Methanol conversion to light olefins over SAPO-34 catalyst: Understanding the fundamental relationship between catalyst's synthesis procedures, properties, activity performance, and deactivation pathway.

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"The years of anxious searching in the dark, with their intense longing, their alternations of confidence and exhaustion, and final emergence into the light—only those who have experienced it can understand that."

Albert Einstein

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Abstract

The current technologies for light olefin production are energy-intensive, have limited feedstock, and are not environmentally friendly. On the contrary, methanol conversion to light olefins (MTO) seems promising as methanol can be produced in large volumes from any carbonaceous resource such as methane, coal, or renewable biomass and waste. The possibility of implementing the so-called closed carbon cycle for sustainable production of light olefins persuaded us to investigate the MTO process. The main objective of this dissertation was to develop techniques that can improve the performance of the MTO catalyst (SAPO-34) by retarding the coke formation and enhancing the catalyst lifetime. After a thorough literature review, 4 main subprojects were defined on topics that have been addressed merely and demanded further investigation. Within each subproject, we attempted to relate the catalyst performance to its physicochemical properties with the aid of comprehensive catalyst characterization methods.

In the 1st subproject, the template's role in the physicochemical properties of SAPO-34 was investigated using the four most popular templates. Possessing a high external surface area (related to macro and mesopores) was recognized to be the dominant parameter affecting the catalyst's lifetime, while optimum acidity and small particle size played inferior roles. For the first time, insitu measurement of coke formation over SAPO-34, with realistic reaction conditions, was conducted in a thermogravimetric reactor (TGR). This led to the proposal of a coke formation mechanism, which was later approved by GC-MS and ¹³C-NMR spectroscopy.

The 2nd subproject concerned the utilization of alkali post-treatment as an efficient route for the introduction of secondary mesopores and improvement of mass transfer in the catalyst. The mild-treated sample exhibited ~50% longer lifetime; however, light olefins selectivity was slightly lower relative to the parent catalyst. TGA-TPO, followed by GC-MS and ¹³C-NMR tests, revealed the formation of heavier coke species (with a lower H/C content) over the treated samples that can provide extra hydrogen for higher alkane production. According to the CD₃CN-FTIR test, it was noticed that Lewis acidic sites remained intact while the Brønsted acidity was depleted after alkali treatment. Our Density Functional Theory (DFT) calculations, complemented by recent findings, depicted a meaningful connection and revealed that methanol adsorption and C-C coupling are

more favorable over Brønsted sites (leading to olefin formation) while Lewis acidic sites facilitate dehydrogenation and aromatization (resulting in enhanced coke generation).

The 3rd subproject attempted to develop a new method regarding catalyst shaping for fluidizedbed application. Since the conventional spray-drying method downgrades the properties of SAPO-34, a novel technique for in-situ mounting of SAPO over the outer shell of γ -Al₂O₃ microspheres was developed. SAPO loadings of 31 and 44 wt.% with different morphologies were achieved using two different templates. Both SAPO-mounted γ -Al₂O₃ catalysts illustrated longer lifetimes in reaction with acceptable light olefin selectivity compared to their parent SAPO counterparts. These catalysts also went through attrition tests and indicated better resistance than the spray-dried sample.

The contradictory results of previous studies on the metal-promoted SAPO-34 encouraged us to examine this technique in our 4th subproject. 20 metals from different groups of the periodic table were tested by the in-situ metal incorporation method. Although the addition of some metals induced faster nucleation and resulted in smaller particles and higher surface area, a major loss in crystallinity was measured for metal-promoted catalysts. Overall, no substantial advancement in the activity performance was recorded over promoted samples that depicted the disability of this technique in SAPO-34 improvement.

Abstrait

Les technologies actuelles pour la production d'oléfines légères consomment énormément d'énergie, ont des matières premières limitées et ne sont pas respectueuses de l'environnement. Au contraire, la conversion du méthanol en oléfines légères (MTO) semble prometteuse car le méthanol peut être produit en grandes quantités à partir de n'importe quelle ressource carbonée telle que le méthane, le charbon ou la biomasse renouvelable et les déchets. La possibilité d'établir un cycle du carbone fermé pour une production durable d'oléfines légères nous a incités à étudier le processus de MTO. L'objectif principal de cette thèse était de développer des techniques permettant d'améliorer les performances du catalyseur MTO (SAPO-34) en retardant la formation de coke et en améliorant la durée de vie du catalyseur. Après une revue approfondie de la littérature, quatre sous-projets principaux ont été définis sur des sujets qui jusqu'à maintenant, n'étaient que partiellement abordés et nécessitaient des investigations approfondies. Dans le cadre de chaque sous-projet, nous avons cherché à relier les performances du catalyseur.

Dans le premier sous-projet, le rôle du modèle dans les propriétés physico-chimiques de SAPO-34 a été étudié en utilisant les quatre modèles les plus populaires. Il a été reconnu que la possession d'une grande surface externe (liée aux macropores et aux mésopores) était le paramètre dominant affectant la durée de vie du catalyseur, tandis qu'une acidité optimale et une petite taille des particules jouaient des rôles inférieurs. Pour la première fois, des mesures in-situ de la formation de coke sur SAPO-34, avec des conditions réactionnelles réalistes, ont été effectuées dans un réacteur thermogravimétrique (TGR). Cela a conduit à la proposition d'un mécanisme de formation de coke, qui a été ensuite confirmé par GC-MS et ¹³C-NMR.

Le deuxième sous-projet portait sur l'utilisation du post-traitement à base d'alcali comme une voie efficace pour l'introduction de mésopores secondaires et l'amélioration du transfert de masse dans le catalyseur. L'échantillon traité de manière douce a montré une durée de vie d'environ 50 % plus longue ; cependant, la sélectivité des oléfines légères était légèrement inférieure par rapport au catalyseur d'origine. Des tests TGA-TPO, suivis de tests GC-MS et ¹³C-NMR, ont révélé la formation d'espèces de coke plus lourdes (avec une teneur en H/C plus faible) sur les échantillons traités, pouvant fournir de l'hydrogène supplémentaire pour la production d'alcane supérieur. Selon le test CD3CN-FTIR, nous avons remarqué que les sites acides de Lewis restaient intacts tandis

que l'acidité de Brønsted était épuisée après le traitement à l'alcali. Nos calculs de la théorie de la fonctionnelle de la densité (DFT), complétés par des découvertes récentes, ont représenté une connexion significative et ont révélé que l'adsorption du méthanol et le couplage C-C étaient plus favorables sur les sites de Brønsted (conduisant à la formation d'oléfines) tandis que les sites acides de Lewis facilitaient la déshydrogénation et l'aromatisation (entraînant une génération de coke accélérée).

Le troisième sous-projet a tenté de développer une nouvelle méthode de mise en forme du catalyseur pour une application en lit fluidisé. Étant donné que la méthode conventionnelle de séchage par pulvérisation dégrade les propriétés de SAPO-34, une nouvelle technique de montage in-situ de SAPO sur la coque externe des microsphères de γ -Al₂O₃ a été développée. Des charges de SAPO de 31 et 44 % en poids avec différentes morphologies ont été obtenues en utilisant deux modèles différents. Les deux catalyseurs SAPO- γ -Al₂O₃ ont montré une durée de vie plus longue dans la réaction avec une sélectivité acceptable pour les oléfines légères par rapport à leurs contreparties SAPO initiales. Ces catalyseurs ont également été soumis à des tests d'attrition et ont montré une meilleure résistance que l'échantillon séché par pulvérisation.

Les résultats contradictoires d'études précédentes sur le SAPO-34 activé par les métaux nous ont encouragés à examiner cette technique dans notre quatrième sous-projet. Vingt métaux provenant de différents groupes du tableau périodique ont été testés par la méthode d'incorporation de métal in-situ. Bien que l'ajout de certains métaux ait induit une nucléation plus rapide et conduit à des particules plus petites et à une plus grande surface spécifique, une perte majeure de cristallinité a été mesurée pour les catalyseurs activés par les métaux. Dans l'ensemble, aucune avancée substantielle dans les performances d'activité n'a été enregistrée pour les échantillons activés par les métaux, ce qui démontre l'inefficacité de cette technique pour l'amélioration de SAPO-34.

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1 Introduction

1.1 Motivation

In recent years, light olefins (i.e., ethylene and propylene) have experienced an upsurge in global demand, with an ever-growing market capacity of 475 MM\$ per annum by 2027 [1] (Fig. 1-1). The leading process for light olefins production is steam cracking of naphtha or gas condensate. Shortage of crude oil resources and severe fluctuation in its pricing, along with increasing awareness of global warming and human impact on the environment, have urged researchers to explore alternative and preferably more sustainable processes and feedstock. Methanol conversion to light olefins (MTO) can be the alternative process [2]. Methanol can be produced in large volumes from syngas obtained via steam reforming or partial oxidation of any carbonaceous resource such as methane, coal, renewable biomass, waste [3], and CO_2 [4,5].



Fig. 1-1 (A) Global ethylene and propylene demand (consumption) from 2015 to 2022. Adapted from [6,7]. (B) Contribution of different processes towards global propylene production in 2020 and 2025 (projected). Adapted from [8,9]

With the aid of MTO technology, the idea of a closed-loop carbon cycle can be implemented. This can be done by steam-reforming or partial oxidation of plastic wastes to synthetic gas, which in turn will be converted to methanol and subsequently to light olefins for plastic production. Consequently, a surge in research towards the MTO process over the last 2 decades has been

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observed (Fig. 1-2), which can project both the importance and emergence of this process as a means for sustainable light olefin production. This also encouraged us to study, understand, and improve the MTO process and its catalyst.



Fig. 1-2 Number of publications related to methanol conversion to light olefins over SAPO-34 published per year. Data collected from the Web of Science Core Collection [10]

1.2 Objectives

As of yet, SAPO-34 remains the most frequently used catalyst for the MTO process, since it seems to drive peak catalytic performance relative to all other examined silicoaluminophosphate catalysts (as observed in Fig. 1-3) [11]. Under optimal MTO reaction conditions, SAPO-34's relatively small pores (3.7 Å) [12], medium acidity (~ 1 mmol g⁻¹) [13–15] and high thermal stability (up to 1000°C) [16,17] have been recognized as the key reasons for high selectivity towards light olefins (~80% total of $C_2^=$ and $C_3^=$) [18–20]. The rather small pore size of SAPO-34 inhibits the diffusion of large hydrocarbon species out of the framework, with only smaller-sized hydrocarbons (mainly light olefins) being capable of diffusing out of SAPO-34's cages- evidently explaining the selectivity towards these species.



Fig. 1-3 Product distribution obtained by application of different silicoaluminophosphate catalysts (alongside their topology structure) in the MTO reaction. (A) SAPO-34 compared to SAPO-41, SAPO-11, and SAPO-46. Reaction conditions: T = 450 °C, P = 1 atm, and WHSV = 1 g_{MeOH} g_{Cat}⁻¹ h⁻¹. Adapted from [21]. (B) Parent SAPO-34 compared to SAPO-35, SAPO-56, STA-7 and SAPO-42. Reaction conditions: T = 400 °C, P = 1 atm, WHSV = 0.35 g_{MeOH} g_{Cat}⁻¹ h⁻¹. Adapted from [22].

In terms of drawbacks, one major issue that exists to this date is the short catalyst lifetime that SAPO-34 encounters. Over time on stream, it has been experimentally validated that large multiring aromatic species (termed coke) build up inside and on the outer surfaces of the catalyst. These species block catalyst pores and in turn inhibit the diffusion of molecules, resulting in catalyst deactivation [23,24]. However, a variety of strategies at the lab scale have been investigated to try and resolve this problem of pore blockage. To this date, research is continuously being allocated towards the redesigning and modifying of the catalyst in the hope of mitigating the catalyst's short lifetime. Fig. 1-4 attempts to decipher the most prominent terms and themes present in MTO-related articles published in the last two decades. It seems there are two distinct clusters that correspond to (i) SAPO-34 synthesis and characterization and (ii) reaction and mechanistic studies. Similarly, our objectives here were.

- 1) to understand the MTO process and the dominant operating parameters affecting the reaction (critical literature review).
- to prepare the SAPO-34 catalysts, and by providing the optimum reaction conditions, reach similar products as the commercialized process.
- 3) to understand the fundamental relationship between synthesis procedures, catalyst properties, activity performance, and the deactivation pathway.
- to propose methods to improve the catalyst performance by lengthening the catalyst lifetime lowering the coke formation rate and advancing the economy of the process.

With that in mind, we did a comprehensive literature review to identify the knowledge gaps and open areas of research and tried to focus on them. Accordingly, after the design and construction of an experimental setup for conducting MTO activity tests, the SAPO-34 catalyst was synthesized, and 4 subprojects were defined and investigated. The 4 subprojects are as follows:

- SAPO-34 catalyst synthesis optimization by template alteration and understanding the coke formation and evolution mechanism.
- SAPO-34 alkali treatment to create a hierarchical structure and investigate the role of Lewis and Brønsted acidic sites of SAPO-34 in the reaction and deactivation pathway.
- Fabrication of SAPO-34 over γ-Al₂O₃ microspheres with high SAPO loading and good adhesion for fluidized-bed application.
- 4) Intensive assessment to see if secondary metal incorporation into SAPO-34 framework genuinely improves its performance in methanol conversion to light olefins reaction.

Throughout the project, detailed characterization techniques were employed to analyze and understand the catalyst features and relate them to its performance within the reaction.



Fig. 1-4 Bibliometric map generated by VOSviewer [25], based on 669 articles (keywords "MTO" and "SAPO-34"), indexed from 2000 to June 2023, from the Web of Science Core Collection [10].

1.3 Organization of the thesis

This dissertation has summarized the work that I have done during the last 4 years of research as a PhD student. Here I commenced with the motivations that encouraged us to conduct a thorough study of this process and objectives that we had in mind in the early stages of the project. The second chapter is dedicated to the theoretical background and the comprehensive review of the relevant literature. It contains the description of the process, followed by the reaction and deactivation mechanism, kinetics, and study of the catalyst design and modification techniques. As the outcome of the literature review, 4 subprojects were defined and implemented. Each of these subprojects, which have been explained in chapters 4 to 7, were eventually formed into a manuscript for publication. Chapter three explains the methodology that was applied for all subprojects and includes catalyst preparation and modification methods, activity tests, and characterization techniques utilized. Chapter 8 summarizes the main findings and results of the entire project and chapter 9 discusses the originality and novelty of the project outcomes. The thesis concludes with the contribution of authors, nomenclature, references, appendix, and finally published works.

2 Comprehensive review of the relevant literature

2.1 MTO process

According to Le Chatelier's principle, due to the increase in number of moles in methanol dehydration to olefins, low pressures are favorable. Methanol conversion reactions to light olefins (reactions 2-1 and 2-2) are highly exothermic and spontaneous. High negative Gibbs free energy changes of the methanol reactions to ethylene and propylene (at 400 °C and atmospheric pressure) make the equilibrium constant extremely large which means methanol can react to olefins up to almost 100% conversion without any thermodynamic limitation. Dimethyl ether (DME, C_2H_6O) is known as an intermediate of the MTO reaction which appears at low temperatures. At higher temperatures, the energy required to overcome the activation energy is provided and methanol would be converted directly to olefins.

$$CH_4 O(g) \Leftrightarrow \frac{1}{2} C_2 H_6 O(g) + \frac{1}{2} H_2 O(g) \quad \Delta G_R = -4.87 \ kJ \ mol^{-1} , \Delta H_R = -10.31 \ kJ \ mol^{-1}$$
(2-1)

$$CH_4O(g) \Leftrightarrow \frac{1}{2}C_2H_4(g) + H_2O(g) \qquad \Delta G_R = -55.62 \ kJ \ mol^{-1}, \Delta H_R = -11.98 \ kJ \ mol^{-1}$$
 (2-2)

$$CH_4O(g) \Leftrightarrow \frac{1}{3}C_3H_6(g) + H_2O(g) \qquad \Delta G_R = -53.75 \ kJ \ mol^{-1}, \Delta H_R = -31.25 \ kJ \ mol^{-1}$$
(2-3)

The simplified process flow diagram of the methanol conversion to light olefins process, based on the technology developed by the Honeywell UOP/Norsk Hydro joint venture, is presented in Fig. 2-1. Methanol diluted with 20 wt.% water is being warmed and vaporized by recovering heat from reactor effluent in E-101 heat exchanger. The methanol feed then passes through the feed distributor and fluidizes the fresh catalyst coming back from the regenerator. The regenerated catalyst (having a temperature of about 600 °C) heats up the feed to the reaction temperature (around 410 °C). The MTO reaction takes place in the reactor riser, and gaseous products along with the fluidized catalyst particles enter the disengagement section of the reactor. The higher cross-sectional area of this section causes an instant drop in the gas velocity, which in turn triggers the fall of most of the catalyst, that is entrained in the gas phase, will be separated using multiple successive cyclones. Simultaneously, a portion of the catalyst is sent to the generator to burn the

partial coke formed via air. The reactor effluent is quenched (to remove the water and unreacted methanol) and then compressed to be directed to product separation and purification units. After caustic wash (to remove carbon dioxide) and drying (to remove moisture), the gas passes through the de-ethanizer where ethylene, ethane, and lighter compounds are separated from heavier ones. After the acetylene converter, the fuel gas (methane and hydrogen) will be removed followed by ethylene purification. In the heavy compounds section, high-purity propylene is produced where C_4^+ species are sent to the olefin cracker to enhance the overall light olefin yield of the process [26]. The basic MTO process can yield 75-80% (carbon-based) ethylene plus propylene, 2-5% coke, 2-5 % alkanes, and 0.5-1.0 % DME, where the olefin cracker can improve the light olefin yield up to 85-90%.



Fig. 2-1 Process flow diagram of MTO process adopted from UOP co. [27]. Unit identification: M-101 Mixer; E-101 Heat Exchanger; R-101 Fluidized Reactor; R-102 Regenerator; K-101 Air Compressor; C-101 Quench Tower; E-102 Air-Cooled Exchanger; C-102 Water Stripper; K-102 Product Compressor; V-101 Phase Separator; C-103 Condensate Stripper; C-104 Caustic Scrubber; C-105 Gas Dryers; C-106 De-ethanizer; R-103 Acetylene Converter; C-107 De-methanizer; C-108 C₂ Splitter; C-109 De-propanizer; C-110 C₃ Splitter.

2.2 Reaction operating conditions

The influence of MTO reaction conditions on SAPO-34 catalytic performance is an area of research that has been well investigated. One important factor that researchers have considered is the operating temperature, which plays a large role in establishing product distribution. It has been found that the optimal temperature exists in the range of 400 to 460 °C (by weighing the combined values of both light olefin selectivity and lifetime, as can be seen in Fig. 2-2(A)) [28–31]. The reaction taking place at a temperature higher than the optimum range sustains an acceptable total average light olefins selectivity but suffers from lower catalyst active lifetime (due to enhanced rate of coke generation) and heightened light alkane (primarily methane) formation [29,32,33]. At lower temperatures (< 400 °C), on the other hand, the heat required to overcome the activation energy of the reaction seems to be too minimal, resulting in incomplete conversion of methanol and overall lower active lifetime [29,33]. In general, higher temperature alteration of 370 °C to 490 °C [29]. Researchers have related the dependency of product distribution on reaction temperature to the type of activating and deactivating species present at specific reaction temperature ranges [33].



Fig. 2-2 (A) Product distribution of MTO reaction over SAPO-34 catalyst at different temperatures [29]. Notation: LOS = light olefin selectivity, OS = olefin selectivity, X = conversion, TOS = time on stream. Reaction conditions: pressure 0.1 barg, WHSV of 1 g_{MeOH} g_{Cat}⁻¹ h⁻¹, and methanol diluted with 20 wt.% water. (B) Effect of WHSV on the conversion of methanol, selectivity to ethylene, propylene, and butylene over time on stream [34]. Reaction conditions: temperature of 450 °C, atm pressure, and methanol diluted with 20 wt.% water. (C) The effects of pressure alteration on methanol conversion, ethylene yield, propylene yield and selectivity towards light olefins. Adapted from [30]. Reaction conditions: temperature of 400 °C, WHSV of 12 g_{MeOH} g_{Cat}⁻¹ h⁻¹, and methanol diluted with 69 wt.% water. (D) Synergistic effect between H₂O and H₂ on the catalytic performance of SAPO-34 in the MTO process. Reaction conditions: temperature of 450 °C, 40 bar, and WHSV of 4.0 g_{MeOH} g_{Cat}⁻¹ h⁻¹. Adapted from

[35]

Other than operating temperature, one should consider the role that weight hourly space velocity (*WHSV*) may impose on catalytic activity. As seen in Fig. 2-2(B), the MTO reaction performs optimally under *WHSVs* of approximately 1 to 2 $g_{MeOH} g_{Cat}^{-1} h^{-1}$ [31,36]. A *WHSV* below 1 $g_{MeOH} g_{cat}^{-1} h^{-1}$ has also been proven to reduce the total average selectivity of C₂⁼ to C₄⁼ species. This has been attributed to the longer residence time of species in the reactor, which can permit

secondary reactions to take place and ultimately alter the product distribution [31]. The use of *WHSVs* larger than the pre-mentioned optimal range results in a shortened catalyst active lifetime and, in even higher values, causes incomplete methanol conversion [34].

Another important consideration is the impact feed composition may have on product distribution and catalyst lifetime. Studies have demonstrated that the use of diluents in the feed, such as water, decreases the partial pressure of methanol, which has correspondingly boosted selectivity towards light olefins and delayed catalyst deactivation [37,38]. Although nitrogen has been utilized as an alternative diluent, water is readily available, possesses a relatively higher heat capacity as a vapor (to carry away the heat of reaction), and has been shown to more effectively reduce the rate of coke formation and further improve catalyst utilization [39,40]. Since water will tend to reversibly adsorb on catalyst acidic sites (primarily strong ones) due to its basic properties, it has been argued to reduce the residence time of coke precursors adsorbed on such active sites as well as inhibit the coke-generating steps involving alkene monomers undergoing oligomerization and cyclization [39,41,42]. Furthermore, problems involving product separation may arise when diluents other than water are employed [40]. Employing 70-80 mol% of water in the feed has proven to process roughly eight times more methanol (within the catalyst active period) than if the feed had consisted of only pure methanol [40]. Going beyond this range (90 mol% water) has proven no substantially better performance [43]. However, the addition of substantial amounts of water will result in the occupation of the reactor volume, which consequently lowers the reactor's nominal processing ability. Besides, heating up the water to the reaction temperature and condensing the outlet water, despite the application of heat recovery methods, can result in heat loss and decreased energy efficiency. Hence, in industrial applications, feed water content is usually kept around 30 mol% (20 wt.% water in methanol) [27].

Other than the conventional use of water/ nitrogen diluent in the feed, groups have also investigated the potential effects that other co-fed gases like hydrogen may impose on catalytic activity [35,44]. According to Fig. 2-2(D), Zhao et al. [35] reported that the SAPO-34 fed with pure methanol lasted for less than an hour; however, following hydrogen addition in the H_2 / MeOH ratios of 8.3, the lifetime was substantially enhanced to around 80 hours. However, the light olefins were inevitably hydrogenated to alkanes, leading to a considerable drop in light olefins selectivity, from around

70% using pure methanol, to around 50% in the presence of hydrogen. Another group [44] claimed milder reduction in light olefins selectivity in response to hydrogen addition (LOS of 76% for 0 H₂/MeOH molar ratio compared to LOS of 70.5% for 231 H₂/MeOH molar ratio) and over 70 times longer lifetime. Nonetheless, the reaction conditions that they employed (WHSV of 40 $g_{MeOH} g_{cat}^{-1} h^{-1}$ over only 4 mg of catalyst) seem to be far from the optimal range. Interestingly, the simultaneous presence of water and hydrogen in the feed seems to trigger a synergistic effect, leading to a long lifetime without compromising LOS (see Fig. 2-2(D)). Preceding studies have claimed that the fed H₂ may play a role in hydrogen transfer reactions and seemingly intercept the pathways that lead to the generation of deactivating multi-ring aromatic species. It was proclaimed that, under combined feeding of H_2 and H_2O [35], heavy aromatic deposits that formed were likely to undergo hydrogenation catalyzed by SAPO-34 Brønsted acidic sites [45], followed by possible cracking (depending on the temperature employed). These species were declared to have likely reverted back to active intermediates and in turn, decelerated the overall evolution of coke species [35]. Periodic density functional theory (DFT) modeling that ensued focused on investigating these hydrogenation-based mechanistic claims that revolved around hydrogen co-feeding [46]. It was uncovered that potential deactivation-inducing precursors such as formaldehyde and dienes, which have been claimed to drive the link between olefinic and aromatic dual cycles (see section 4.3.1 on polyalkylaromatics formation), are selectively hydrogenated (i.e., at a higher rate) relative to desired light alkene species. Hence, the elimination of such potential aromatic precursors by hydrogenation, via high-pressure H₂ co-feeding, may be the plausible cause for the extended lifetime observed in pre-mentioned studies. Recently, the potential of undertaking MTO catalysis in the presence of syngas reagents (co-feeding a mix of H₂ and CO under high pressure) has been examined [47]. However, under elevated methanol partial pressure, which begins to more closely resemble the MTO process, co-feeding CO (in both the presence and absence of H₂) resulted in no clear improvement in any catalytic performance metric.

2.3 MTO reaction mechanism and deactivation pathways

The uncovering of the MTO mechanism has been and continues to be a challenge for researchers. Over the last 60 years, a vast number of mechanistic proposals have been put forward. The pathways that have gained increasing popularity over the years are depicted as a simplified schematic in Fig. 2-3. In general, the elementary steps of the first C-C coupling (in the formation of light olefins) are still under debate. However, it has been widely accepted that early-stage constructed light olefins are likely to undergo further reactions. These include hydrogen transfer, alkylation, cyclization, and aromatization to form the following species: paraffins, larger olefins, naphthene, and aromatics. The generation of large multi-ring aromatic species can in turn lead to the "coking" and hence, deactivation of the zeolite catalyst. The most probable path behind the first C-C bond formation has been the main topic of discussion in many articles. A large number of mechanistic proposals have been put forward; however, the two most widely discussed and relevant mechanisms have been explored as follows.¹



Fig. 2-3 Simplified schematic of the MTO overall reaction.

2.3.1 Oxonium ylide mechanism

During early mechanistic research, the oxonium ylide mechanism (as seen in Fig. 2-4) has received recognition as one of the viable paths for the formation of the initial C-C bond [48–50]. It has been suggested that, in the presence of Brønsted acidic sites (H⁺) of zeolite catalysts, the initial step (A) consists of the dehydration of two methanol molecules to a singular dimethyl ether (DME). This DME intermediate may interact with a Brønsted acidic site of the zeolite catalyst, to in turn form a dimethyl oxonium ion. These two preceding species can react further to produce a trimethyl oxonium ion (i.e., step B). This is then followed by a deprotonation step (C) of one of the methyl groups by a basic site, to in turn formulate a surface-associated dimethyl oxonium methyl ylide species. The subsequent step comprises of two options, either a Stevens rearrangement (step D) or an intermolecular methylation (step D'). Via the Stevens rearrangement, the ylide species is converted to a methylethyl ether (as well as a singular methanol molecule), which is then ultimately transformed to ethylene via a β -elimination step (E). On the other hand, with intermolecular methylation (the second option), an ethyldimethyl oxonium ion forms. This is once again followed by a β -elimination step (E') to produce the ethylene species while regenerating a DME molecule in this case. An isotope labeling study [51] reached the conclusion that intermolecular methylation (step D') is the preferred pathway in comparison to the potential 'Stevens rearrangement' (step D).



Fig. 2-4 Oxonium ylide mechanism. Adapted from [48].

2.3.2 The Hydrocarbon pool concept

As mechanistic research in the methanol conversion to olefins process developed, much research during the 1990s was allocated towards the understanding of a more novel parallel-type reaction concept i.e., the notion of the hydrocarbon pool (HCP). The initial formal suggestion of this concept was pronounced by Dahl and Kolboe [52,53]. By isotope labeling experiments, the authors were able to provide experimental evidence to back up the carbon pool idea they proposed. The experiments involved co-feeding ¹³C-methanol and ¹²C ethanol and propanol, simulating ethylene and propylene absorbed on the surface of the SAPO-34 catalyst. In the case of the methanol and ethanol co-fed reaction, in view of the product isotopic distribution, propene, and butene species were generated primarily from ¹³C, coming from methanol, rather than a combination of ¹³C and ¹²C. This can demonstrate that the produced hydrocarbons were not generated via successive methylations of ethylene, but instead via a sort of ambiguous 'carbon pool' mechanism. As research to uncover the details expanded, the concept began to receive much recognition as the major contributor for both olefin formation as well as coke production for advanced times on stream [54–61]. With analysis of the species confined in catalyst pores during the reaction,

substantial amounts of polyalkylaromatics were detected. This finding spawned the idea that a pool of intermediate carbonaceous species exists, in which polyalkylaromatics (generally polymethylbenzenes) are the active centers. In this pool, a variety of elementary reaction steps, including chain extension, cyclization, and aromatization take place on linear chain aliphatic hydrocarbons (detected during early stages of MTO) [62], in turn leading to the generation of aromatic species. As these aromatic species begin to alter and evolve, ethylene and propylene have been suggested to 'split off' as products. This in turn offers a path for light olefin generation, as opposed to the previously discussed ordinary formulation of these species. The HCP concept possesses two underlying mechanisms that are said to be generally responsible for light olefin formation. These are termed the exocyclic methylation route (i.e., the side chain mechanism) and the pairing mechanism (also commonly referred to as the expansion- contraction mechanism) [56–58], which will be discussed, along with other noteworthy HCP means of light olefin formation, in the following section.

The 'exocyclic methylation route', also commonly referred to as the 'side chain mechanism', is one of the two central mechanisms under the HCP concept. To the best of our knowledge, this pathway was first proposed by Mole et al. [63] during the early 1980s and has been subsequently modified [64]. Over recent years, the side chain mechanism has received recognition as a means of explaining how light olefins may form within the MTO reaction [56–58,65,66]. Fig. 2-5 (A) provides a close examination of this mechanistic route over zeolite catalyst utilizing either polymethylbenzene (top row) or polymethylnaphthalene (bottom row) i.e., the previously mentioned active components of the hydrocarbon pool concept [67]. Nonetheless, the mechanism proceeds in the same manner for both scenarios. Studying the case of the PMB cycle (top row), commencing with hexamethylbenzene, this species first undergoes gem methylation with methanol (M1) to form 1,1,2,3,4,5,6-heptmethylbenzenium cation (heptaMB+). Its subsequent deprotonation (D1) generates hexamethyl-methylene-cyclohexadiene (HMMC). The exocyclic double bond of HMMC reacts with an electrophilic methenium species (derived from a methanol molecule) to form an ethyl group on the benzenic ring (i.e., an extension of the benzenic species side chain) (M2). As suggested by a different group [56], dealkylation of this ethyl group may take place, resulting in the formation of ethylene. However, there is the alternative possibility that deprotonation occurs instead (D2), which would regenerate the exocyclic double bond, forming hexamethyl-ethylene-cyclohexadiene. Further reaction with a methenium species (M3) leads to the formation of an isopropyl group attached to the benzenium cation. Dealkylation of this propyl group takes place via an internal hydrogen shift (E1), resulting in the formation of propylene. It should be noted that butene formation is highly unlikely to occur with respect to this mechanism due to steric hindrance [56]. Overall, groups [58,67] have backed up this mechanistic proposal as a plausible route for light olefin formation via the use of theoretical modeling DFT calculations (as seen in Fig. 2-5 (B) and (C)).



Fig. 2-5 (A) Side chain mechanism via the top: polyMB cycle (commencing with hexamethylbenzene) and bottom: polyMN cycle (commencing with dimethylnapthalene) for the MTO reaction over zeolite catalyst [67]. (B) Free energy profiles of the polyMB based side chain mechanism (at 673 K) for different commencing polyMBs in the MTO reaction over zeolite catalyst. The commencing polyMBs studied are p-xylene (PX), 1,2,4-trimethylbenzene (TMB), 1,2,4,6-tetramethylbenzene (TeMB), and hexamethylbenzene (HMB). The zeolite framework, methanol, and different polyMBs in the gaseous phase are taken as the reference state. A1, A3, and A4 are the adsorption of methanol, while A2 is the additional adsorption of polyMB [67]. (C) Free energy profiles of the polyMN based side chain mechanism (at 673 K) for different commencing polyMNs in the MTO reaction over zeolite catalyst. The

commencing polyMNs studied are 1,4-dimethylnaphthalene (DMN), 1,4,5-trimethylnaphthalene (TMN), and 1,4,5,8-tetramethylnaphthalene (TeMN). The zeolite framework, methanol, and different polyMNs in the gaseous phase are taken as the reference state. A1, A3, and A4 are the adsorption of methanol, while A2 is the additional adsorption of polyMN [67].

The second major mechanistic route that falls under the HCP concept is commonly termed the expansion-contraction mechanism or the paring mechanism. The introduction of this pathway came about in 1961 when Sullivan et al. [68] sought to explain the formation of light olefins from polyalkyl benzenium ions. Since then, research fixating on this mechanistic proposal has taken flight, with many research groups agreeing on the viability of this path [56–58,66,69]. The generalized paring route can be observed in Fig. 2-6 (A). The mechanism suggests alkyl side chain growth by ring contraction and expansion (as opposed to the alkylation steps involving methenium species of the side chain mechanism). Specifically, the six-membered ring (heptamethyl benzenium ion) is contracted to a five-membered ring (step A), followed by subsequent dealkylation of the isopropyl and isobutyl groups (which leads to the formation of propylene and isobutene, respectively). This can be seen in steps B', B and C. The five-membered ring undergoes deprotonation and carbon atom interchange to in turn expand to a six-membered ring (steps D and F). Methylation involving methanol leads to the ultimate formation of hexamethylbenzene (hexaMB) (steps E and G). This process is then repeated as hexaMB is converted back to the starting species (heptamethyl benzenium ion) via gem methylation with methanol (step H). Isotope labeling experiments conducted by Bjørgen et al. [70] promoted the idea that the paring mechanism may be the dominant route in olefin formation over zeolite catalysts. Precisely, the group reacted ¹³C-methanol and ¹²C-benzene over H-beta zeolite catalyst. In turn, methylbenzene species (comprised of a ¹²C-benzene ring) with ¹³C methyl groups were generated. The gas-phase product isotopic distribution provided evidence in support of the existence of the paring mechanism. A great portion of the propene product molecules contained carbon atoms (¹²C) from the benzene ring, which is in line with the notion of the ring contraction-expansion of the paring mechanism. Furthermore, as seen in Fig. 2-6(B), one study [66] utilized DFT based modeling to analyze the most crucial reaction steps of the paring mechanism (i.e., up to ethylene formation (step B')). It was uncovered that the paring mechanism may be an energetically feasible pathway for certain zeolite catalysts (such as H-ZSM-5) but argued that in the case of H-SAPO-34, the side chain mechanism seems to be more favorable in comparison (due to both the less favorable kinetics and thermodynamics of the B' step).



Fig. 2-6 (A) Paring mechanism via the polyMB cycle for the MTO reaction over zeolite catalyst. Adapted from [56] and [57]. (B) Free energy profile of the most crucial steps of the polyMB based paring mechanism (at 725 K), initiated from the most favorable gem-methylated carbenium intermediate (6MBC1⁺) over H-SAPO-34. The energy reference is the free energy of the adsorbed gem-methylated carbenium intermediate (ZO⁻-6MBC1⁺) alongside three gas-phase methanol molecules. Adapted from [66].

Hence, overall, in terms of the two key mechanisms ('side chain' and 'expansion- contraction'), the articles studied have suggested that both are likely to take place, but that it is largely dependent on the zeolite's acid site strength, leading to the favoring of one over the other [56–58]. From a theoretical perspective, as dictated by Olsbye et al. [56], the side chain mechanism could be favored over the expansion-contraction mechanism by utilizing a zeolite catalyst with active sites of relatively low acidic strength.

2.3.3 Deactivation pathways

The consensus amongst articles regarding coke formation is that the mechanism commences with polyalkylnaphthalene. This group of molecules is said to undergo molecular rearrangement, ring expansion, and aromatization, which leads to the formation of multi-ring aromatics (such as anthracene and phenanthrene), as seen in Fig. 2-7. Ultimately, these heavy aromatics (so-called coke) block zeolite catalyst pores, preventing the diffusion of reactant molecules (methanol) towards active sites, and resulting in catalyst deactivation [67,71]. Interestingly, as multi-ring aromatics begin to formulate, the necessary hydride transfer reactions between intermediate species and surface-associated methoxy groups lead to the formation of methane molecules.

Hence, this can provide a justification as to why methane and coke production seem to rise concurrently during the MTO reaction since the hydride transfer step (which generates methane) is necessary for the building up of aromatic rings to form coke species. Referring back to Fig. 2-7, the free energy profile associated with the mechanistic scheme developed for the pre-mentioned anthracene and phenanthrene formation has also been illustrated [67]. The conducted DFT modeling indicated that anthracene and phenanthrene production in zeolite cages is kinetically more difficult relative to the generation of benzene and naphthalene. Moreover, the free energy barriers of methylation and olefin elimination steps in the previously discussed polyMN-based side chain mechanism are much lower in comparison to the hydride transfer reactions for anthracene and phenanthrene formation. Hence, it can be concluded that (poly)MB and (poly)MN are more likely to assist in the formation of olefins, the more favorable pathway, rather than build up to form polycyclic aromatics. In other words, these species take on more of a role as the active components of the hydrocarbon pool mechanism rather than the precursors for inactive species.



Fig. 2-7 Proposed mechanistic path for the formation of polycyclic aromatic species (anthracene and phenanthrene) during the MTO reaction over a zeolite catalyst. The top left plot presents the free energy profile for both anthracene (ant.) and phenanthrene (phen.) production (at 673 K) in the MTO reaction over a zeolite catalyst. In addition to the zeolite framework, naphthalene and adsorbed butene (A1) are taken as the reference state for the formation of

anthracene and phenanthrene. A2, A3, and A4 represent methoxyl generation at the active site prior to the hydride

transfer reactions. For each of the elementary steps, the optimized transition states have been presented schematically. Notation: O1 refers to oligomerization, HT1–HT3 refers to hydride transfer reactions, and C1 is for the 1,6-cyclization. Atom colorings: yellow (Si), red (O), white (H), pink (Al) and blue (C). Bonding distances are presented in Å. Adapted from [67].

2.4 MTO reaction and deactivation kinetics

As seen by the highly varied and complex mechanistic scheme that constitutes the MTO reaction (discussed in section 2.3), no kinetic model from research till the present day has been able to fully encapsulate MTO's extensive reaction network. Research groups that have delved into the field of MTO kinetics (with SAPO-34 as the catalyst) have largely presented simplified lumped kinetic models that are derived from reaction schemes comprising a small number of steps. Iterative approaches were tried and tested until model predictions of MTO performance were comparable to that of the experimental data. Different approaches to developing these models have been utilized, ranging from the use of simple power laws to the application of the Langmuir-Hinshelwood (LH) approach. As an example, Taheri Najafabadi et al. [19] utilized both LH and power law kinetic models to derive their rate equations. The developed simple mechanism consisted of five reaction steps, involving the adsorption of methanol on the surface of the zeolite (in place of a Brønsted acidic site), followed by the formation of a surface-associated dimethyl ether, which could subsequently desorb or instead convert to light olefins. With the use of the LH formulation, it was assumed that the reactant methanol molecules were able to adsorb on the surface of the catalyst, diffuse in close proximity to the surface, and in turn react with surfaceassociated molecules. Evidently, the generated products on the surface are assumed to desorb into the fluid phase without constraint. Other than the LH mechanism, all other possible paraffinic products were lumped together as a singular species, and the corresponding reaction rate expression was formulated as a simple power law. Reaction steps 3 to 5 were presumed to be ratedetermining. The group established this via an iterative approach of altering the assumed ratedetermining steps, and in turn comparing the predictions from a variety of suggested rate models with experimental data.

Reaction pathway*	Rate expressions**
MeOH + S $\stackrel{k_m}{\underset{k'_m}{\Rightarrow}}$ MeOH · S	_
2 MeOH · S $\stackrel{k_d}{\underset{k'_d}{\mapsto}}$ DME · S + H ₂ O + S	_
$DME \cdot S \xrightarrow{k_{\mathrm{r}}} DME + S$	$r_{r} = \frac{k_{r}K_{d}K_{m}^{2}P_{MeOH}^{2}}{P_{w}(1 + K_{m}P_{MeOH} + (K_{d}K_{m}^{2}P_{MeOH}^{2}/P_{w}))}$
$DME \cdot S \xrightarrow{k_e} C_2H_4 + H_2O + S$	$r_{e} = \frac{k_{e}K_{m}^{2}P_{MeOH}^{2}}{P_{w}(1 + K_{m}P_{MeOH} + (K_{d}K_{m}^{2}P_{MeOH}^{2}/P_{w}))}$
$DME \cdot S + MeOH \cdot S \xrightarrow{k_p} C_3H_6 + 2H_2O + 2S$	$r_p = \frac{k_p K_d K_m^3 P_{MeOH}^3}{P_w (1 + K_m P_{MeOH} + (K_d K_m^2 P_{MeOH}^2 / P_w))^2}$
_	$r_{Paraffin} = k_{Paraffin} P_{Paraffin}^{n}$

Table 2-1 Reaction mechanism and final reaction rate expressions used to describe the MTO process over SAPO-34 catalyst, based on both Langmuir-Hinshelwood and power law kinetic models [72].

*Reaction rate constants (k_j) are in units of mol $g^{-1}h^{-1}$, except for $k_{Paraffin}$, which is in units of mol $g^{-1}h^{-1}$ bar⁻ⁿ (where n = 0.31).

Moreover, some groups considered coke formation as part of their reaction rate expressions, as it influences the distribution of the product substantially [73–76]. Accordingly, one group [74] formulated a kinetic model including the coke-dependent parameter by using a thermogravimetric reactor and measured the coke content over time on stream. Both rate expressions, involving feed consumption (methanol and dimethyl ether, lumped as MDOH) and rate of production of different species *i*, contain the parameters a' and α_i , which, respectively, are indicative of the catalyst activity and the dependency of each species production on the coke content (see Table 2-2). The group tested a range of catalyst activity functions (a') and found that the exponential function provided the best fit for the experimental data, justified by its higher correlation coefficient (0.9965). This catalyst activity expression is a function of only the coke content (C), determined

^{**} r_i refers to the rate of species *i* production (mol g⁻¹ h⁻¹). K_j refers to the equilibrium constant for a reaction *j*. P_w and P_{MeOH} refer, respectively, to the partial pressure (bar) of water and methanol in the feed.

by the TGA. The coke content *C* in turn is a function of the temperature *T*, time *t*, weight hourly space velocity WHSV ($g_{MeOH} g_{cat}^{-1}h^{-1}$), and methanol partial pressure *p*.

Reaction	Rate expressions**				
pathway [*]	Rate of consumption of species A (MDOH)	Rate of production of species i			
	$\mathbf{r}_{A} = \mathbf{a}' \cdot \mathbf{r}_{A0} = \mathbf{a}' \cdot \mathbf{k}_{A}^{0} \mathbf{e}^{-\left(\frac{\mathbf{E}\mathbf{a}_{A}}{\mathbf{R}T}\right)} \mathbf{p}_{A}$	$r_i = a' \cdot r_{A0} \cdot \alpha_i = a' \cdot k_A^0 e^{-\left(\frac{Ea_A}{RT}\right)} p_A \cdot \alpha_i$			
MDOH $\stackrel{k_1}{\rightarrow}$ CH ₄	$r_A = a' \cdot k_A^0 e^{-\left(\frac{Ea_A}{RT}\right)} p_0 y_A$	$r_i = a' \cdot k_A^0 e^{-\left(\frac{Ea_A}{RT}\right)} p_0 y_A \cdot \alpha_i$			
$MDOH \xrightarrow{k_2} C_2 H_4$	$r_{A} = a' \cdot k_{A}^{0} e^{-\left(\frac{Ea_{A}}{RT}\right)} p_{0} \cdot \frac{1 - X}{1 + X \cdot \sum_{i} \alpha_{i} + \frac{N_{N_{2}}}{F_{A} \cdot T_{T}}}$	$r_{i} = a' \cdot k_{A}^{0} e^{-\left(\frac{Ea_{A}}{RT}\right)} p_{0} \cdot \frac{1 - X}{1 + X \cdot \sum_{i} \alpha_{i} + \frac{N_{N_{2}}}{1 - X}} \cdot \alpha_{i}$			
$MDOH \xrightarrow{k_3} C_3H_6$ $MDOH \xrightarrow{k_4} C_4H_8$	catalyst activity	function: $a' = e^{-\beta C}$			
$\text{MDOH} \xrightarrow{k_5} C_n H_m^{***}$	$C = C_0 \left(1 - e^{\left\{ \left[a + b \left(\frac{T}{1000} \right) + \right. \right. \right\} \right\}} \right)$	$c\left(\frac{T}{1000}\right)^2 + d\left(\frac{T}{1000}\right)^3 + f \cdot p \cdot WHSV \cdot t$			
	stoichiometric coefficient fur	nction: $\alpha_i = x_i(e^{u_i \cdot C} + z_i) \cdot e^{v_i/T}$			

Table 2-2 MTO reaction pathways and rate expressions, with inclusion of a coke dependency term [74].

*Reaction pathway presented as simplified unbalanced reactions (side products omitted). MDOH refers to the lumped species of MeOH and DME.

** N_{N_2} refers to the molar flow rate of N_2 (mol/h). F_A is the molar flow rate of methanol feed (mol/min). t_p is the pulse duration (min). p_A and p_0 respectively refer to the partial pressure of compound A (MDOH) and the initial total system pressure (both in MPa). R is the gas constant (8.314 J mol⁻¹ K⁻¹). *C* is the weight percentage of coke on the catalyst in $g_{coke}/100 g_{cat}$.

*** C_nH_m refers to the rest of hydrocarbons (i.e., $C_5^=$ and paraffins).

Overall, considering the dependency of the products' distribution on the catalyst coke content, feed dilution, and temperature (as explained in section 2.2), a universal and acceptable kinetic model should consider all the aforementioned affecting parameters. In addition to that, the activity tests that resulted in the estimation of the kinetic rate constants ought to be conducted in conditions like industrial/realistic ones. Regrettably, some of the kinetic studies overlooked the influence of

catalyst coke content on product distribution [19] [72] [77], while others conducted the experimental tests under unrealistic conditions such as a heavily diluted feed with water [19] (as opposed to the industrial case of 20 wt.% dilution with water [26]). A few points need to be highlighted here concerning the derivation of a kinetic model. Firstly, to simulate a differential reactor with limited conversion, a very high WHSV must be employed, but one should be aware that the SAPO-34 catalyst tends to deactivate quite rapidly upon these conditions. Hence, utmost attention should be given to not collect data over partially deactivated catalyst. Intermittent (pulse) flow of feed could be a possible solution. Secondly, since the methanol conversion to light olefins reaction is not thermodynamically limited and backward reactions are not probable, the dependency of the methanol conversion rate on its concentration can be mirrored by different levels of dilution using an inert gas instead of products. However, the diluent should not block the active sites or alter the reaction mechanism, hence water is not a suitable fit, as one group [77] varied the water content in the feed from 0 to 75 wt.% and observed an influence of water dilution on the rate of each specific species' production. Besides this, to accurately mimic the actual reaction conditions, the diluent should impose similar molecular diffusion resistance as the actual products of the reaction (on methanol penetrating into the pores). For instance, methanol diffusion in dominant MTO products such as ethylene, propylene, and butene is not similar to methanol in argon. Table 2-3 summarizes the parameters and specifications of proposed kinetic models so once can assess the alignment of these models with the mentioned considerations.

Ref.	Temp (°C)	WHSV $(g_{MeOH}$ $g_{cat}^{-1}h^{-1})$	Dilution (wt. % of diluent in the feed)	Rate equation type	Produced and lumped species considered	Coke formation or deactivation consideration
[19]	400 - 450	10.7 - 37.2	69 wt% water	Power law	DME, CH ₄ , C ₂ H ₄ , C ₃ H ₆ , C ₄ H ₈ , C ₅ H ₁₀ , CO, CO ₂ , C ₂ H ₆	The effect of coke was not considered
[73]	400 - 550	57 - 2558	Helium as diluent, N/A wt%	Power law	C_2H_4 , C_3H_6 , C_4H_8 , C_5H_{10} , C_6H_{12} Lumped species: oxygenates (MeOH + DME), paraffins	Coke was included as a parameter C, referring to the wt % of coke on the catalyst
[72]	375 - 425	3.2 - 12.8	36 wt% water	Langmuir– Hinshelwood Power law	MeOH·S, DME·S, C ₂ H ₄ , C ₃ H ₆ Lumped species: paraffins	The effect of coke was not considered

Table 2-3 Evaluation of the proposed kinetic models for the MTO reaction over SAPO-34.

[74]	375 - 475	7.08 - 35.91	Nitrogen as diluent, N/A wt%	Power law	$\begin{array}{c} CH_4, C_2H_4, C_3H_6, C_4H_8\\ Lumped species: MDOH\\ (MeOH + DME), and rest\\ of hydrocarbons (paraffins,\\ except CH_4, and C_5^+) \end{array}$	Coke was included as a function of the final coke content, temperature, time, <i>WHSV</i> and methanol partial pressure
[77]	350 - 475	2.27 - 100	0 – 75 wt% water	Power law	C_2H_4 , C_3H_6 , C_4H_8 Lumped species: oxygenates (DME + MeOH) and rest of hydrocarbons (paraffins and C_5H_{10})	The effect of coke was not considered
[75]	450	1 – 500	~0.02 wt% Helium	Power law	$\begin{array}{c} CH_4, C_2H_4, C_3H_6, C_3H_8, \\ coke \\ Lumped species: C_4 (C_4H_8 \\ + C_4H_{10}), C_5 (C_5H_{10}, \\ C_5H_{12}, C_6H_{12} \text{ and} \\ paraffins) \end{array}$	Coke was included as a function of time
[78]	400 - 470	31.7 – 339.4	~69 wt% water	Power law	$\begin{array}{c} CH_4, C_2H_4, C_3H_6, C_3H_8, \\ C_4H_8 \\ \\ Lumped species: MDOH \\ (MeOH + DME), C_4 \\ (C_4H_{10} + 1, 3\text{-butadiene}), \\ and C_5^+ (includes C_2H_6) \end{array}$	A deactivation rate was introduced (in terms of grams of catalyst that deactivates per unit time)
[76]	450	1.68 - 8.40	20 – 60 wt% water	Power law	C ₂ H ₄ , C ₃ H ₆ Lumped species: C ₄	Coke was included as a function of time, the maximum coke content, methanol feed concentration, <i>WHSV</i> , and the density of the catalyst bed
[79]	400 - 490	1.5 – 3	40 – 70 wt% water	Langmuir– Hinshelwood –Hougen– Watson approach	DME, CH4, C2H4, C2H6, C3H6, C3H8, C4H8, C4H10, C5H10, H2, CO, CO2	The effect of coke was not considered
[80]	400 - 500	3 - 6	N/A	Langmuir– Hinshelwood –Hougen– Watson approach	DME, CH4, C2H4, C2H6, C3H6, C3H8, C4H8, H2, CO, CO2	A catalyst activity function was introduced as a function of temperature, time and <i>WHSV</i>

Note on commercial conditions: *WHSV* of 2-3 $g_{MeOH} g_{cat}^{-1}h^{-1}$; temperature of 400-450 °C; methanol dilution with 20 wt.% water [26].

2.5 Catalyst design and modification

2.5.1 Introduction to SAPO-34

SAPO-34 is a microporous silicoaluminophosphate that possesses a topology analogous to that of the naturally-occurring silico-aluminate chabazite (CHA) zeolite [81]. The structure consists of a three-dimensional pore system of alternating D6R (double-six rings) cages and large CHA cavities (~9.4 Å in diameter) that are accompanied by smaller sized eight-ring (8r) windows/ pore openings (3.8 Å) [81,82]. This 3D structure, alongside SAPO-34's molecular sieving capabilities, has been depicted in Fig. 2-8 in a variety of manners by different research groups. This ability makes SAPO-34 suitable for its application in the MTO process, allowing for the diffusion of primarily desired C₂ and C₃ olefinic products out of its framework. In comparison to the neutral aluminophosphate (AlPO₄-34) structure, which predominantly consists of alternating Al-O-P bonds, SAPO-34 possesses a similar framework, one in which primarily phosphorous atoms (of PO₄ tetrahedra) are substituted by silicon [83–86]. This is considered the first (and well-acknowledged) substitution mechanism (SM1), which forms Si (4A1) (isolated) structures, however, the second potential mechanism (SM2) involves the double substitution of neighboring Al and P by Si atoms, generating island-based entities i.e., Si (nAl) (n ranging from 3 to 0) [84-86]. Overall, the incorporation of Si⁴⁺ for P⁵⁺ (SM1 route) yields a negatively charged framework, hence, protons (as additional cations) with Brønsted acid properties are introduced into the structure as part of bridging hydroxyl groups (i.e., Si-OH-Al) for total charge compensation [84–86]. These ultimately play a major role as the active sites for the MTO reaction.


Fig. 2-8 (A) SAPO-34 (CHA type framework) topology structure alongside the composite building units [87]. (B) Geometry-optimized SAPO-34 structure, with the four O connectivities, indicated (Si–O–Si, Si–O–Al, Si–O–P, and Al–O–P). Here, the Si–O–Si species exists due to the presence of a Si island configuration. The illustrated Si–O–P linkage, which may be generated via the SM I mechanism, has not been experimentally observed [88]. (C) H-SAPO-

34 cell with two adjacent cages containing hydrocarbon pool species [89]. Color code: Al (pink), P (green), Si (yellow), O (red), H (white), C (gray). (D) H-SAPO-34 pore system demonstrating the large cages connected via 8-ring windows [89].

To this day, the hydrothermal synthesis approach exists as the most commonly used procedure for the generation of SAPO-34 molecular sieves [81,83]. The synthesis commences with gel formation via the mixing of different precursors (i.e., sources of Al, P, and Si) and the template (commonly tetraethylammonium hydroxide (TEAOH)). This is followed by the crystallization step, typically conducted in a Teflon-lined stainless-steel autoclave at 175-215 °C, with the total period of crystallization typically lasting ~24 h [83,90]. The subsequent steps utilized in the final formulation of SAPO-34 are separation of the solid from the liquid phase (via filtering or centrifugation), drying, and calcination (550-600 °C for 4-5 h, to remove volatile organic compounds, i.e., the template) [83,90]. Typically, the resulting catalyst particles are of a cube-like morphology [91,92], in the size range of hundreds of nanometers [93,94] to tens of microns [95,96]. However, alteration of the types of precursors utilized in synthesis (as well as the overall

procedure used) has shown to have varied effects on particle shaping, capable of generating sheetlike particles [97,98] and micro-spherical ones [97,99].

Overall, since SAPO-34 suffers from relatively rapid deactivation as a result of pore blockage by organic species, there exists a need to uncover methods to prolong the catalyst lifetime [23,24]. As will be seen in the following sections, research groups have begun to do so by employing techniques during synthesis as a means of reducing the catalyst particle size (to shorten the molecular diffusion pathway) as well as introducing secondary meso- and macro-pores, resulting in a hierarchical SAPO structure (to facilitate intra-particle diffusion). Furthermore, procedures involving template/ OSDA (organic structure directing agent) alteration alongside modifications in catalyst silicon content (which directly impacts active site content) have also been utilized to improve catalyst activity effects.

2.5.2 Catalyst modification by template alteration

Altering the structure-directing agent (i.e., template), a vital component utilized in zeolite synthesis could be an approach to tuning the performance and costs of the MTO catalyst. In general, tetraethyl ammonium hydroxide (TEAOH) is used as the primary template to produce a pure SAPO-34 structure. Due to its high cost, other cheaper templates such as morpholine (MOR), triethylamine (TEA), and diethylamine (DEA) have also been employed. These three alternative templates produce SAPO-34 with larger particle sizes, lower crystallinity, and substantial impurities [100]. Other templates have also been utilized for SAPO-34 synthesis, like piperidine [101], but the crystalline products included other phases of the SAPO family-like SAPO-17, SAPO-20, and SAPO-35. Recently, mixed-template SAPO-34 has gained considerable attention with the idea of initial nucleation of pure SAPO-34 crystals using TEAOH and further growth of crystals by adding cheaper alternative templates [102]. By implementing this method, researchers aim to produce cheaper SAPO-34 catalysts without sacrificing phase purity and particle size. In addition to that, mixed-template SAPO-34 samples have shown a longer lifetime by introducing new intergrowth structures. This makes internal active sites more accessible to the reactants and delays catalyst deactivation due to coke formation.

To date, several groups have investigated both single and mixed template SAPO-34 synthesis utilizing MOR/TEAOH [102], DEA/TEAOH [103], and TEA/TEAOH [104]. These groups have reported superior catalytic performance of mixed-template ones but failed to provide a clear justification as a distinct trend could not be seen among the samples concerning particle size, surface area, Si incorporation mechanism, acidity, and activity test results (i.e., the values were highly fluctuating). One group [103] inferred that the longest catalyst lifetime, achieved by a mixed-template sample (with 50% DEA and 50% TEAOH), was because of having an optimal average crystal size of about 1.15 μ m. Smaller crystals in the case of pure TEAOH template and bigger ones in the case of using pure DEA resulted in a shorter activity lifetime. This interpretation contrasts with other articles [24,105] that believe a smaller crystal size would result in a longer catalyst lifetime. Furthermore, discrepancies among the samples' silicon content and acidity were also observed [102]. According to the literature [106,107], the larger the Si content as part of the bulk composition, the greater the number of acid sites that should be formulated.

To summarize, although a few research groups have tried altering or combining templates, there are still some issues that need to be addressed. Firstly, no meaningful trends can be observed in the prementioned articles- this is with respect to the physicochemical properties of the catalyst upon the change of template ratios. Secondly, these articles have neglected the role of the gel pH and have used the same amounts of templates regardless of their basicity strength. Thirdly, there is still the need for a more in-depth justification for the superior performance of mixed-template synthesized SAPO-34. Fourthly, in the literature, the product distribution was presented excluding the coke formation, neglecting the fact that the coke formation rate plays an important role in process economy and the selection of the optimum catalyst. Furthermore, considering TEAOH, MOR, TEA, and DEA as the most popular and well-known templates for SAPO-34 synthesis, there is yet to exist any article that has assessed all templates in single and mixed forms under similar synthesis and reaction conditions to introduce the superior template. Finally, although articles have tried different orders with regard to precursor addition during the synthesis stage, no research group has compared the effect of this order on catalyst properties.

Hence, one of our subprojects was defined to address the pre-mentioned issues through in-depth experimental investigation and analysis to shed light on the relationships between (1) synthesis

procedure and catalyst properties, and between (2) catalyst properties and activity. In detail, we compared SAPO-34 catalysts prepared via single and mixed templates (TEAOH/MOR, TEAOH/DEA, TEAOH/TEA) using a variety of characterization tools, conducted MTO activity tests and in-situ measurement of the coke formation during the reaction using a thermogravimetric reactor coupled with mass spectrometry (TGR-MS). To the best of our knowledge, the work by Hu *et al.* [11] is the only study that has carried out TGR experiments. However, they exposed the catalyst to a 10 times higher weight hourly space velocity than for commercial reactors (i.e., *WHSV* of 21.8 *vs.* 2 $g_{MeOH} g_{Cat}^{-1} h^{-1}$), resulting in a very fast catalyst deactivation. Within our study, we used *WHSV* of 1 $g_{MeOH} g_{Cat}^{-1} h^{-1}$ and monitored the gradual coke formation and product evolution simultaneously. Subsequently, we did ¹³C-NMR spectroscopy over partially and completely coked catalysts to theorize a mechanistic pathway for coke evolution that aligns with the activity tests and characterization results.

2.5.3 Catalyst modification by silicon content adjustment

Due to the strong correlation that exists between silicon content and its incorporation mechanism in SAPO-34's crystalline structure with the amount and strength of generated Brønsted acidic sites (BAS), a large number of studies have adjusted the Si quantity in the commencing catalyst synthesis gel to decipher the optimal acidity leading to superior catalyst performance [106–109]. According to ²⁹Si NMR analysis, illustrated in Fig. 2-9, starting with a low Si content in the gel (up to a SiO₂/Al₂O₃ ratio of roughly 0.2), the Si incorporation mechanism is mainly dominated by SM1 (P atom substitution for Si), resulting in so-called isolated Si (i.e., Si(4Al)). However, when employing a higher amount of Si in the commencing gel, the Si incorporation mechanism is also contributed by SM2 (simultaneous adjacent Al-P pair substitution by two Si atoms), leading to Si-rich (island-like) environments (Si(nAl), n = 0-3) [110].



Fig. 2-9 ²⁹Si NMR spectrum for SAPO-34 (S-*x*) samples, where *x* stands for different SiO₂/Al₂O₃ ratios. (A) Adapted from [106]. (B) Adapted from [90]. (C) Adapted from [111]. (D) Adapted from [112].

The general observance, according to the literature [106,107], is that the larger the Si content incorporated into the bulk catalyst structure, the greater the total number of Brønsted acid sites generated - although, there is the possibility that a portion of Si forms as an extra-framework amorphous silica phase. This trend occurs up to the point in which isolated Si environments begin to transform into island-like configurations. It is worth mentioning that the number of BAS per incorporated Si is lower for Si islands relative to isolated Si environments. As a result, the trend shifts to either a stagnation [107] or slight depletion [106] in overall acidic site amount, as seen for the larger Si-containing samples in the NH₃ temperature programmed desorption (TPD) results of different research groups (Fig. 2-10).



Fig. 2-10 NH₃ temperature programmed desorption of SAPO-34(-*x*) samples with different SiO₂/Al₂O₃ (*x*) ratios. Adapted from (A) [106] and (B) [107]. The values beneath the peaks of (B) refer to acidic site density in $mmol_{NH3}/g_{cat}$.

By employing the pre-mentioned Si alteration method, groups have found that the optimal starting SiO_2/Al_2O_3 molar ratio, with the aim of achieving a superior catalyst lifetime, exists between 0.2 and 0.3, as seen in Fig. 2-11 [106,107,113]. With regards to light olefins selectivity, on the other hand, the greatest value was attained utilizing SAPO-34 of low acid site density (with a SiO_2/Al_2O_3 the molar ratio between 0.1 to 0.2 in the gel) [106,107,114], which possesses a framework structure of primarily isolated silicon environments (see Fig. 2-9). It has been generally found that exceeding the SiO₂ to Al₂O₃ molar ratio of roughly 0.2 to 0.3 results in an excess of strong Brønsted active sites, which can facilitate both aromatization of cycloalkanes, along with intermolecular hydrogen transfer reactions between polymethyl-benzenes/naphthalenes (PMBs and PMNs) and light olefins [115]. This can in turn amplify the formation rate of polycyclic aromatic compounds (as well as paraffinic species), ultimately resulting in much more rapid catalytic deactivation. The resulting decreased number of PMBs/ PMNs, which are active components of the hydrocarbon pool mechanistic concept, can also result in a concurrent depletion of light olefin production. Furthermore, samples constructed with too large silicon content in the gel have been found to possess dense cubic crystals with little to no macroporous cracks, relative to low Si-containing samples which seem to contain hollow, thin wall, SAPO crystals holding a large range of pore sizes (meso- and macro-, in addition to micropores) [106]. Macropore presence in SAPO-34 can permit the diffusion of reactant and product species despite the formation of coke (which initially

blocks microporous pathways only). Hence, the elimination of such macro-cracks in high Sicontaining samples can partly be blamed for the shortening of the catalyst lifetime. On the other hand, moving below the optimal SiO_2/Al_2O_3 range of 0.2-0.3 can result in a catalyst that does not possess the required number of acidic/ active sites to sustain long-term light olefin production. Once coke species begin to develop on these limited number of active sites, no further sites would be available for the adsorption and subsequent reactions involving further reactant methanol molecules. Although lower Si-containing samples (i.e., a lower SiO_2/Al_2O_3 ratio such as 0.1-0.2) is beneficial for light olefin production, as it suppresses the hydrogen transfer and aromatization reactions leading to coke, it is still important to introduce enough silicon during the gel stage of synthesis to ensure an adequate active site density in the SAPO framework to achieve timeextended methanol conversion [106].



Fig. 2-11 Methanol conversion activity test results for SAPO-34 (S-*x*) samples, where *x* stands for different
SiO₂/Al₂O₃ ratios. (A) At 450 °C and WHSV of 3 g_{MeOH} g⁻¹_{cat} h⁻¹. Adapted from [106]. (B) At 425 °C and WHSV of 1 g_{MeOH} g⁻¹_{cat} h⁻¹. Adapted from [107]. (C) At 400 °C and WHSV of 2 g_{MeOH} g⁻¹_{cat} h⁻¹. Adapted from [111].

2.5.4 Sub-micron SAPO-34 synthesis

SAPO-34 catalyst morphology with reduced particle size is highly desired due to its contribution in prolonging of catalyst lifetime [24,105]. Groups have declared that smaller particles are able to increase the exposure and accessibility of catalyst active sites as well as enhance the mass transfer properties of the catalyst. It also implies a shortened diffusion pathway and subsequently lower residence time of reactant and product species in SAPO micropores and cavities, which correspondingly yields lower rates of coke formation. This notion seems rational and has been well accepted, hence we speculate that a mere conflicting report [103], which introduced an optimum catalyst particle size $(1.15 \ \mu m)$ and claimed that smaller ones have inferior catalytic performance, may have overlooked the other affecting parameters (i.e., surface area, acidity, etc.). Accordingly, a large range of research groups have modified the conventional synthesis method to optimize this metric.

Microwave-assisted hydrothermal synthesis is one such method that has claimed to be capable of synthesizing nanocrystalline SAPO-34 catalysts relative to the conventional hydrothermal method i.e., 75-150 nm (see Fig. 2-12(A)) compared to the parent of a few microns [105,116,117]. This approach involving microwave irradiation of the synthesis gel under static conditions allowed for the reduction in crystallization time to only a few hours and allowed for more homogeneous nucleation of particles, yielding SAPO particle morphologies that were thin, smaller, more plate/sheet-like, and uniform. This ultimately resulted in roughly 50 to 60% enhanced catalyst lifetime (alongside maintained light olefins selectivity), justified by reductions in the diffusion pathway and decreased residence time of reactant and product species in the micropores of the catalyst [118].

Seed-assisted synthesis is an alternative technique that has been employed for the generation of higher surface area, nano-sized SAPO-34 within the range of 200-700 nm (Fig. 2-12 (B)) [93,119], which has displayed both a 4-fold enhanced catalyst lifetime and improved average light olefins selectivity in the MTO reaction [119–122]. In brief, this method operates via the addition of preconstructed SAPO-34 seed crystals to the initial synthesis gel, followed by the normal hydrothermal synthesis approach [123]. The seed crystals, which partially dissolve in the gel, take on the role of surfaces/ nuclei for newly growing crystals. As a result, one study [120] demonstrated that this method allowed for rapid nucleation, which effectively reduced the time for synthesis, as well as decreased consumption of template (OSDA) by up to 52%, which was declared to lower synthesis costs.

Alternatively, the generation of SAPO-34 nano-particles (50–350 nm in size, as seen in Fig. 2-12(C), relative to the parent of a few μ m) has been achieved through the use of a top-down approach known as post-synthesis milling and recrystallization [124–126]. In turn, the implementation of this technique has brought about improved MTO catalytic performance in terms

of both lifetime (a 5-fold enhancement) and LOS [126]. This method commences with synthesized SAPO crystals that are crushed via bead milling (such as using a planetary ball mill with water as a dispersing phase), followed by crystallinity recovery via hydrothermal recrystallization (utilizing an aluminophosphate solution). The use of X-ray photoelectron spectroscopy (XPS), in one study, was able to reveal that milling followed by post-recrystallization resulted in decreased Si content on the surface of SAPO particles relative to the bulk interior [126]. Hence, other than the reduction in particle size, this reduction in particle surface acidity could suppress the hydrogen transfer and aromatization reactions responsible for coke formation, retaining the interior active sites accessible.

Solvent-free hydrothermal synthesis, also termed dry gel conversion, exists as another method employed for the generation of nano-sized SAPO-34 crystals (in the range of 75 to 500 nm, as seen in Fig. 2-12 (D)) [127–131]. This method can operate either by evaporating the solvents contained in the final catalyst gel prior to the hydrothermal step [132], or alternatively, by grinding and mixing the required precursors in the absence of a solvent entirely [127]. In order to achieve a desirable H₂O/Al₂O₃ ratio, a certain quantity of water may potentially be introduced into the dry precursor, which is then followed by the typical hydrothermal portion of the synthesis [132]. Solvent-free hydrothermal allows for significantly reduced template consumption, which is obviously beneficial from an economic standpoint and has also meaningfully reduced the time for crystallization, with ~6 h of synthesis till successfully fully crystalline SAPO-34 [129–131]. Nanosized catalysts constructed via this methodology possess a hierarchical structure containing mesopores (in addition to the traditional microporous pathways) due to the stacking of nanocrystals, which has been claimed to enable the mass transfer of reactant and product species [132]. Overall, the implementation of this method has resulted in a prolonged catalyst lifetime (roughly two to four-fold increase) with equivalent to slightly greater light olefins selectivity, relative to that under the conventional hydrothermal method [129,131,132].

Sono chemical-based synthesis is introduced to be another technique utilized in the construction of SAPO-34 nano-catalysts (in the range of 50 nm to 450 nm, Fig. 2-12 (E)) [20,133–135]. This method involves the use of ultrasonic irradiation (rather than mechanical stirring) during the aging step, followed by a shortened hydrothermal step to minimize the overall growth of the crystal

nuclei. Due to the chemical effects ultrasonic waves impose (as a result of acoustic cavitation phenomena in the solution), the rate of nucleation enhances while the agglomeration of particles diminished, resulting in a catalyst with a larger total and external specific surface area than the traditionally prepared parent counterpart. Due to the reduced residence time of hydrocarbons species in nano-catalyst particles (i.e., as a result of shorter intercrystalline diffusion length), sono-synthesized catalysts have displayed reduced coke generation rate, and thus prolonged activity (roughly two-fold), alongside a similar product distribution to the conventionally prepared parent SAPO-34 (displaying a 2 μ m average particle size) [133].

Lastly, some groups have utilized crystal growth inhibitors (CGIs) during synthesis such as polyethylene glycol (PEG) (see Fig. 2-12 (F)), polyoxyethylene lauryl ether (Brij-35), methylene blue (MB), and surfactant, cetyltrimethylammonium bromide (CTAB)) [136,137]. This method consists of the addition of one or more of these pre-mentioned compounds as either the final precursor(s) or prior to template addition during the gel stage of SAPO synthesis. The added inhibitors are generally removed during the final calcination step. The CGIs are suggested to interact with reactive sites of inorganic precursors in solution, such as to give rise to an enhanced rate of nucleation. This is ensued by the adsorption of CGIs onto the external surface of generated nuclei, allowing for their separation, and thus lowering the rate of crystal growth. Overall, this results in the formulation of a larger number of smaller-sized crystals, without imposing any significant structure-directing effects during the generation towards the final catalyst framework (i.e., no clear major presence of competing phases). This method has resulted in catalysts with a much larger BET surface area than the conventionally prepared parent catalyst. A study that investigated the use of CTAB during SAPO-34 synthesis found that the optimal resulting catalyst, sized between 0.8-1 µm (compared to the parent of nearly 7 µm), displayed three times longer catalyst lifetime than the parent counterpart alongside higher selectivity towards light olefins [136].



Fig. 2-12 SEM/TEM images of the catalysts prepared via different sub-micron SAPO-34 synthesis techniques: (A)
 Microwave-assisted hydrothermal synthesis [118]; (B) Seed-assisted synthesis [121]; (C) Post-synthesis milling and
 recrystallization [126]; (D) Solvent-free hydrothermal synthesis [129]; (E) Sonochemical-based synthesis [20]; (F)
 Crystal growth inhibitors (CGIs) involved synthesis [137].

Although nano-sized SAPO-34 has proven useful in enhancing catalyst performance in the MTO reaction, the catalyst synthesis methods generally still face issues involving low yield, higher production costs, and serious difficulties concerning scale-up. Hence, a comprehensive costbenefit analysis of each technique seems to still be required to truly assess whether the benefits of improved catalyst performance outweigh the costs associated with these synthesis procedure adaptations. Furthermore, only a limited number of groups have investigated the effect of the combined application of these pre-mentioned methods e.g., the hydrothermal approach involving seed assistance followed by dry gel conversion [129]. A detailed exploration of the possible synergistic effects of multiple technique integration (in a singular synthesis procedure) seems yet to be undertaken.

2.5.5 Hierarchical SAPO-34 synthesis by pre- and post-treatment methods

Another strategy that has been utilized by research groups for the conquering of fast catalyst deactivation by coke involves the introduction of secondary macro- and mesopores to naturally

microporous SAPO-34 (i.e., resulting in a hierarchical structure) [138–141]. While micropores enable the molecular sieving process of SAPO-34, to maintain a high selectivity to light olefins, these secondary macro- and meso-pores are capable of improving the mass transfer properties of the catalyst. They have been shown to keep interior active sites accessible to reactants despite progressive coke blockage of micropores over time, which can accordingly prolong catalyst lifetime. To achieve the pre-mentioned, research groups have employed a variety of bottom-up (pre-treatment) and top-down (post-treatment) synthesis methods, which have been described as follows.

Pre-treatment methods generally involve the addition of secondary soft or hard templates into the catalyst gel during synthesis, which generally speaking, will burn during calcination, leaving behind macro- and meso-sized pores within catalyst particles that depend on both the size and morphology of these secondary templates. With regards to soft templates, one that is commonly employed is the organosilane surfactant [3-(trimethoxysilyl)propyl]-octadecyldimethylammonium chloride (i.e., TPOAC) [142,143]. This secondary template has been observed to adopt a dual role as a mesopore-generating agent and an alternative silica source precursor (alongside tetraethyl orthosilicate (TEOS) [142]) during synthesis. Due to the surfactant's adsorption behavior with regards to SAPO precursors, it has been also declared to possess crystal growthinhibiting capabilities (see Fig. 2-13(A), displaying the spherical agglomeration of nanosheet-like crystals for the pre-treated catalyst). The resulting catalyst has displayed an improved catalyst lifetime (two to four-fold) as well as maintained comparable [142] to enhanced [143] selectivity (by ~10%) towards light olefins (relative to the conventionally prepared parent counterpart). However, it can be argued that the use of organosilane surfactants as secondary templates is a relatively expensive approach [144,145]. Hence, another largely explored soft template includes the use of cost-effective polyethylene glycol (PEG) in a variety of molecular weights [146–150]. This compound has demonstrated similar capability in formulating hierarchical SAPO-34 catalysts with intercrystalline micro-, meso-, and macro-porosity (see Fig. 2-13 (B)). The resulting catalysts generated via this soft template have exhibited two to six times higher catalytic lifetime, alongside comparable to 10% improvement in light olefins selectivity. PEG employment has been shown to trigger a conflicting mix of either greater [148] or lower [147] concentrations of strong acidic (primarily Brønsted) sites, however, generally, groups have reported a depletion in average

Brønsted acidic strength upon its use (with reference to PEG of higher molecular weight i.e., 2000-4000 g/mol).

Other than the pre-mentioned soft templates, the use of hard (solid) structure directing agents has been used as an alternative approach by groups to introduce mesoporosity in SAPO-34 crystals. Here, groups have primarily investigated the use of carbon nanoparticles and nanotubes as secondary (hard) templates added during the culmination of the gel stage of catalyst generation (prior to the crystallization step) [144,145]. Then, as previously touched upon, the combustion of these secondary templates during calcination is ultimately responsible for the mesopore generation seen in the catalyst structure. One group that investigated the use of carbon nanoparticles as a hard template demonstrated its ability to enhance the catalyst's external surface area and increase the total pore volume, but the structures formulated were cavity-like rather than interconnected pores. This would have seriously hindered the catalyst mass transfer properties and internal diffusivity and also limited the accessibility of reactant species to internal active sites [145]. In turn, the resulting catalyst displayed no significant improvement in catalytic performance (i.e., with regards to lifetime and light olefins selectivity) relative to the parent catalyst. In order to alleviate the prementioned issues associated with nanoparticle templating, carbon nanotubes have been utilized instead as an alternative secondary template [144,145]. With respect to Fig. 2-13 (C), its implementation has led to the generation of mesoporous channels (of varying diameters and orientations) that connect the inner section of the catalyst to the external surface. This has resulted in a three-dimensional multi-pore network, rather than simple cave-like and unconnected pores. This approach demonstrated a prolonged catalytic lifetime in the MTO reaction with only slightly lower light olefin selectivity relative to the conventionally-prepared sample [144]. However, the slight reduction in LOS could be argued to be related to the greater collapse of the SAPO crystalline framework structure, which could hinder its molecular sieving capabilities.

On the contrary, the top-down method involves (generally chemically selective) post-treatment of the synthesized catalyst via the employment of acid or alkali-based etching agents that result in somewhat preferential extraction of framework cations [151–153]. Chemically selective etching, specifically desilication, of SAPO-34 catalysts has been undertaken, under ultrasonic conditions, via a fluoride medium post-treatment route involving HF-NH₄F mixed aqueous solutions

[151,152]. The resulting post-treated catalysts (prepared individually with one of MOR, TEA or TEAOH as micropore generating agents [152]) displayed the desired hierarchical-like structure (see Fig. 2-13 (D)) with slightly reduced average Brønsted acidic site strength, in turn performing better in terms of average light olefins selectivity (by $\sim 2\%$). In terms of catalyst lifetime, one study displayed a range of worse (by 25-30%) to comparable values for post-treated samples compared to the parent counterparts [152]. This was largely blamed on the observed SAPO crystallinity depletion alongside insufficiency in the number of catalyst active sites (due to reduced strong (primarily Brønsted) acidic site quantity). However, contrastingly, another group [151] observed a slightly enhanced lifetime (less than 2-fold) of their treated samples despite a similar large reduction in active site (BAS) concentration. Other than fluoride-based post-treatment, etching using TEAOH aqueous solution is another procedure that has been employed for the preparation of hierarchical SAPO-34 crystals [153]. The resultant catalysts here have displayed a doubling in catalyst lifetime alongside well-maintained average light olefins selectivity relative to the parent catalyst. However, the concentration of strong acidic sites (as well as strength) was reported to have been increased over treated samples, which seems to conflict with the observed and expected preferential desilication upon treatment. Generally, the choice of etching agent is crucial when it comes to controlling the preparation of hierarchical SAPO-34. For instance, the use of sodium hydroxide instead as a basic etching agent in the post-treatment of SAPO-34 has been observed to lead to a substantial reduction in crystallinity and selectivity remove phosphorus from the bulk structure, yielding amorphous aluminosilicate [154]. Another important consideration is the time duration associated with etching post-treatment, which has also been partly investigated by groups with regards to its effect on catalyst properties [151,152]. It was uncovered that increased treatment time resulted in reduced SAPO-34 crystallinity, more deeply etched crystals, larger secondary pores and greater desilication (which resulted in decreased Brønsted acidic site concentration).



Fig. 2-13 SEM images of the catalysts (fixated on one particle) produced via application of the different pre- and post-treatment techniques: (A) TPOAC as a secondary (soft) template. Adapted from [142]; (B) PEG as a secondary (soft) template. Adapted from [148]; (C) Carbon nanotube as a secondary (hard) template. Adapted from [144]; (D) HF-NH₄F mixed aqueous solution as an acid-based etching agent. Adapted from [152].

Discrepancies in the results of the alkali-treatment studies encouraged us to further study this technique. In our second subproject, diethylamine (DEA), a weak alkali, was utilized to better control the etching process and to avoid the destruction of the parent SAPO-34 framework. It seems acid or basic post-treatment alters the ratio of strong/weak acidic sites (more specifically, Brønsted to Lewis acidic sites), which may correspondingly affect the product distribution. However, there still exists a lack of studies fixated on the role of Brønsted and Lewis acidic sites (BAS and LAS) in the MTO reaction over the treated catalysts. Hence, we took a step further, and after precise measurement of the acidic site's density and the product distribution over the parent and treated catalysts, we tried to uncover the role of BAS and LAS in the MTO reaction by DFT modeling. With the aid of comprehensive catalyst characterization techniques, DFT modeling, and precise analysis of the products over parent and treated samples, we aim to assess the effect of etching on the catalyst physiochemical properties (with emphasis on the LAS to BAS ratio) and relate them to the catalytic activity performance.

2.5.6 SAPO-34 promotion using secondary metal

metal modification of SAPO-34 has been studied in the hope of prolonging catalyst lifetime and boosting light olefins selectivity. To the best of our knowledge, so far, the following metals have been tested in this respect: Co, Ni, Fe, La, Ce, Y, K, Ag, Ca, Cu, W, Mg, Mn, Ge, Zn, Ti, and Zr [155–172]. Secondary metal promotion via one-pot synthesis (so-called direct incorporation or isomorphous substitution) has shown superior results over impregnation and physical mixing techniques [155]. This is due to the fact that the metal-incorporated catalyst (Me-SAPO-34) results

in higher dispersion of the promoter in the framework as well as enhanced interaction with the parent catalyst while imposing less negative effect on the surface area and crystallinity. The majority of the research groups have inferred that metal-promoted SAPO-34 displays superior performance with respect to lifetime and LOS. On the contrary, some articles have even partially backed up the idea of metal-incorporated catalysts performing worse than the parent [158,161,165,168]. The groups who have observed catalytic enhancement upon metal incorporation have primarily attributed this to a reduction in acidity. It is generally declared that the acidity is sufficient to catalyze the dehydration of methanol to light olefins, but too low to promote side reactions involving aromatization and intermolecular hydrogen transfer of hydrocarbon species. Hence, this reduces the production of alkanes and multi-ring aromatics (i.e., coke), which in turn lengthens the catalyst's active period and improves light olefins selectivity [155–160]. However, these articles overlook the fact that the acidic content can be easily manipulated by altering the silica content in the starting catalyst gel. Several research groups [173,174] have tried different silica content and found an optimum SiO_2/Al_2O_3 ratio of 0.2-0.4. These pre-mentioned articles already use the ideal silica content/ acidity in preparation of the parent catalyst, hence, acidity changes upon metal incorporation (which generally reduces silica content/ acidity to below optimum levels) cannot possibly be the justification of better catalytic performance. Since metal promotion is usually coupled with negative catalytic consequences, such as a loss in acidity, surface area, and crystallinity, a fundamental reasoning as to why metal promotion boosts activity still needs to be established.

In terms of the metal loading, a majority of the articles have tried a 0.05-0.08 Me/Al₂O₃ ratio in the initial gel [156,158,160,169,172], while some groups have tested lower values (0.005-0.01) [161,162,164], and some higher (around 0.1-0.12) [163,166]. Some studies [162,163] have fixated on deciphering the optimum loading amount and have found that the metal content has a crucial effect on the promoted catalyst performance, but it should be noted that this optimum metal content cannot be generalized to all metals and could vary from one metal to another. A more comprehensive outlook into the metal-promoted SAPO-34 studies, including the reaction conditions, metal loading, gel formula, and catalyst performance, can be found in Table S 1.

Overall, by observing the results of the conducted research in metal modification of SAPO-34, clear contradictions can be spotted. Even while employing similar metals, opposing catalytic performances have been reported. For instance, in the case of Ni-incorporated SAPO-34, there have been reports of significantly improved [160], unchanged [161], and slightly worsened [168] light olefins selectivity (relative to the parent catalyst). This demands a comprehensive study on metal-promoted SAPO-34. Our fourth subproject looks to examine a wider range of metalincorporated catalysts than typically seen in the literature. By utilizing seven of the metals that have already been evaluated (Mg, Ca, Mn, Fe, Ni, W, Ce), alongside thirteen additional metals that have not been investigated (Li, V, Zr, Mo, Ga, In, Sn, Tl, Pb, Ru, Nd, Sm, Gd), we aim to offer a thorough comparison of the similarities and distinctions of metals of diverse periodic groups (with correspondence to their performance). Our study also seeks to better clarify the link between characterization outcomes and catalytic results. Furthermore, we will take a step further by co-feeding hydrogen to metal-promoted SAPO-34. Hence, the possible synergistic effects of metal promotion and hydrogen can be examined that may in theory selectively crack heavy hydrocarbons, leading to a boost in LOS and a longer catalyst lifetime. In contrast to the previous hydrogen co-feeding attempt [175] at high pressure, that resulted in substantial LOS depletion, we will instead utilize ambient pressure conditions- a more economically and commercially favourable approach.

2.5.7 Catalyst shaping

Despite the intense research on SAPO-34 catalyst modification to lengthen the catalyst lifetime and mitigate the coke formation, the study of the catalyst final shaping for fluidized-bed application has remained sparse. Due to the fast deactivation of the SAPO-34 catalyst (within a few hours) by coke formation, a fluidized-bed reactor with simultaneous catalyst regeneration is essential on an industrial scale [176]. As the gaseous products leave the MTO reactor from the top, the catalyst particles entrained in the gas phase are collected using multi-stage cyclones by centrifugal force. The as-synthesized SAPO-34 cubic particles are generally in the range of 1-5 microns, whereas efficient catalyst recovery using cyclones demands larger sizes. As a result, further catalyst shaping is required to form SAPO-34 agglomerates with a size bracket of 50-100

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 μ m [177]. In-situ synthesis of large SAPO-34 crystals (45-50 μ m) using morpholine as the template has been investigated, but long intraparticle mass transfer distance caused fast deactivation (the conversion depleted from 100% to 50% in less than 20 min time on stream at WHSV of 2.85 g_{MeOH} g_{cat}⁻¹ h⁻¹ and reaction temperature of 450 °C) [178]. Mixing the SAPO-34 particles with a binder (usually silica or alumina) and using a spray dryer to form agglomerates is the conventional technique that is subject to major drawbacks. Blocking the pores of the SAPO-34 catalyst by the binder and substantial reduction in the catalyst's surface area, inaccessibility of the portion of the catalyst which lies in the middle of the agglomerates, undesired physicochemical changes of the parent catalyst after mixing with the binder slurry, and intense erosion and loss of the catalyst due to the irregular coarse shape of the agglomerates. Recently, the in-situ formation of SAPO-34 catalyst on the external surface of micro-spherical Kaolin has been tried [179]. By this method, precious SAPO-34 catalyst will not be buried in the middle of the agglomerate, instead, affordable Kaolin microspheres would provide the supporting bulk and their external surface will be covered by SAPO-34 particles. In addition to that, the abrasion will be less intense due to the spherical shape of the Kaolin particles. The group [179], prepared the SAPO-34 synthesis gel and added it to the kaolin microspheres before the hydrothermal step (dry kaolin to gel weight ratio of 0.4). They treated the kaolin microspheres with different concentrations of NaOH aqueous solution to make a rough surface on the microspheres to enhance SAPO-34 loading on the external surface. More intense NaOH treatment resulted in higher SAPO-34 loading. They reported 9 times longer activity over the SAPO/Kaolin sample (that was treated with 4% NaOH solution and contained 9 wt% SAPO-34) than the pure SAPO-34 catalyst. They didn't provide any reasoning for this longer lifetime as in the best scenario, the SAPO/Kaolin should have had the same activity as the pure SAPO-34 showing a successful mount of SAPO-34 over the support (i.e., Kaolin) without any change in its physicochemical properties. In another study, Jie et. al [179] attempted to adhere SAPO-34 crystals to the support by providing the silica and alumina required for SAPO-34 synthesis from kaolin (Al₂Si₂O₅(OH)₄). SAPO-34 loading reached almost 22 ± 1 wt.% over kaolin and illustrated superior performance compared to the conventional spraydried SAPO-34 sample (which was prepared using silica as the binder with 25% SAPO-34 content). The surface area of the spray-dried SAPO-34 was not reported but pore size distribution for the two catalysts clearly showed a more developed mesoporous structure in SAPO/Kaolin

sample which was referred to by the authors as the main reason for improved performance. Zhou et. al [178], on the other hand, tried SAPO-34 assembly on the α -Al₂O₃ spheres (0.8 m² g⁻¹ surface area). The SAPO-34 content on α -Al₂O₃ spheres was measured to be around 6.5 wt.% This can be a main downside as it may lead to a completely different reactor design to meet a longer contact time of the reactant and the catalyst (to compensate for the low loading of SAPO-34). As a reference, free SAPO-34 with the same gel formula and spray-dried SAPO-34 (SAPO-34/silica mass ratio of 1/3) were also manufactured. All three catalysts were tested for DME conversion to olefins based on the SAPO-34 content of the catalyst (as the active phase for the reaction). The free SAPO-34 catalyst and SAPO-34 / α -Al₂O₃ sample had almost similar activity while the spray-dried sample showed inferior performance. They also showed the importance of the microsphere's surface structure and chemical properties as an important role in the initiation of SAPO-34 particles' formation on silica microspheres and α -Al₂O₃ ones. Over silica microspheres, in contrast to α -Al₂O₃, SAPO-34 crystals were populated unevenly. Fig. 2-14 summarizes the SEM images of the produced SAPO-34 mounted catalysts from the literature.



Fig. 2-14 SEM images depicting the morphology of composites: (A) SAPO-34/kaolin microsphere. Adapted from [180]; (B) SAPO-34/silica microsphere. Adapted from [181]. (C–G) SAPO-34 on calcined kaolin microspheres treated with NaOH solutions of (C) 0, (D) 2, (E) 4, (F) 10, and (G) 14 wt.% concentrations (prior to use in the MTO reaction). Adapted from [182].

The poor adhesion and low SAPO loading of the composite catalysts prepared in former studies, motivated us to delve into this technique and try to improve the catalyst for the fluidized-bed application. By utilizing kaolin microspheres (having equimolar Si and Al elements), controlling the silica incorporation into the SAPO-34 framework, which determines the acidic strength and has a crucial effect on the catalyst performance, is challenging. α -Al₂O₃ microspheres (MS), on the other hand, have low surface area and reactivity which results in low SAPO-34 loading and poor adhesion. In our third subproject, we will attempt to mount SAPO-34 over γ -Al₂O₃ in high-weight content. γ -Al₂O₃ has a higher surface area than α -Al₂O₃ and kaolin (190 m² g⁻¹ compared

to 1 and 35 m² g⁻¹, respectively) and has been widely tested for methanol conversion to DME, a known intermediate in the MTO reaction [183]. Furthermore, a novel fabrication technique using microwave heating will be employed. Microwave-assisted SAPO-34 synthesis due to homogeneous heating and enhanced nucleation compared to conventional heating via oven has proved to shorten crystallization time and yield smaller particles [184,185]. Spray-dried SAPO-34 will also be prepared and studied comprehensively to truly assess the consequences of SiO₂ addition on the physicochemical properties of SAPO-34.

3 Methodology

3.1 Catalyst synthesis and modification methods

3.1.1 Parent catalyst synthesis method

Gel composition ($n_1Al_2O_3/n_2P_2O_5/n_3SiO_2/n_4T/n_5H_2O$), type of precursors and templates, time and temperature of mixing, aging, hydrothermal and calcination are crucial in resulting the optimum SAPO-34 catalyst. After a thorough review of the literature and preparing over 30 batches of catalysts, the optimum parent catalyst with similar performance as the commercialized SAPO-34 was developed. The parent SAPO-34 synthesis procedure has been explained as follows but further explanation of the techniques used in each subproject has been elaborated in the following sections.

Parent SAPO-34 was synthesized using aluminum isopropoxide (AIP 99% Sigma Aldrich), phosphoric acid (85% aqueous solution, Sigma Aldrich), colloidal silica (Ludox 40% aqueous solution, Sigma Aldrich), and tetraethylammonium hydroxide (TEAOH 40% aqueous solution, Sigma Aldrich) as the precursors of Al, P, Si, and the template, respectively. The molar composition of the synthesis gel was $1.0 \text{ Al}_2\text{O}_3$: $1.0 \text{ P}_2\text{O}_5$: 0.3 SiO_2 : 2.0 TEAOH: $70.0 \text{ H}_2\text{O}$ (using the optimum silica content [186,187]). For the synthesis of a catalyst batch, as illustrated in Fig. 3-1, typically 16.34 g AIP was dissolved in 30 g of deionized water at 50 °C for 2 h, then 1.8 g SiO₂, 29.45 g TEAOH, and 9.22 g H₃PO₄ aqueous solutions were added dropwise using a syringe pump and one hour mixing time was considered in between each step. The flask containing the prepared gel was capped and further stirred for 20 h at 50 °C as the aging step. Then, the gel was transferred into a stainless-steel Teflon-lined autoclave (Berghof, Germany) heated up to 200 °C by 1 °C min^{-1,} and kept for 48 h under autogenous pressure. After hydrothermal crystallization, the solid particles were separated from the liquid by repeated washing and centrifugation, dried overnight at 90 °C, and calcined at 550 °C for 5 h.



Fig. 3-1 Simplified scheme of SAPO-34 catalyst preparation.

3.1.2 Catalyst synthesis regarding template alteration method (concerning chapter 4)

SAPO-34 samples were prepared using aluminum isopropoxide (99%, AIP), silica solution (40% in water, LUDOX), tetraethyl ammonium hydroxide (40% in water), morpholine (99%), triethylamine (98%), diethylamine (98%) and orthophosphoric acid (85% in water, H₃PO₄) as precursors (all purchased from Sigma Aldrich in ACS grade). In this study, two methods were utilized to prepare SAPO-34 molecular sieves, which differed with regard to the order used for precursor addition. Method 1 commences with AIP dissolving in water for 2 h under rigorous mixing. Concurrently, in a separate breaker, an appropriate quantity of silica suspension was dissolved into the template to get a clear solution in 2 h. These two mixtures were combined gradually, and phosphoric acid was added dropwise as the final step. Concerning method 2, the order of addition of precursors was different: it commenced with AIP, followed by phosphoric acid addition, and finally, the Si solution with template was added. The prepared gels in both methods were aged for 24 h under agitation and transferred to a 120 ml PTFE-lined (polytetra-

fluoroethylene) stainless steel autoclave (Berghof, Germany). Hydrothermal crystallization was conducted at 200 °C for 2 days. The produced crystals were recovered from the parent solution by centrifugation and washing several times with deionized water. The resulting precipitate was dried at 90 °C overnight and calcined at 550 °C for 5 h. The molar composition of the synthesis gels was kept constant in terms of all precursors as $1.0 \text{ Al}_2\text{O}_3/ 1.0 \text{ P}_2\text{O}_5/ 0.3 \text{ SiO}_2/ 1.5-3.0 \text{ Template}/ 70 \text{ H}_2\text{O}$. In the case of the mixed-template samples, TEAOH was mixed with one of MOR, DEA, or TEA to decrease the TEAOH consumption as it is substantially more expensive than the other templates. The crystallization started with TEAOH with the initiation of pure SAPO-34 nucleation, and then a complimentary template (MOR, DEA, or TEA) was added for the crystal growth. The ratio of TEAOH to the second template was kept constant at 1/3 to satisfy the limited usage of TEAOH. The total amount of template used was adjusted to reach the optimum gel pH, which would result in higher crystallinity and surface area. The type and amount of templates used for different samples have been presented in Table 3-1.

	Template molar ratios				Total template used	
Sample*	ТЕАОН	MOR	TEA	DEA	$(mol/mol_{Al_2O_3})$	
TEAOH-1	1	0	0	0	2.0	
TEAOH-1β**	1	0	0	0	2.0	
TEAOH-2	1	0	0	0	1.5	
MOR-1	0	1	0	0	2.5	
MOR-2	0	1	0	0	2.0	
DEA-1	0	0	0	1	2.5	
DEA-2	0	0	0	1	2.0	
TEA-1	0	0	1	0	3.0	
TEA-2	0	0	1	0	3.0	
TEAOH/MOR-1	1	3	0	0	2.5	
TEAOH/MOR-2	1	3	0	0	2.0	
TEAOH/DEA-1	1	0	0	3	2.5	
TEAOH/DEA-2	1	0	0	3	2.0	
TEAOH/TEA-1	1	0	3	0	3.0	
TEAOH/TEA-2	1	0	3	0	3.0	

Table 3-1 Catalyst samples notation and template molar ratios

* The suffix digits (1 and 2) refer to synthesis methods 1 and 2, respectively.

** This sample was prepared with the same order of precursor addition as method-1; however, silica was added separately from the template.

3.1.3 Alkali treatment method (concerning chapter 5)

The molar composition of the synthesis gel was 1.0 Al₂O₃: 1.0 P₂O₅: 0.4 SiO₂: 2.0 TEAOH: 70.0 H₂O (using the optimum silica content [186,187]). For the synthesis of a catalyst batch, 16.34 g AIP was dissolved in 30 g deionized water at 50 °C for 2 h, then 1.8 g SiO₂, 29.45 g TEAOH, and 9.22 g H₃PO₄ aqueous solutions were added dropwise using a syringe pump and one hour mixing time was considered in between each step. The flask containing the prepared gel was capped and further stirred for 20 h at 50 °C as the aging step. Then, the gel was transferred into a stainless-steel Teflon-lined autoclave (Berghof, Germany) heated up to 200 °C by 1 °C min⁻¹ and kept for 48 h under autogenous pressure. After hydrothermal crystallization, the solid particles were separated from the liquid by repeated washing and centrifugation, dried overnight at 90 °C, and calcined at 550 °C for 5 h.

The Alkali post-treatment method was conducted by mixing the prepared parent SAPO-34 with 0.5, 1.0, 2.0, and 4.0 molar DEA aqueous solution using an orbital shaker. The samples were named 0.5, 1.0, 2.0, and 4.0 DEA/SAPO-34, respectively. More specifically, 3 g of the dried parent catalyst was added to 10 ml DEA solution and stirred for 5 h. This was followed by solid-liquid separation by centrifugation, drying, and calcination which were analogous to the parent catalyst preparation method. To find the optimum DEA concentration and mixing time, a few preliminary blind tests were conducted which can be found in the supplementary information (Fig. S 7 and Fig. S 8).

1

3.1.4 Catalyst synthesis for fluidized-bed application (concerning chapter 6)

The molar composition of the synthesis gel was 1.0 Al₂O₃: 1.0 P₂O₅: 0.3 SiO₂: 1.5 TEAOH/ 2.5 TEA: 70.0 H₂O (using the optimum silica content [186,187]). Typical synthesis commenced with dissolving AIP in water followed by dropwise addition of phosphoric acid, template, and silica. The prepared gel was transferred into a stainless-steel Teflon-lined autoclave (Berghof, Germany) and heated up to 200 °C by 1 °C min⁻¹ and kept for 48 h under autogenous pressure. After hydrothermal crystallization, the solid particles were separated from the liquid by repeated washing and centrifugation, dried overnight at 90 °C, and calcined at 550 °C for 5 h. The samples were named TEAOH-SAPO and TEA-SAPO according to the type of template utilized.

For comparison, the spray-dried (SD) catalyst was also prepared. Parent catalyst (i.e., TEAOH-SAPO) was mixed with SiO₂ solution (in the SAPO-34 over SiO₂ mass ratio of 1/1) and spray dried using countercurrent hot air. The agglomerates were sieved later to collect particles within the range of 30-60 μ m and labeled as SD-TEAOH-SAPO.

The SAPO-34 mounted over γ -Alumina microspheres (MS, 30-60 µm, Fisher) were synthesized in two steps. First, the surface of γ -Alumina microspheres was treated using phosphoric acid and template (with the molar ratio of 1.0 Al₂O₃: 0.5 P₂O₅: 1 template: 30.0 H₂O) at 90 °C for 10 min via microwave heating at 200 W (CEM microwave oven MARS6). The microspheres (now having AlPO₄-34 on the outer surface) were washed using deionized water and retrieved using centrifugation from the gel residue (that contains the extra acid, template, and dissolved alumina). A certain amount of silica and template were added (analogous to the parent counterparts with the aim of reaching 50 wt% loading of SAPO-34 over γ -Alumina microspheres) and the mixture went through microwave-assisted hydrothermal at 200 °C for 2 h (using 800 W power). Washing, centrifugation, drying, and calcination steps were implemented similarly to the parent catalysts and the samples were identified as TEAOH-SAPO/ γ -Al₂O₃ MS and TEA-SAPO/ γ -Al₂O₃ MS based on the template employed, where MS denotes microsphere.

3.1.5 Metal-incorporated catalyst synthesis (concerning chapter 7)

The synthesis procedure typically commenced by dissolving AIP in water under rigorous mixing. This is followed by the dropwise addition of template, silica, the aqueous solution of the secondary metal (Table 3-2), and finally phosphoric acid. The prepared gel was aged for 24 h under agitation and transferred to a 120 ml PTFE-lined (polytetrafluoroethylene) stainless steel autoclave (Berghof, Germany). Hydrothermal crystallization was conducted at 200 °C for 2 days. The produced crystals were recovered from the parent solution by centrifugation and washing several times with deionized water. The resulting precipitate was dried at 90 °C overnight and calcined at 550 °C for 5 h. The molar composition of the synthesis gels was kept constant for all the samples as 1 Al₂O₃/ 1 P₂O₅/ 0.3 SiO₂/ 0.05 Me/ 2 TEAOH/ 100 H₂O, where Me refers to the metal.

Index	Metal precursor	Formula	Mw	purity (%)
1	Lithium hydroxide monohydrate	$LiOH\cdot H_2O$	41.96	99.00%
2	Magnesium nitrate hexahydrate	Mg $(NO_3)_2 \cdot 6H_2O$	256.41	99.00%
3	Zirconium (IV) oxynitrate hydrate	ZrO (NO ₃) ₂ · xH ₂ O	231.23	99.00%
4	Thallium (I) nitrate	TlNO ₃	266.39	99.90%
5	Iron (III) nitrate nonahydrate	Fe $(NO_3)_3 \cdot 9H_2O$	404	98.00%
6	Vanadium (III) chloride	VCl ₃	157.3	97.00%
7	Indium (III) nitrate hydrate	In (NO ₃) ₃ · xH ₂ O	300.83	99.90%
8	Tin (II) chloride	SnCl ₂	189.62	98.00%
9	Lead (II) nitrate	Pb (NO ₃) ₂	331.21	99.95%
10	Manganese (II) nitrate hydrate	Mn (NO ₃) ₂ · xH_2O	178.95	98.00%
11	Nickel (II) nitrate hexahydrate	Ni (NO ₃) ₂ · 6H ₂ O	290.79	98.00%
12	Ammonium molybdate (VI) tetrahydrate	(NH4) 6M07O24·4H2O	1235.86	99.00%
13	Ammonium meta tungstate hydrate	$(NH_4)_6 H_2 W_{12} O_{40} \cdot x H_2 O_{40}$	2956.3	99.99%
14	Calcium nitrate tetrahydrate	$Ca~(NO_3)_2\cdot 4~H_2O$	236.15	99.00%
15	Gallium (III) nitrate hydrate	Ga (NO ₃) ₃ · xH ₂ O	255.74	99.50%
16	Neodymium (III) nitrate hexahydrate	Nd $(NO_3)_3 \cdot 6H_2O$	438.3	99.90%
17	Samarium (III) nitrate hexahydrate	Sm ((NO ₃) ₃ · 6H ₂ O	444.5	99.90%
18	Cerium (III) nitrate hexahydrate	Ce $(NO_3)_3 \cdot 6H_2O$	434.22	99.50%
19	Gadolinium (III) nitrate hexahydrate	Gd $(NO_3)_3 \cdot 6H_2O$	451.4	99.90%
20	Ruthenium (III) nitrosyl nitrate solution, Ru 1.5 wt.%	Ru (NO)(NO ₃) ₃	317.09	99.0%

Table 3-2 Metal precursors tested as promoters of SAPO-34 catalyst.

3.2 Catalyst characterization

3.2.1 Phase determination and crystallinity

X-ray diffraction (XRD) is generally the first characterization tool employed for crystallinestructured catalysts. It is utilized to verify that the desired phase has been formed via peak matching of the sample with that of its reference pattern. The tool operates via the emission of incident X- ray beams onto the specimen usually within the desired 2θ angle range [188,189]. With reference to Bragg's law, either constructive or destructive wave interferences will take place; hence, based on the interplanar distances, only the constructive interferences will result in a diffraction pattern that acts as a fingerprint for each specific material. It should be noted that for most crystalline materials, the copper *K*- α radiation (with a wavelength of 1.5418 Å) was employed as opposed to radiation from other metallic anodes, due to its appropriate wavelength which maintains d-spacing accuracy i.e., does not shift the diffraction pattern towards low or high Bragg angles.

For crystalline phase recognition, X-ray diffraction patterns of our calcined samples were recorded on a Bruker D8 Advance diffractometer equipped with a LYNXEYE linear position sensitive detector (Bruker AXS, Madison, WI). Data was collected using a continuous coupled $\theta/2\theta$ scan with Ni-filtered Cu *K* α ($\lambda = 1.54178$ Å) radiation operating at 40 kV and 40 mA. The scans were collected at increments of 0.02° and in 2 θ range of 5 to 60°.

3.2.2 Surface area and pore size measurements

Physisorption analysis is one of the most commonly used tools today to measure the specific surface area of porous materials [190,191]. Typically, the linear region of the N₂ adsorption isotherm data at 77 K (i.e., the 0.05 to 0.35 region of the $P/(V(P^0 - P))$ vs. P/P^0 graph) is used as the basis of BET methodology calculations in the determination of the total specific surface area over porous catalysts [192,193]. By interpretation of the linear region's slope and intercept, one can uncover the values of the constants V_m and C. Here, V_m refers to the gas volume required to form a complete monolayer. C is a constant that is proportional to the exponential of the difference between the enthalpy of adsorption of the 1st layer and that of all subsequent layers. The value of V_m , once uncovered, is subsequently utilized to compute the total specific surface area. This is accomplished by multiplication of V_m with the Avogadro's constant (N_A) and the cross-sectional area of the adsorbed molecules, divided by both the molar volume of adsorbed gas and the mass of sample.

Physisorption analysis via the t-plot method has been demonstrated to be a useful tool in the measurement of the external surface area (macro- and meso-pores) and the specific micropore volume of SAPO-34 catalysts. By plotting the volume of adsorbed nitrogen (V_a) as a function of

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the statistical thickness (t) of the adsorbed layer, one should expect a linear region in the medium thickness range. By extrapolating this linear region to the V_a axis, the specific micropore volume and external surface area can be retrieved from the y-intercept and slope, respectively [194]. It should be noted that the thickness curve should be preferentially derived from N₂ adsorption tests conducted on non-porous reference materials (with the same physicochemical properties). However, considering the pore-containing structure that SAPO-34 possesses, universal thickness curves are normally used instead [195].

The Barrett, Joyner, and Halenda (BJH) methodology is commonly used to uncover the pore size distribution of a material by use of the desorption curve, retrieved from physisorption isotherm data [196]. The theory is based on two underlying statements. Firstly, it assumes that pores are of a cylindrical shape and are non-connected. Secondly, the quantity adsorbed is assumed to be the sum of both physisorption on pore walls, as well as capillary condensation in mesopores. In turn, the pore radius computed by the BJH method is the sum of both the physical desorption multilayer thickness (i.e., the thickness of the film adsorbed on pore walls, computed via the empirical Halsey equation) and the liquid-vapor meniscus radius (from the Kelvin equation) [197,198]. Although this method has been generally utilized to determine the pore size distribution of microporous material, due to its stringent hypotheses, it has been shown to yield somewhat unreliable results (a 20% error) for pore diameter calculations on pores sizes smaller than 5 nm [198,199]. Although other methods, such as non-local density functional theory (NLDFT), have demonstrated greater accuracy in depicting sub-meso pore sizes, the BJH method, nevertheless, follows the general distribution trend like that of other methods. Overall, the BJH method still provides a semiquantitative analysis of the contribution of different pore sizes with regard to microporecontaining materials like SAPO-34 [200].

Nitrogen physisorption isotherm on our samples was obtained at -198.5 °C using the Micromeritics Gemini VII device with a p/p_0 precision of 10⁻⁴. In a typical measurement, 150-200 mg of the sample was weighed, dried, and degassed under 50 ml min⁻¹ of helium (99.999% Linde) at 250 °C for 2 h reweighed and then degassed by high vacuum (0.02 mmHg). The adsorption and desorption isotherms were each recorded over 40 relative pressure values (p/p_0) ranging from 0 to 1.

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3.2.3 Morphology

Morphological characterization was carried out via the use of imaging/ microscopic techniques, such as scanning electron microscopy (SEM). SEM operates by employing a focused incident beam of accelerated electrons (using electrostatic or electromagnetic lenses) from a cathode onto a sample, which in turn ejects a mixture of X-rays, primary backscattered electrons, and secondary electrons. These are collected at a detector and are subsequently used to formulate an image on a corresponding display screen [201,202]. The morphological characterization of multi-phase materials is generally conducted via the analysis of the back scattered electrons (BSE) emitted by the sample in a scanning electron microscope [203]. Heavier elements (i.e., elements possessing a greater number of protons/ Z-number) can generate more BSEs, and in turn appear brighter, relative to lighter elements [204]. Hence, this presents as a useful tool when performing the morphological analysis of SAPO-34 catalyst modified with secondary metal species. Since the metals utilized for promotion are typically derived from both the transition and rare earth series (which are heavier relative to Si, P, and Al), SEM-BSE can help distinguish the secondary metal and can be correspondingly used to evaluate the distribution uniformity of the promoted metal in the SAPO-34 structure. Generally, zeolites and SAPO materials are not electrically conductive, hence, the SEM images generated tend to be blurry and highly bright. The two easiest approaches to counteract this problem are to utilize low electron volts (2-5 keV) during SEM operation or conduct the test in a low vacuum mode (which injects air molecules into the chamber, essentially absorbing some of the incident electron beams) [205,206]. A final approach can be to coat the sample of interest with either carbon or a highly conductive metal (such as platinum) [205].

The morphology of our catalysts was observed using a scanning electron microscope (Hitachi SU-3500), with an accelerating voltage of 5 kV, under partial vacuum mode (40 Pa). A technique used to avoid blurry images due to the charging effect in the case of non-conductive materials like SAPO-34. Also, a back-scattered electron (BSE) detector was applied as it provided an enhanced contrast between the catalyst particles and the carbon tape as the background.

3.2.4 Bulk elemental composition

In order to investigate the bulk elemental composition of a produced catalyst, the most commonly employed methods are inductively coupled plasma (ICP) spectroscopy and X-Ray fluorescence (XRF) spectroscopy. The ICP-based technique can operate in a variety of manners depending on the spectroscopy method utilized (e.g., mass spectrometry (MS) and atomic emission spectroscopy (AES)). ICP-MS elemental analysis, for instance, consists of using a plasma torch (usually made from argon gas) to induce the first ionization events in a sample [207,208]. The corresponding generated ions are directed to the mass spectrometer which then undergoes segregation based on their mass/charge ratio. A detector subsequently formulates a spectrum of ion signals of different intensities which can be used in tandem with reference data to uncover the concentration of elements within the sample. ICP-AES, on the other hand, is based on utilizing plasma to induce excitation events (rather than ionization) in a sample [208]. Photons are released during deexcitation, resulting in electromagnetic (EM) radiation at characteristic wavelengths of the elements present in the sample. An optical spectrometer is subsequently utilized to analyze the different wavelengths of EM radiation emitted by the sample, as well as quantify its presence. This can then be correspondingly converted to data on elemental composition/ concentration. XRF spectroscopy, on the other hand, utilizes high-energy, short-wavelength radiation (e.g., in the form of incident X-Ray photons) to initiate ionization events of inner shell (usually K and L) electrons in a sample [209]. Consequently, during the de-excitation of outer shell electrons which replace the inner shell vacancies, EM radiation is emitted to a detector in the form of X-Ray fluorescence, i.e., secondary X-Rays characteristic to each element. The detector here depends on whether an energy-dispersive (i.e., EDXRF) or wavelength-dispersive (i.e., WDXRF) spectrometer is being utilized, as both the energy and wavelength of the photons released to act as a fingerprint of the elements being detected. The intensity of the emissions can then be related correspondingly to the concentration of elements in the sample.

Bulk elemental analysis of our samples to determine the Al, P, and Si content was done using an energy dispersive X-ray fluorescence (EDXRF) spectrometer; Epsilon 1 (Malvern Panalytical), equipped with a 50 kV silver anode X-ray tube and a high-resolution Silicon Drift Detector (SDD).

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The samples were loaded in powder shape without any preparation, and fast mode (10 min acquisition time) was applied.

Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES, iCAP 6500 dual view Thermo Scientific) was also employed for bulk elemental composition measurement of our catalysts. Typically, 100 mg of SAPO-34 catalyst was digested in a 10 ml aqueous solution of triplicate trace-metal-grade acids (2 HF: 1 HCl: 3 HNO₃ molar ratios) at 200 °C for 2 h using a microwave oven. The clear fully dissolved catalyst-containing solutions were filtered and further diluted for ICP analysis.

3.2.5 Surface elemental composition

X-Ray photoelectron spectroscopy (XPS) and scanning electron microscopy with energydispersive X-Ray spectroscopy (SEM-EDXS) are the techniques typically utilized in the revelation of a catalyst's surface elemental composition. With regards to the former, XPS operates by emitting a focused beam of monochromatic X-Rays (photons) from an X-Ray source, usually in the form of aluminum or magnesium K α , onto a sample [210]. This leads to electrons on the surface of the sample absorbing energy and ejecting as photo-emitted electrons possessing a specific kinetic energy (which roughly equates to the difference in the photon energy and the electron's binding energy to the nucleus). A detector correspondingly measures the kinetic energy (which is later converted to binding energy) and intensity of the ejected photoelectrons, which can be used to identify the type of elements present and their surface elemental concentration in a sample, respectively. This technique is able to provide a complete surface analysis (for the top 10-200 Å) of any solid sample that is (or can be made) vacuum stable, whereby the concentration of all elements, except hydrogen and helium, can be deduced [210]. SEM-EDXS, the other commonly used surface analyzing tool, works via the examination of the ejected X-Rays emitted during scanning electron microscopy (see morphology subsection for further details) [201,202]. These characteristics X-Rays (which are emitted as a result of electron transitions of outer shell electrons to inner vacancies) are collected via a photon-energy sensitive detector that measures both its energy and intensity [211]. In turn, the gathered data can be used to determine the type of elements present on the surface of the sample alongside their corresponding concentration. We utilized SEM-EDX for surface elemental analysis of our samples.

3.2.6 Acidity

Since the active site for the MTO reaction is well known to be the Brønsted acid site (i.e., the bridging hydroxyl groups, Si-OH-Al) over the catalyst, acidity measurements play an important role in catalyst characterization. The easiest and most commonly used tool in the determination of acidic site quantity and strength is NH₃ temperature programmed desorption (TPD) [142,212,213]. This tool generally provides two peaks that correspond to weak sites (a combination of Lewis and Brønsted acidic sites) and strong sites (primarily Brønsted) in ranges of 150 to 200 °C and 350 to 450 °C, respectively [186,214,215]. Considering the plot generated by this tool, i.e., the thermal conductivity detector (TCD) signal as a function of the ammonia desorption temperature (from ~60 °C to 550 °C), the computed integral under the peaks can be related to the amount of desorbed ammonia [216]. This can be achieved via a comparison of the desorption peak areas with that of successive pulse calibration using a pre-known volume sample loop. In turn, the amount of desorbed ammonia (in millimoles of ammonia per gram of catalyst) can be an indication of acidic site quantity. The relative acidic site strength, on the other hand, is positively correlated with the NH₃ desorption temperature [216]. It can be determined by recording the temperature corresponding to the tip of each of the two peaks.

The NH₃-TPD does not reveal any information regarding the nature of the acidic sites (i.e., Lewis or Brønsted acidic sites, abbreviated as LAS and BAS). Hence, the FTIR technique with the aid of a probe molecule was employed to assess the LAS and BAS exclusively. Pyridine, having a molecular kinetic diameter of 5.33 Å, is not able to penetrate the small pores of SAPO-34 (pore size of 3.7 Å) and cannot be used as the probe molecule [217]. NH₃-FTIR was not viable either, as the region where the vibrational modes of ammonia adsorbed on Lewis centers and Brønsted ones (LAS at 1625 cm⁻¹, and BAS-related peaks at 1457 and 1405 cm⁻¹ [218]) interferes with the characteristic peaks related to SAPO-34 framework in the range of 500-1700 cm⁻¹. Therefore, deuterated acetonitrile (CD₃CN) was employed as the probe molecule. The C=N stretching vibration of CD₃CN, interacting with BAS and LAS, appears within 2100-2500 cm⁻¹ where no

interference exists. The CD₃CN-FTIR test provides a qualitative analysis; to study the acidic sites quantitatively, CD₃CN-TPD was also conducted and related to the CD₃CN-FTIR test.

In our study, the acidic site quantity and strength over the samples were measured by the ammonia temperature-programmed desorption (NH₃-TPD) technique using Altamira AMI-300. In a typical test, 150 mg of the samples were loaded into the sample tube; it was then dried at 300 °C for 2 h under helium (99.999% Linde), subsequently cooled down to 50 °C, and saturated with ammonia (10 vol% NH₃ in He, Linde) for 1 h. The sample was purged by helium at 60 °C for 1 h to desorb weakly adsorbed ammonia molecules. Finally, the sample temperature was raised by 2 °C min⁻¹ up to 550 °C while the desorbed ammonia was measured by a thermal conductivity detector (TCD). Acetonitrile-TPD was similarly done by passing argon through CD₃CN saturator. The saturation and degassing of the catalyst were performed at 30 °C while other steps were analogous to the NH₃-TPD test. To distinguish between Brønsted acidic sites (BAS) and Lewis's ones (LAS) on the catalyst, the samples were dried and then saturated with 10 mol% deuterated acetonitrile (C₂D₃N, 99.8 atom% D, Millipore Sigma) in argon (99.999% Linde) at 30 °C. The weakly adsorbed acetonitrile molecules were purged from the catalyst with argon at 40°C for 1h. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) spectra were recorded on a Thermo Scientific[™] Nicolet[™] iS50 FTIR Spectrometer equipped with a diffuse-reflectance attachment. 50 scans for signal accumulation were collected, using MCT detector, in the range of 600-4000 cm⁻¹, with a resolution of 2 cm⁻¹. Harrick Praving Mantis[™] enclosed chamber (with ZnSe window) capable of programmed heating was used, and the data was analyzed using OMNIC 9.11.706 software. DRIFT spectra at temperatures of 30, 100, 200, 300, and 400 °C under argon atmosphere (40 ml min⁻¹) were collected.

3.2.7 Coke analysis

It is well known that the primary drawback associated with the MTO reaction is catalyst deactivation due to coke formation, which occurs inevitability over time on stream. The development of coke species ultimately leads to the blockage of catalyst pores, resulting in a rapid decline in methanol feed conversion and reduced light olefins selectivity [23,24,219–221]. As a result, due to its massive implications on the process economy, ample research has focused on deciphering the mechanistic pathways responsible for coke formation [67,222], as well as

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uncovering ways to limit its generation rate [223,224]. Characterization tools such as thermogravimetric analysis- temperature programmed oxidation (TG-TPO) have been utilized by researchers as a means to quantify the coke content over deactivated SAPO catalysts [93,225]. Generally, the weight loss observed in the temperature range of 50 to 200 °C corresponds to the desorption of water from the sample, while a second weight loss is observed gradually between 200 to 600 °C and can be attributed to the combustion of coke species from the catalyst sample [93,164,226]. Another technique is to transform the thermogravimetric analyzer into a reactor in the pursuit of performing live/ in-situ measurements of coke generation during the MTO reaction over SAPO-34 [11].

Other than identifying the coke generation rate (over time on stream) and the content corresponding to catalyst deactivation, deciphering the types of species that constitute coke can help in viewing the larger picture pertaining to coke analysis. For instance, the identification of coke species that are distinctly responsible for ultimate pore blockage may provide the initial step in developing the deactivation mechanistic sequence. One method to accomplish this involves analysis of the coke species in a deactivated catalyst via ¹³C or ¹H nuclear magnetic resonance (NMR) spectroscopy [17,115,227]. Although this technique does not necessarily analyze the detailed structure of the species contained in coke, it can still provide an indication of the type of functional groups present. Groups who have utilized this method have indicated that coke species are largely aromatic-based as opposed to linear chain aliphatic compounds [115,227]. If a more in-depth analysis of the structure is desired, a technique involving gas chromatography-mass spectrometry (GC-MS) may be utilized instead, depicting coke species as ranges of multi-ring aromatics [35,228,229]. Here, the deactivated catalyst may be digested in hydrofluoric acid, with the hydrocarbon phase extracted using dichloromethane (CH_2Cl_2) [35]. The organic compounds can be subsequently injected into the GC as a means of separating the different coke species by their retention time, which can then be analyzed via MS successively. Although this technique may seem promising with regards to structural identification, there are some inconsistencies between the types of coke species entrained in deactivated SAPO-34 reported by research groups. One group was able to analyze and identify insoluble hydrocarbons (up to 55 C atoms in size)

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within coke species [230], while another suggested that pyrene (16 C atoms) i.e., a soluble hydrocarbon, was the largest identifiable coke species [13]

In our study, solid-state ¹³C NMR spectra were acquired on a 400 MHz Varian VNMRS spectrometer using a 4 mm double-resonance Varian Chemagnetics HX probe. Approximately 60 mg of samples were packed into rotors and spun between 12-13 kHz. The multiCP pulse sequences were used [231] with 8 periods of 1 ms contact time at 60 kHz RF field and recycle delay of 3 s. 4000 scans were collected. Spectra were referenced to the CO resonance of α -glycine at 176.5 ppm.

Moreover, to identify the coke species that was formed in the pores of the catalyst, gas chromatography in tandem with the mass spectroscopy technique (GC-MS) was employed. Firstly, the confined coke molecules were released from the pores by catalyst digestion. Although the commonly used acid for zeolite digestion is hydrofluoric acid, due to its safety concerns, we tested alternative acids (i.e., H₂SO₄, HCl, HNO₃, H₃PO₄). H₂SO₄ and H₃PO₄ appeared to be able to digest SAPO-34. Hence, 20 mg of deactivated catalyst was digested in 4 ml of 25 vol% H₃PO₄ aqueous solution. The organic phase was later extracted using 3 ml of hexane containing 15 ppm of m-dichlorobenzene as the internal standard. Afterward, 0.5 µl of the organic specimen was injected into the GC-MS (Agilent 6890N GC with 5975B Quadrupole Mass Spec used in scan mode from 50 to 500 m/z) equipped with Rtx-5MS column with the following temperature program: hold for 1 min at 50 °C, then raise the temperature to 350 °C at a rate of 15 °C min⁻¹. The molecules annotated on the chromatograms were identified through fragmentation peak analysis and matching with the NIST database.

The coke deposition amount on our deactivated catalysts was determined via temperatureprogrammed oxidation with a thermo-gravimetric analyzer (Netzsch TG 209, Germany). 20-40 mg of spent sample was loaded, then heated to 200 °C for 2 h to remove moisture and then hat a rate of 10 °C min⁻¹ under synthetic air to 600 °C, while the weight change was recorded.

3.2.8 Elemental environment

Nuclear magnetic resonance (NMR) spectroscopy is also a commonly employed tool in the field of catalysis, where it is capable in determining the types of environments prevalent in a catalyst
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structure. A wide range of NMR studies, generally comprising ²⁷Al-, ³¹P-, and ²⁹Si-based NMR, have been employed in the context of silicoaluminophosphates such as SAPO-34. With respect to ²⁹Si-NMR, five different peaks close to -90.5, -94.4, -99.6, -104.3 and -109.8 ppm are often observable, respectively corresponding to environments of Si(4Al) (i.e., isolated Si), and silica islands such as Si(3Al, Si), Si(2Al, 2Si), Si(Al, 3Si) and Si(4Si) [232–234]. Generally, it has been observed that the greater the amount of silicon incorporated into the SAPO framework, the more likely the formation of Si islands in comparison to isolated Si environments [100]. The range of isolated Si generated in the SAPO framework, relative to islands, can be an important factor to consider when deciphering the reasons for a catalyst's particular performance. A general consensus amongst research groups exists that the formation of primarily isolated silicon environments (as opposed to Si islands) is more desirable from a catalyst activity standpoint, which is often justified by the lower acidity strength associated with isolated Si sites [235,236].

In our study, solid-state ²⁹Si NMR spectra were acquired on a 400 MHz Varian VNMRS spectrometer using a 7.5 mm double-resonance Varian Chemagnetics HX probe. Approximately 300 mg of samples were packed into rotors and spun at 3 kHz. 512 scans were collected via direct excitation with 1H decoupling and a relaxation delay of 100 s. The ²⁹Si was referenced to DSS (1.4 ppm).

3.2.9 Attrition test

The resistance of the composite catalysts (mounted over γ -Al₂O₃ microspheres) to abrasion and erosion (simulating the fluidized bed environment) was examined using a tapping sieve shaker (Gilson company). 1 gram of the composite catalyst was sieved for 100 h at a frequency of 60 taps/min. Since the catalyst has shaped within the range of 30-60 µm, the portion of the catalyst that was shattered by electromagnetic vibrator taps and passed through the bottom sieve (with the mesh number of 635 equivalent to 20 µm pore size) was weighted, and reported as the metric of abrasion vulnerability. The portion that was separated in the first 5 h was discarded as it may have passed due to its small size rather than crushing.

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3.3 Activity tests

For methanol conversion to light olefins activity tests, we designed and constructed a micro-fixedbed reactor (Fig. 3-2), which consists of a quartz tube (7 mm ID and 200 mm L) surrounded by an electrical furnace. In a typical test, 250 mg of the dried catalyst was loaded (catalyst bed of 2-4 cm), and a methanol solution containing 20 wt% water (similar to commercial feed, [26]) was injected by a syringe pump providing the methanol weight hourly space velocity (WHSV) of 1 g_{MeOH} g_{Cat}⁻¹ h⁻¹. Methanol was diluted with argon (Ar, 99.999% Linde) to avoid condensation (molar composition of the feed: 10% water, 20% methanol, and 70% argon). All the connecting lines were heat-taped and maintained at 130 °C to keep the methanol feed and products in the gaseous phase. For all the experiments, the reaction temperature was within 400-450 °C and pressure was in the range of 0.2-0.35 barg. The products were analyzed using a calibrated online gas chromatograph (SRI GC-8610) equipped with a flame ionization detector (FID) and HP-Plot Q capillary column (Agilent, 30 m long, 0.32 mm inside diameter, 20 µm thickness of the stationary phase). The GC oven program can be described as follows: the oven was kept at 50 °C for 3 min, went up to 210 °C with a heating ramp of 20 °C min⁻¹, and kept at 210 °C for 5 min. In total, the heating program of the oven took 16 min while the fast cooling (to the initial temperature) took 4 min; hence, every 20 min a sample of the reactor effluent was acquired and analyzed by the GC. Methanol conversion and selectivity of the products were based on carbon number, and dimethyl ether (DME) was counted as unreacted methanol in the calculation of methanol conversion. The catalyst lifetime was defined as the time on stream from the beginning of the reaction until the time that methanol conversion to hydrocarbons (other than DME) dropped below 90%.



Fig. 3-2 Our micro-reactor experimental setup (left) P&ID (right) real picture. PG=Pressure Gauge, PR=Pressure Regulator, TIC=Temperature Indicator Controller, 3WV= 3-way valve, MFC=Mass Flow Controller, GC =Gas Chromatograph, V=Plug Valve.

To measure the rate of coke formation as a function of time on stream (TOS), the thermogravimetric reactor with online mass spectrometry (TGR-MS) was employed. In contrast to the traditional method [237] of taking the catalyst out of the reaction at different time intervals and burning the coke, which encounters difficulties and considerable error, in-situ measurement of catalyst weight change due to coke formation during the reaction is precise, easy, and more reliable. A stainless-steel sieve (mesh number 350) was formed into a small cup and used instead of the usual ceramic crucible to facilitate the permeation of reactant into the catalyst bed. Argon at 5 ml_N min⁻¹ flowed through a methanol saturator kept at 25 °C (producing almost 15 vol% CH₃OH, 85 vol% Ar mixture based on the methanol vapor pressure) diluted with 5 ml extra argon to avoid methanol condensation within the machine and passed through the catalyst bed (holding 60-65 mg of catalyst). This simulates reaction conditions similar to the fixed-bed reactor (i.e., the same *WHSV*, temperature, and pressure). A calibrated online mass spectrometer (HPR-20, Hide Analytical, UK) was used to monitor evolved products such as argon (Ar, m/z = 20), ethylene (C₂H₄, m/z = 27), methanol (CH₃OH, m/z = 31), DME (CH₃OCH₃, m/z = 46) and the aggregation of C₄-C₆ olefins (m/z = 56).

3.4 Calibration and reproducibility tests

To address the growing concern about non-reproducible experimental work presented in scientific articles, 10% of the lab work was randomly chosen and replicated to assess the validity and reproducibility of the results. This includes catalyst synthesis, activity runs, and characterization tests. The numerical values should be presented not based on the raw data acquired from different machines in the lab (i.e., the molar composition of the products using a gas chromatograph with 3 decimal numbers or absolute surface area with two decimal numbers) but rather according to the deviation of the replicates (i.e., uncertainty or error).

All the machines were calibrated according to the specific procedures recommended by their suppliers. Here are some of the calibration procedures that were employed in our lab.

The gas chromatograph (GC) was calibrated using a standard gas (Linde Co.) containing the typical gaseous products of the MTO reaction with similar quantities. The standard gas was injected into the GC using a 100µl sample loop and the optimum oven program and carrier gas flow that resulted in symmetric peaks with no interferences or overlaps were developed. Finally, methane, ethylene, ethane, propylene, propane, C₄ olefins, and C₅ olefins were calibrated using multiple injections of the standard gas. The surface areas under the peaks were recorded with an average 0.7% relative deviation. DME and methanol were calibrated using another standard gas containing methane, methanol, and DME. The key point is that to do separate calibrations, always one gas should be common among calibration gas mixtures, and the calibration factors will be normalized by keeping the common gas. The calibration factor is the ratio of surface area under a specific gas peak over its molar percent in the calibration gas. Later, the peaks will be identified based on their retention time in the chromatogram and the related calibration factor will be used to convert the surface area under the peak to the molar percent.

The mass flow controllers (Vögtlin, red-y series, 0-25 ml min⁻¹) with a turndown ratio of 1:100 and accuracy of 0.1 ml/min were employed for argon and hydrogen cofeeding with methanol. The gas flow controllers had been calibrated for a specific gas in the factory and in case of using another gas due to differences in gas densities, additional calibration was required. We utilized a gas-soap

flow meter to calibrate the MFC for each specific gas. The results were reproducible with an accuracy of 0.2 ml min^{-1} .

The mass spectrometer (MS) was also calibrated using the same standard gases used for GC calibration. The argon was used as the internal standard. Due to multiple fragmentation states during electron bombarding of the molecules in the MS chamber, each molecule results in several peaks at different mass-to-charge ratios. This can make it difficult to interpret the spectrum, especially when several species are present in the specimen. Therefore, those mass-to-charge ratios should be chosen as the characteristic peak of a specific compound that has less overlap or interference with other molecules. Also, in the case of minor overlaps, the contribution of one compound from the identification peak of another one was excluded to enable us to compute the amount of each species with acceptable accuracy. The following mass-to-charge ratios were picked accordingly: (Ar, m/z = 20), ethylene (C₂H₄, m/z = 27), methanol (CH₃OH, m/z = 31), DME (CH₃OCH₃, m/z = 46) and the aggregation of C₄-C₆ olefins (m/z = 56).

3.5 Documentation of the experimental work using eLab

In the world of scientific research and innovation, documenting experimental procedures and observations in the laboratory is an indispensable practice. Documenting experimental procedures is essential for ensuring the reproducibility and reliability of scientific experiments and making it possible for others to replicate the experiments accurately. This transparency allows for independent verification of results and helps to eliminate potential sources of bias or error. The credibility of scientific findings hinges on the ability to replicate experiments, and thorough documentation is key to achieving this. Catalytic and Plasma Process Engineering (CPPE) lab is equipped with an encrypted eLab (https://www.elabftw.net/) that enables the group research members to steadily record their experimental studies online. Documenting the experimental work online makes them easily accessible and securely preserved. These records are regularly stored as backup copies on a local hard disk. Some of the capabilities of this tool have been listed below:

 User-friendly environment and having almost all Microsoft office tools to make a goodlooking document (with various fonts, symbols, equations, highlights, tables, and so on)(Fig. 3-3).

- 2- Decent organization of the experiments and easy accessibility by consistent naming, search tools, categorization according to the subgroups and research projects, and adding tags.
- 3- Ability to add figures and observations, attach documents, and cross-reference to other protocols and procedures.
- 4- Ability to manipulate the level of access to the reports and records for each member.
- 5- Ability to book the common devices in the lab to avoid any conflict and interference.

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Fig. 3-3 eLab interface

Additionally, documenting observations during experiments is equally vital. It provides a record of unexpected outcomes, anomalies, and deviations from the expected results. These observations can also lead to valuable insights and discoveries. This helps scientists understand the cause-and-effect relationships between various parameters, leading to a deeper understanding of the processes involved. This can easily be done by taking a picture and adding it to the relevant report on eLab. Fig. 3-4 indicates the eLab report concerning an experiment done on SAPO-34 digestion is acids. Images of the clear solutions while using H₃PO₄ and H₂SO₄ approve the successful digestion of the catalyst.

Moreover, documented experimental procedures and observations serve as a solid foundation for patent applications, providing evidence of the novelty and inventiveness of an idea. On eLab, by

using the timestamp tool (Fig. 3-4), one can disable any further change on a report or observation and later use it as evidence for filing a patent or reporting a discovery or an invention.



Fig. 3-4 eLab report on an experiment concerning SAPO-34 digestion in acids bearing the visuals of the test.

3.6 Computational method

This section was done via our collaborators from the chemistry department of the University of Calgary. Vienna Ab initio Simulation Package "VASP" [238–242] was used to carry out periodic DFT calculations. Structures were relaxed to meet the energy and force convergence criteria of

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 10^{-8} eV and 0.01 eV Å⁻¹, respectively. The PBE functional [243,244] was used to account for the electronic exchange and correlation effects, and Grimme's zero damping D3 dispersion corrections to include long-range interactions [245]. The Projector-Augmented-Wave (PAW) method [238–240] was used and plane-wave energy cut-off was set to 400 eV, except for the convergence of lattice parameters, where 800 eV was used instead. Gamma-only *k*-point sampling was found to be sufficient to model the zeolite. The unit cell of H-SAPO-34 (chabazite framework), consisting of 36 tetrahedral atoms (36T), is converged with lattice parameters of *a* = 13.88, *b* = 13.87 and *c* = 15.04, with angles $\alpha = 90$, $\beta = 90$ and $\gamma = 120$ (trigonal cell with space group R3m). Transition state scans were performed using automated relaxed potential energy surface scans (ARPESS) [246]. Gibbs Free energies were computed at 400 °C, where vibrational frequencies were calculated using the finite difference scheme, rigid rotator/oscillator, and harmonic approximation. No imaginary frequencies were found for any relaxed structures, except for transition states, where a single imaginary frequency along the reaction vibrational mode is expected.

The ratio of Al: P: Si in our models is 18:17:1 respectively. This corresponds to a single Brønsted active site per unit cell, where a P atom was replaced with Si, and a proton was added to the neighboring oxygen to compensate for the charge imbalance. Similar to the Brønsted acid site, P was replaced by Si, and extra-framework Lewis sites were modeled by attaching Al(OH)₂ to framework oxygen atoms closest to the substituted Si atom. The two additional hydroxyls constitute the resting state of the active site. Further information regarding the stability of the formation CHA-Al-(OH)₂ is included in the DFT discussion.

4 Effect of template alteration on SAPO-34 properties4.1 Introduction

Although a few research groups altered or combined templates, there are still some issues that need to be addressed. Firstly, no meaningful trends can be observed in the prementioned articles- this is with respect to the physicochemical properties of the catalyst upon the change of template ratios. Secondly, these articles have neglected the role of the gel pH and have used the same amounts of templates regardless of their basicity strength. Thirdly, there is still the need for a more in-depth justification for the superior performance of mixed-template synthesized SAPO-34. Fourthly, in the literature, the product distribution was presented excluding the coke formation, neglecting the fact that the coke formation rate plays an important role in process economics and the selection of the optimum catalyst. Furthermore, considering TEAOH, MOR, TEA, and DEA as the most popular and well-known templates for SAPO-34 synthesis, there is yet to exist any article that has assessed all templates in single and mixed forms under similar synthesis and reaction conditions to introduce the superior template. Finally, although research groups have tried different orders with regard to precursor addition during the synthesis stage, no research group has compared the effect of this order on catalyst properties.

Hence, this chapter was defined to address the pre-mentioned issues through in-depth experimental investigation and analysis to shed light on the relationships between (1) synthesis procedure and catalyst properties, and between (2) catalyst properties and activity. In detail, we compared SAPO-34 catalysts prepared via single and mixed templates (TEAOH/MOR, TEAOH/DEA, TEAOH/TEA) using a variety of characterization tools, conducted MTO activity tests and in-situ measurement of the coke formation during the reaction using a thermogravimetric reactor coupled with mass spectrometry (TGR-MS). To the best of our knowledge, the work by Hu *et al.* [11] is the only study that has carried out TGR experiments. However, they exposed the catalyst to a 10 times higher weight hourly space velocity than for commercial reactors (i.e., *WHSV* of 21.8 *vs.* 2 $g_{MeOH} g_{Cat}^{-1} h^{-1}$), resulting in a very fast catalyst deactivation. Within our study, we used *WHSV* of 1 $g_{MeOH} g_{Cat}^{-1} h^{-1}$ and monitored the gradual coke formation and product evolution simultaneously. Subsequently, we did ¹³C-NMR spectroscopy over partially and completely coked catalysts to theorize a mechanistic pathway for coke evolution that aligns with the activity tests and characterization results.

4.2 The influence of silica addition to the template

The silica suspension is a milky liquid containing micron-sized SiO₂ particles. Following the addition of silica suspension to the template aqueous solution, a clear liquid forms which illustrates the dissolution of silica into the template, resulting in a faster and uniform catalyst nucleation. Here, while holding the other synthesis parameters constant, we tried silica dissolution into the template (sample TEAOH-1) and compared it to the sample prepared by a separate addition of silica and template (sample TEAOH-1 β). By employing the pre-mentioned strategy, surprisingly, the average particle size reduced considerably (Fig. 4-1). Evidently, smaller catalyst particles provide a shorter pathway for methanol to diffuse. This means a higher portion of active sites will be near the outer layer of the catalyst particles. Hence, following the partial blockage of pores, the lower portion of the active sites will be concealed from the reactant molecule. Another hypothesis suggests that, as the diffusion route gets shorter, there is a smaller probability for hydrocarbon products (which are diffusing out) to further grow. This is because, in a shorter diffusion path relative to a prolonged one, there is less of surface-associated reactive groups available to react with the diffusing product. This favors the production of lighter compounds (i.e., especially light olefins) and reduces the coke formation rate by avoiding the build-up of long hydrocarbon chains.



Fig. 4-1 SEM images of SAPO-34 samples prepared by different silica addition methods. Left: TEAOH-1 β silica added separately. Right: TEAOH-1 silica added to the template.

Activity results over the TEAOH-1 sample, as an example, have been illustrated in Fig. 4-2 ; the catalytic behavior and the product distribution profiles are similar for both samples. Over time on stream, gradual and continuous coke formation results in the narrowing of the catalyst pores, favoring the production of smaller molecules and hence increasing the selectivity towards lighter compounds (methane, ethylene, and ethane) [247]. For instance, ethylene selectivity experienced an upsurge (between the start of the activity test and the onset of catalyst deactivation) of ~30% to ~47% and ~31% to ~48% over TEAOH-1 β and TEAOH-1, respectively. Propylene production slightly decreases over time on stream (by ~1% and ~0.5%, correspondingly), whereas the selectivity towards heavier compounds like C₄ and C₅⁺ olefins reduces more substantially over time. In line with the notion that coke deposition until a certain amount can increase the selectivity towards light olefins, the highest light olefin selectivity (85.9% and 86.1%, respectively) was recorded on the partially coked catalysts. Following advanced times on stream, catalyst activity diminishes abruptly due to deactivation (as illustrated by the evolution of the GC chromatograms over TOS in Fig. 4-3).



Fig. 4-2 (a) Methanol conversion and main products' selectivity, (b) selectivity of the less abundant products vs time on stream over TEAOH-1 catalyst. Reaction condition: T = 425 °C, P = 0.2-0.35 barg, $WHSV = 1 g_{MeOH} g_{Cat}^{-1} h^{-1}$, and feed composition 10 mol% H₂O, 20 mol% CH₃OH and 70 mol% Ar.

Even after catalyst deactivation (i.e., following a steep decrease in olefins production), DME as an intermediate was being produced at methanol-DME equilibrium conversion corresponding to the reaction temperature (Fig. 4-2). This demonstrates that methanol to DME conversion can continue over a much lower number of acidic sites than needed for the MTO reaction. As expected, the submicron SAPO-34 catalyst (i.e., TEAOH-1) lasted longer (by 10%, i.e., the period in which methanol conversion remained higher than 90%) at *WHSV* of 1 $g_{MeOH} g_{Cat}^{-1} h^{-1}$ with a superior average light olefin selectivity (76.0% compared to 74.8%, as seen in Table 4-2). Furthermore, the average coke formation rate, using TGA, was determined to be higher for the catalyst with the larger particles (Table S 2). Since both catalysts exhibited a similar acidity and surface area (Table 4-1), it is evident that the reduction in particle size would be the sole cause of any alteration in catalytic performance.



Fig. 4-3 GC chromatograms of the MTO reaction over TEAOH-1 catalyst at different times on stream

A similar behavior was observed by Peng *et al.* [115], where SAPO-34 was synthesized using TEA and pressed, crushed, and sieved to assess the particle size influence on catalytic activity. Catalysts with an average particle size of 60 μ m had almost 25% longer lifetime compared to those possessing an average size of 700 μ m. This finding contrasts with the study regarding SAPO-34 particle size assessment by Yang *et al.* [105], where the acidity of the samples was not reported and surface areas were considerably different.

Sample name	$S_{BET}{}^{a}$ (m ² g ⁻¹)	SMicro + SMeso+Macro (m ² g ⁻¹) ^b	Weak acid sites ^{c,d,f} (mmol _{NH3} g _{cat} -1)	Strong acid sites ^{c,d,f} (mmol _{NH3} g _{cat} ⁻¹)	Al (mol%)	P (mol%)	Si (mol%)	Crystallinity ^g (%)
ΤΕΑΟΗ-1β	533	519 + 14	0.97 (160 °C)	0.74 (401 °C)	47.4	43.7	8.9	84.5
TEAOH-1	549	532 + 17	0.99 (160 °C)	0.73 (403 °C)	47.2	44.0	8.8	81.2
TEAOH-2	524	503 + 21	0.90 (160 °C)	0.63 (401 °C)	48.5	43.0	8.5	79.9
MOR-1	534	534 + 0 ^e	1.07 (160 °C)	0.83 (409 °C)	47.5	42.7	9.8	68.4
MOR-2	561	561 + 0 ^e	0.97 (157 °C)	0.79 (399 °C)	47.3	43.4	9.3	72.3
DEA-1	565	565 + 0 ^e	1.15 (164 °C)	0.96 (410 °C)	48.1	43.4	8.6	75.0
DEA-2	511	511 + 0 e	0.79 (155 °C)	0.65 (401 °C)	48.8	43.8	7.5	71.5
TEA-1	567	552 + 15	0.60 (153 °C)	0.56 (380 °C)	51.8	43.1	5.1	82.4
TEA-2	575	558 + 17	0.73 (157 °C)	0.63 (376 °C)	50.8	43.2	6.0	81.4

Table 4-1 Physicochemical properties of the prepared catalysts. Total, micro- and combined meso + macro surface area. NH₃ uptake for weak and strong acid sites. Bulk molar composition (using XRF), crystallinity (using XRD).

^a S_{BET} = BET total specific surface area obtained from adsorption data in the p/p_0 range from 0.06–0.2; all reported data are within ±4 m² g⁻¹ based on repeated analysis.

^b S_{Micro} = micropore; $S_{Meso+Macro}$ = meso + macropore surface areas.

^c Precision $\pm 2\%$ relative ^d Precision $\pm 3^{\circ}$ C ^e negligible amount

^f value in brackets refers to peak temperature in ^oC

^g This was calculated based on the ratio of reduced area to global area, where the reduced area is the global area minus the amorphous surface area (using DIFFRAC.EVA V4.1).

The particle size reduction via the direct addition of Si to the template was further examined using other templates and a similar behavior was observed (Fig. S 1). Hence, all the samples were prepared with silica addition to the template, except samples prepared by TEA, as TEA is insoluble in aqueous solution. It is worth mentioning that the only substantial physicochemical alteration from sample TEAOH-1 β to TEAOH-1 is a slight increase in external surface area (Table 4-1).

Referring to Fig. 4-4, both samples using TEAOH as the template showed the typical X-ray diffraction pattern corresponding to the reference SAPO-34 phase [248], depicting the successful synthesis of catalysts.



Fig. 4-4 X-ray Diffraction pattern for single-template samples with corresponding references: SAPO-34 (PDF # 00-047-0617), SAPO-5 (PDF # 00-047-0619), and SAPO-11 (PDF # 00-047-0613).

4.3 Single template SAPO-34 synthesis

The next step was preparing SAPO by single template using one of the 4 most popular templates (TEAOH, MOR, DEA, and TEA) according to the two mixing methods described earlier. Since the basicity strength of the templates is different (with TEAOH as the strongest and TEA as the weakest), the amount of the template used varied to keep the final gel pH within the optimum

range (Table 3-1). This fact has been widely ignored by previous research groups . The optimum pH value for all catalysts (apart from TEA-incorporated samples) was in the range of 6.5-7.5. With respect to the TEA-directed catalysts, the highest crystallinity was achieved using a pH bracket of 8.0-8.5. It should also be noted that the second mixing method generally demanded a lower quantity of templates to reach the same gel pH as the first method.

All the single-template samples were examined at the same WHSV, T, and p (Table 4-2 and Fig. 4-5). In contrast to most of the articles that overlooked the coke formation in presenting the product distribution, here, by measuring the coke content of the deactivated catalyst, the average coke selectivity was also reported. This holds great significance in evaluating catalytic performance and behavior. Since it is widely mentioned that the coke formed during the MTO reaction has an aromatic structure [115,230,249], C_nH_n can be an acceptable formula for estimating the carbon content of the coke. Dividing the weight of carbon in the precipitated coke (over the deactivated catalyst) by the accumulated carbon entering the reactor during the catalyst lifetime (in the form of methanol), one can compute the average coke yield; sequentially, dividing this value by methanol conversion gives coke selectivity. Sample calculation for coke selectivity has been presented in the supplementary information. With reference to Table 4-2 and Fig. 4-5, firstly, it can be noted that the catalyst lifetime and product selectivity were similar between catalyst samples prepared using the same template but via different methods (i.e., different order of addition of precursors). This validates the successful preparation of zeolite catalysts and the reproducibility of the results regardless of the variance in the order of precursor addition chosen for the synthesis procedure. These results also demonstrate the significance of considering the final gel pH rather than the quantity of template used during catalyst preparation. In terms of the catalyst active period, the TEAOH samples achieved a lifetime of ~11 h, while surprisingly, the TEA-directed samples possessed a lifetime that was roughly 50% longer in comparison (Fig. 4-5). The MOR and DEA samples, on the other hand, experienced a much shorter lifetime relative to the TEAOH samples (by ~90% and 80% respectively). Concerning the average light olefins selectivity metric, the highest value was recorded over the TEAOH samples (~76%). The TEA-incorporated catalysts experienced only a slight reduction in light olefins' selectivity (LOS) by roughly 1-3% (mainly due to lower ethylene formation). On the other hand, using the other two templates (DEA and

MOR) led to a significantly lower light olefins selectivity, ranging from \sim 55 to \sim 65%, along with a greater production of heavier olefins

Fig. 4-4 displays the X-ray diffraction patterns of all the single-template samples, along with the reference diffraction patterns corresponding to SAPO-34, SAPO-11, and SAPO-5, as the presented phases within the synthesized samples. While the use of TEAOH resulted in a pure SAPO-34 phase, the application of alternative templates instead of TEAOH (i.e., MOR, DEA, and TEA) introduced diffraction peaks at 2θ of 7.4° and 8.1°, which are assigned to SAPO-5 and SAPO-11 respectively (the competing phases in the SAPO-34 formation). SAPO-34 (CHA zeolite) possesses pores of 3.72 Å, while SAPO-5 (AFI Zeolite) and SAPO-11 (AEL zeolite) contain larger pores with effective diffusivity of 7.42 Å and 4.63 Å, respectively. The usage of MOR and TEA produced a mixture of SAPO-34 and SAPO-5, while DEA introduction, on the other hand, generated both SAPO-34 and SAPO-11. The lower light olefin selectivity (as a result of higher production of heavier compounds) for samples that utilize templates other than TEAOH could be explained by the existence of structures with larger pore sizes (i.e., SAPO-5 and SAPO-11). Up to now, the Hydrocarbon Pool mechanism (HP) has been recognized as the most acceptable pathway for olefin formation over SAPO-34 [250] through either side-chain methylation or paring mechanisms, with multi-methyl benzenes as the active intermediates. The study by Song et al [251] has revealed that ethylene formation is more favorable via benzene having two or three methyl groups attached and propylene would form dominantly through benzene with 4-6 methyl groups. Lower $C_2^{=}/C_3^{=}$ values on TEA-1&2 compared with TEAOH-1&2 (as presented in Table 3) can be reflected from bigger pore openings of TEA-1&2 samples (due to the existence of SAPO-5 phase) that can contain benzene molecules with a higher number of methyl groups. Substantially lower LOS and $C_2^{=}/C_3^{=}$ ratios over DEA-1&2 and MOR-1&2 samples can have two reasons. One is the existence of large-pore phases (SAPO-5 and SAPO-11). The second reason can be the short lifetime of the catalysts as they couldn't experience the pore restriction by partial coke formation and the rise of light olefins formation. Crystallinity was also calculated based on the ratio of the areas under the crystalline diffraction peaks over the total area (including the crystalline and amorphous peaks) [252], which is presented in Table 4-2. All the samples displayed 80-85% crystallinity except the ones prepared using MOR and DEA that fall in the range of 68-75%.



Fig. 4-5 (a) Methanol conversion and (b) light olefins selectivity over the single template samples as a function of time on stream. Reaction condition: T = 425 °C, p = 0.2-0.35 barg, WHSV = 1 g_{MeOH} g_{Cat}⁻¹ h⁻¹, and feed composition 10 mol% H₂O, 20 mol% CH₃OH and 70 mol% Ar.

The SEM images of the single-template samples have been presented in Fig. 4-6, and the particle distribution graphs can be found in the supplementary information (Fig. S 3). The samples prepared with TEAOH generally possessed uniform and pure crystals of roughly 0.5-1.3 μ m. The MOR-directed samples, on the other hand, attained large cubic crystalline particles of 8-16 μ m (using method 1) and 5-12 μ m (using method 2), as well as amorphous or irregularly shaped particles (depictive of partial impurity in the sample). The DEA-introduced samples also contained large-sized particles (~5-14 μ m) with likewise particles. In the previous section (i.e., the influence of silica addition to the template), it was observed that a substantial size reduction in particle size (roughly from 3-7 to 0.2-1.3 μ m) only imposed a 10% boost in catalyst lifetime. Evidently, reducing the particle size only plays a limited role in enhancing catalytic performance. Hence, the substantially prolonged lifetime for the TEAOH-based samples (~11 h) and TEA-directed samples (~16 h) relative to the DEA and MOR samples (~1-2 h) can only be partially justified by the particle size reduction. Hence, another explanation for this considerable difference in lifetime must be uncovered.



Fig. 4-6 SEM images of single-template SAPO-34 samples

Table 4-2 Catalyst lifetime and average products selectivity (single-template catalysts)

Average products selectivity (mol%) *													
Sample name	C1	C2 ⁼	C2	C3 ⁼	C ₃	C4 ⁼	C5=	C6=	Coke	C ₂ =/C ₃ =	LOS	Lifetime (h)	
ΤΕΑΟΗ-1β	0.9	37.6	0.9	37.2	3.3	12.1	2.3	0.5	4.9	1.01	74.8	9.8	
TEAOH-1	1.0	39.6	0.9	36.5	3.1	11.7	2.3	0.4	4.2	1.08	76.0	10.9	
TEAOH-2	1.2	38.3	0.8	37.4	2.6	12.4	2.7	0.6	3.7	1.02	75.7	11.1	
MOR-1	1.0	29.3	1.6	34.2	5.0	15.2	4.5	1.1	8.0	0.86	63.4	1.7	
MOR-2	0.8	23.9	1.2	30.5	3.4	21.5	7.2	3.6	6.6	0.78	54.4	2.2	
DEA-1	1.1	30.8	1.8	34.5	7.7	13.3	3.0	0.6	6.8	0.89	65.3	2.4	
DEA-2	0.9	27.6	1.5	29.6	6.3	15.7	7.2	2.5	8.7	0.93	57.2	1.4	
TEA-1	1.0	34.4	0.4	38.7	1.2	15.1	4.5	1.4	2.8	0.89	73.1	15.7	
TEA-2	1.1	35.8	0.6	39.1	1.3	14.0	4.0	1.2	2.7	0.92	74.9	16.1	

* At reaction temperature of 425 °C, pressure of 0.2-0.35 barg, *WHSV* of 1 $g_{MeOH} g_{Cat}^{-1} h^{-1}$, feed molar composition: 10% water, 20% methanol and 70% Argon. Lifetime and average values were taken from the reaction beginning until conversion drops to 90%.

 C_1 is methane, C_2 is ethane, C_2^{-1} is ethylene and similarly for other hydrocarbons.

Concerning the acidity, all the samples, regardless of the template and synthesis method, presented two peaks, as seen in Fig. S 4. One peak appeared at lower temperatures (tip of the peak at 155-165 °C), representing a combination of Lewis and Brønsted acidic sites, while the other peak emerged at relatively higher temperatures (tip of the peak at 380-410 °C), which can be attributed

to Brønsted acidic sites. Before delving into the comparison of the samples' acidity, by first performing a simple computation, the validity associated with the NH₃-TPD results can be examined. Based on the catalyst gel composition, and by applying the assumption that silica substitutes for phosphorus only (i.e., such that isolated silica is only present in the zeolite framework), a tentative molecular formula of Al₄₀P₃₄Si₆O₁₅₇ can be considered as the final solid synthesized catalyst. Considering this formula, 1.25 millimole of silica is expected to exist per gram of catalyst, which corresponds to the same amount of Brønsted acidic sites per gram of catalyst, since every isolated silica is associated with 1 proton (H⁺). Assuming that a portion of the low-temperature peak and the entirety of the high-temperature peak is attributed to Brønsted acidic sites, the values presented in Table 4-1 are in line with the theoretical calculation of the Brønsted acidic sites quantity. Further analysis of the nature of the acidic sites was conducted by using DRIFT over the TEAOH-1 sample saturated with deuterated acetonitrile (CD₃CN) as the probe molecule. As depicted in Fig. 4-7 (a), characteristic peaks related to the SAPO-34 framework have emerged in the range of 700-1700 cm⁻¹ [168,170,253,254]. The CD₃CN-saturated sample pointed out peaks at 2117, 2269, and 2314 cm⁻¹ that are attributed to the symmetric vibration of CD₃, and C≡N interactions with BAS and LAS, respectively [255,256]. The blank sample, as expected, had no peaks in the interval of 2100-2400 cm⁻¹. The broad peak in the band region of 3100-3700 cm⁻¹ ¹ was due to adsorbed water that diminished at elevated temperatures. BAS-related peak (at 2269 cm⁻¹) transformed to two peaks at 2271 and 2283 cm⁻¹ as the temperature went up. At 100 °C, the intensity of the BAS-related peak decreased, and the LAS peak almost disappeared. There was no sign of the LAS peak at 200 °C while the BAS-related peak vanished in the range of 300-400 °C. Although the BAS peak was significantly larger than the LAS-related peak, the surface area under those peaks couldn't necessarily represent the abundance of such acidic sites. This is because the stretching vibration of C=N interacted with each of these different acidic sites, and may have different extinction coefficients according to Lambert-Beer law [255,256]. To investigate the BAS and LAS over SAPO-34 in a semi-quantitative manner, CD₃CN-TPD was performed, and the results were related to DRIFT tests. The total amount of CD₃CN adsorbed was almost the same as the aggregation of weak and strong acidic sites using NH₃-TPD (1.73 vs 1.72 mmol g_{cat}^{-1}) as these chemicals adsorbed equimolar on acidic sites. This consistency can support the reliability of the tests conducted. Since the LAS-related peak almost disappears at around 100 °C (Fig. 4-7 (a)), the low-temperature peak that has appeared in the CD₃CN-TPD test can be attributed to both LAS and

BAS while the other two peaks at higher temperatures are almost solely related to Brønsted acidic sites. Overall, it can be said that the majority of acidic sites presented over SAPO-34 are BAS rather than LAS.



Fig. 4-7 a) Temperature-dependent DRIFT spectra of TEAOH-1 catalyst saturated with CD₃CN (blank sample is without CD₃CN). b) Deuterated acetonitrile temperature programmed desorption (CD₃CN-TPD) over TEAOH-1 sample and deconvolution of the peaks.

By taking a close look at the results (Table 4-1), it is evident that all the single-template samples prepared via method 2 had a lower number of acidic sites (in both strong and weak ones) relative to their method 1 synthesized counterparts. This may be explained by the assumption that within method 2, silica incorporation into the framework would be more difficult since it was added following the formulation of the aluminum phosphate phase, while in method 1, the addition of silica took place in early-stage synthesis (prior to phosphorous addition). In terms of a comparison of the different single template-based samples, assessing TEAOH-directed samples versus MOR-incorporated samples, it was found that both have almost the same quantity of weak acidic sites, however, the MOR-directed catalysts possessed approximately 15 to 30% more of strong ones (Table 4-1). Furthermore, relative to the TEAOH-based samples, DEA-1 had roughly 20% greater weak and strong acidic sites while DEA-2, on the other hand, had 20% less weak and strong ones. For TEA-prepared samples (concerning both methods), much lower acidity was observed (the lowest one in single-template samples), roughly 40% less in weak and strong ones relative to

TEAOH-directed catalysts. Recalling the catalytic performances, milder acidity could not be the sole reason for a longer lifetime, although it has been widely used in other articles. This can be explained by the fact that DEA samples with both higher (DEA-1) and lower (DEA-2) acidity demonstrated a short lifetime (1-2 h). MOR-based samples also experienced fast deactivation while the acidities were similar to that of TEAOH samples. Therefore, it can be asserted that by commencing with the optimum silica content during synthesis (Si/Al ratio of 0.1-0.2, as investigated elsewhere [257]), the generated catalysts would possess slightly different acidities, but still remain in an acceptable range suitable for catalytic activity in MTO reaction. Hence, a superiority or inferiority in a lifetime for those catalysts cannot be addressed solely by exploring the acidic content.

The elemental composition of the prepared samples has been reported in Table 4-1 using the XRF technique. Overall, the Si content for all samples agreed with its corresponding NH₃-TPD results, asserting the accuracy of the tests, in which it was observed that increasing Si content strongly correlated with a greater acidity. Commencing with the prementioned gel formula and assuming Si incorporation by substitution for phosphorous (i.e., mechanism type I, forming isolated silica) gives the ultimate molar composition of 50% Al, 42.5% P, and 7.5% Si. However, the XRF results show that aluminum has also been substituted by silicon which is feasible through other Si substitution mechanisms (i.e., type II). Generally, it can be asserted that in low Si content samples, such as TEA-1 and -2, the type I mechanism of Si incorporation is dominant, as the Al content has remained intact (~50%, based on the preliminary gel formula). On the other hand, as the Si content increases, which occurred more and less for all other samples, the type II silica incorporation mechanism also transpires, which leads to the simultaneous substitution of Al and P by Si.

The total surface area, the contribution of the external surface areas, and pore size distribution of the different single-template catalysts (computed by the Brunauer-Emmett-Teller (BET), (Barrett, Joyner, and Halenda) BJH and t-plot methods) are presented in Table 4-1. Further information concerning BJH and t-plot models has been provided within the supplementary information. With reference to Table S 3, the cumulative pore volume up to a diameter of 194 nm was measured using a single point total pore volume at $p/p_0 = 0.99$ according to the BJH model. Then, the contribution of the macro- and mesopore's volumes was uncovered using the BJH method for a pore diameter interval of 4 to 194 nm (the region where the Kelvin equation is valid). Agreeably,

the difference between these two values represents the micropore volume and is consistent with the one retrieved from the t-plot method. Analogously, the contribution of macro and mesopore volumes agree with the computed external surface areas. TEAOH-assisted samples possessed an external surface area of 2-4% of the total area and the aggregated contribution of the macro- and mesopore volumes was 20-25% of the total volume (Table 4-1 and Table S 3). On the contrary, DEA- and MOR-directed samples demonstrated negligible values with correspondence to the prementioned characteristics. The reflection of having macro and mesopores is an enhancement in mass transfer capabilities, which results in better accessibility to the catalyst interior sites for the reactant despite coke formation. This will lead to a prolonged catalyst lifetime and higher coke content threshold (i.e., the point at which complete catalyst deactivation occurs). Accordingly, DEA and MOR samples deactivated completely with 7.5-8% coke content while the other samples continued generating hydrocarbons until 20-21% of coke was deposited within the catalyst (Table S1). Referring to the formerly described calculation method, coke selectivity depends on the coke deposition rate of the fully deactivated catalyst, average methanol conversion, and catalyst lifetime. Hence, despite the low coke deposition amounts over DEA- and MOR-based catalysts (7.5-8 wt%), due to their very short active lifetime (1-2 h), almost a 2-fold coke selectivity resulted relative to TEA- and TEAOH-incorporated samples, that retained up to 20-21% coke content but experienced a much longer lifetime.

By considering the external surface area as the dominant factor affecting the catalyst lifetime, a comparison of TEAOH-1&2 with TEA-1&2 (which both retain a high external surface area) can reveal the influence of catalyst acidity and pore size. As explained earlier, the existence of SAPO-5 in TEA-incorporated samples (Fig. 4-4) induced higher propylene and heavier olefins production (Table 4-2), along with decreased ethylene formation, which resulted in slightly lower light olefin selectivity over TEA samples compared to TEAOH ones (Fig. 4-5). Other than that, by taking a closer look at the product distribution (Table 4-2), one can uncover the fact that alkanes (especially ethane and propane), as well as coke, are substantially lower over TEA samples (roughly 50% less). This can help validate the proposed mechanism of coke formation by former research works [258,259], which suggest that coke generation and alkane production are interdependent steps. According to their mechanistic outlooks, the cyclization of hexene, and the subsequent steps involving the aromatization of cyclohexene, coincide with hydrogen transfer reactions in which neighboring alkoxy groups on the zeolite surface are converted to alkanes. Accordingly, the ratio of alkanes to alkenes formed is referred to as the hydrogen transfer index (HTI) [250] which qualitatively assesses the influence of zeolite structure on directing the process of methanol dehydration ((CH₂)H₂O) to olefins ((CH₂)n) formation or towards alkanes (CnH_{2n+2}) and hydrogen-deficient species such as aromatics. A lower coke formation rate over TEA-assisted catalysts compared to TEAOH samples can be partially attributed to milder acidity, which in turn improves the catalyst lifetime. Methane formation, on the other hand, had similar quantities between the TEA-directed versus TEAOH-based samples. Hence, it can be insinuated that methane formation may be dominated by other factors and follow a different mechanistic route.

4.4 Mixed-template SAPO-34 synthesis

Regarding the optimum gel pH that resulted in higher crystallinity and surface area, mixedtemplate SAPO-34 samples also displayed the same behavior as the single-template ones. The catalysts prepared by the combination of TEAOH with either DEA or MOR, had the optimum pH of 6.5-7.5 whereas the TEAOH/TEA samples were optimal in the pH bracket of 8.0-8.5. The ratio of TEAOH to the second template was kept constant (1 to 3) and the total template consumption lied between 2-3 mol (per mole of Al_2O_3) in the gel based on the mixing procedure and type of template used. For the sake of consistency, all the reaction parameters were kept analogous to those of the single-template section. Similarly, catalysts produced with the same type of templates, but varying procedures, demonstrated somewhat equivalent activity performance. According to Table 4-2, TEAOH/MOR samples demonstrated the longest lifetime (16-17 h); however, the light olefin selectivity fell within the range of 55-60 % due to the excessive formation of C_4^+ species. On the other hand, both TEAOH/DEA and TEAOH/TEA catalysts experienced a slightly higher light olefin selectivity (77-78 %), and roughly 25% longer lifetime relative to the single-template TEAOH-directed sample (Table 4-3). Generally, it can be mentioned that by employing the second synthesis method, catalysts with slightly superior catalytic performance were prepared. To summarize, all the four TEAOH/DEA or TEAOH/TEA samples had acceptable performance (in terms of light olefins selectivity and catalyst lifetime, and it seems that the optimal one can be appointed to be the TEAOH/DEA-2 sample (Fig. 4-8).



Fig. 4-8 (a) Methanol conversion and (b) light olefins selectivity over the mixed template samples as a function of time on stream compared to the TEAOH-1 sample. Reaction condition: T = 425 °C, P = 0.2-0.35 barg, WHSV = 1 $g_{MeOH} g_{Cat}^{-1} h^{-1}$, and feed composition 10 mol% H₂O, 20 mol% CH₃OH and 70 mol% Ar.

Average products selectivity (mol%) *												
Sample name	C ₁	C ₂ =	C ₂	C3 ⁼	C ₃	C4 ⁼	C5 ⁼	C ₆ =	Coke	C ₂ =/ C ₃ =	LOS	Lifetime (h)
TEAOH/MOR-1	0.7	25.5	0.4	30.6	1.6	25.9	8.6	3.5	2.4	0.83	56.1	17.3
TEAOH/MOR-2	0.8	30.1	0.6	29.8	1.4	19.4	6.0	2.1	2.8	1.01	59.9	16.3
TEAOH/DEA-1	1.0	41.1	0.9	36.2	2.6	11.2	2.4	0.5	3.9	1.14	77.2	13.3
TEAOH/DEA-2	1.0	41.7	0.8	36.5	2.4	10.6	2.2	0.5	4.0	1.14	78.3	13.7
TEAOH/TEA-1	1.2	39.1	0.8	37.1	2.4	12.1	2.7	0.6	3.6	1.05	76.3	13.7
TEAOH/TEA-2	1.2	40.4	0.9	37.0	2.1	11.4	2.4	0.5	3.9	1.09	77.5	14.1

Table 4-3 Catalyst lifetime and average products selectivity (mixed-template samples)

* At reaction temperature of 425 °C, pressure of 0.2-0.35 barg, *WHSV* of 1 $g_{MeOH} g_{Cat}^{-1} h^{-1}$, feed molar composition: 10% water, 20% methanol and 70% Argon. Lifetime and average values were taken from the reaction beginning until conversion dropped to 90%.

 C_1 is methane, C_2 is ethane, $C_2^{=}$ is ethylene, and similarly for other hydrocarbons.

With reference to Table 4-4, it can be seen that the crystallinities of all the mixed-template samples are high (in the range of 83-90%). X-ray diffraction patterns of the mixed-template samples were also collected to assess the phases that have been formed (Fig. 4-9). Via peak-matching, it can be concluded that nucleation with TEAOH followed by the addition of the complimentary template (either DEA or TEA), as anticipated, resulted in pure SAPO-34 production. However, TEAOH/MOR samples still have a noticeable coexistence of SAPO-5 as is evident from the

characteristic peak at 20 of 7.4°. This can in turn potentially justify the higher production of heavier components over these catalysts, which resulted in lower light olefin selectivity. The SAPO-5 phase in TEAOH/MOR samples is even more visible and distinguishable, as illustrated by the SEM images in Fig. 4-10. The hexagonal prism-shaped crystals are characteristic of the SAPO-5 phase [260,261] and can be easily differentiated from the cubic SAPO-34 particles. Owing to TEAOH usage, all mixed-template catalysts have smaller particles compared to their single-template counterparts (Fig. S 3). Furthermore, the TEAOH/TEA catalyst, in contrast to the TEA sample, has no sheet-like particles (Fig. 4-10). Both TEAOH/MOR samples (prepared with both methods) are in the range of 2-10 microns, whereas TEA-TEAOH and DEA-TEAOH catalysts are smaller especially whilst using the second synthesis procedure.



Fig. 4-9 X-ray Diffractions for the mixed-template samples with corresponding references: SAPO-34 (PDF # 00-047-0617), SAPO-5 (PDF # 00-047-0619), and SAPO-11 (PDF # 00-047-0613).

In terms of acidic site strength and abundancy determination, there is a consensus that the second synthesis procedure facilitated higher Si incorporation into the framework, and consequently, resulted in a higher quantity of acidic sites per gram of catalyst (as seen in Table 4-4). All four TEA-TEAOH and DEA-TEAOH catalysts had similar weak acidic sites and around 20% higher strong ones compared to the single-template TEAOH-assisted sample. This again supports the fact that the amount of Brønsted acidic sites is not the underlying factor behind the desirable catalytic performance if it is in the acceptable range, which in the case of our samples is 0.5 to 0.9 mmol g_{cat}^{-1} (for strong sites specifically). According to the XRF data seen in Table 4-4, alongside the NH₃-TPD results (Table 4-4), it can be observed that the catalysts' Si contents are positively correlated with acidic strength. The surface area was also improved by employing the mixed template method and the highest surface area was recorded for TEAOH/DEA samples, where around a 20% enhancement was observed in comparison to the single-template DEA-directed ones (as seen in Table 4-4). It should also be noted that all the samples had a high external surface area, which again supports the fact that possessing macro- and mesopores is the principal characteristic of a durable SAPO-34 catalyst. Surprisingly, even after the catalyst's complete deactivation due to pore blockage by coke, the macro and mesopores are intact in comparison to the fresh catalyst, while the microporous area has depleted to almost 1% of the fresh catalyst (Table S 3). This again confirms the hypothesis about the role of macro and mesopores in facilitating the mass transfer to the interior active sites despite coke formation.

Sample name	S _{BET} ^a (m ² g ⁻¹)	S _{Micro} + S _{Meso+Macro} (m ² g ⁻¹) ^b	Weak acid sites ^{c,d,f} (mmol _{NH3} g _{cat} ⁻¹)	Strong acid sites ^{c,d,f} (mmol _{NH3} g _{cat} ⁻¹)	Al (mol%)	P (mol%)	Si (mol%)	Crystallinity ^g (%)
TEAOH/MOR-1	600	589 + 11	0.74 (158 °C)	0.61 (380 °C)	50.3	43.0	6.7	84.0
TEAOH/MOR-2	618	607 + 11	1.01 (161 °C)	0.84 (398 °C)	49.8	41.9	8.3	84.4
TEAOH/DEA-1	641	632 + 9	1.00 (160 °C)	0.84 (395 °C)	48.6	43.2	8.2	89.5
TEAOH/DEA-2	652	640 + 12	1.07 (160 °C)	0.90 (400 °C)	48.0	43.5	8.5	86.4
TEAOH/TEA-1	595	586 + 9	0.95 (160 °C)	0.76 (391 ℃)	49.0	43.5	7.6	83.6
ТЕАОН/ТЕА-2	597	585 + 12	1.09 (163 °C)	0.91 (403 °C)	47.5	44.6	7.9	83.2

Table 4-4 Physicochemical properties of the prepared catalysts. Total, micro- and combined meso + macro surface area. NH₃ uptake for weak and strong acid sites. Bulk molar composition (using XRF), crystallinity and particle size

^a S_{BET} = BET total specific surface area obtained from adsorption data in the p/p_0 range from 0.06–0.2; all reported data are within $\pm 4 \text{ m}^2 \text{ g}^{-1}$ based on repeated analysis.

^b S_{Micro} = micropore; $S_{Meso+Macro}$ = meso + macropore surface areas.

° Precision $\pm 2\hat{\%}$ relative d Precision $\pm 3^{\circ}C$ e negligible amount

^f value in brackets refers to peak temperature in ^oC

^g This was calculated based on the ratio of reduced area to global area, where the reduced area is the global area minus the amorphous surface area (using DIFFRAC.EVA V4.1).

Referring back to Fig. 4-8, two interesting points can be inferred; first, higher LOS for the TEAOH/DEA and TEAOH/TEA mixed-template samples (compared to the TEAOH-directed single-template one) is not because of the change in reaction mechanism or pore-size of the catalysts (making it more favorable towards smaller molecules like light olefins) as the LOS for all catalysts are roughly equivalent in early stages of the activity test. In fact, this superior LOS is due to the ability of the mixed-template ones in prolonged survival over advanced times on stream where the pores are partially coked and light olefins are being produced in larger quantities. This is due to the introduction of secondary macro- and mesopores, as previously demonstrated, which keep the interior active sites accessible to the reactant. Secondly, a gradual increase of LOS over time due to partial pore restriction by coke until catalyst deactivation can be seen over all samples except TEAOH/MOR ones. This is due to the fact that TEAOH/MOR samples contain two completely separate phases of SAPO-5 and SAPO-34, as shown in Fig. 4-10. It seems that SAPO-34 with higher LOS deactivated faster, hence, responsible for the first observable hill in the LOS

curve of Fig. 4-8, while SAPO-5 particles remained active for longer (possessing lower LOS) until complete deactivation of the sample.



Fig. 4-10 SEM images of mixed-template SAPO-34 samples

Table S 4 compares the activity of the optimum catalyst in the present work with catalysts studied in the literature. Light olefin selectivity has not been presented as some articles have overlooked the coke contribution and reported unrealistic values of 85-95%. It is worth mentioning that the

light olefins selectivity of the commercially established process by UOP/Hydro is within the range of 75-80% (carbon-based) with almost 3% coke and 1% CO_x formation [26]. These values have been achieved in a fluidized bed reactor that has better mass and heat transfer characteristics than lab-scale fixed-bed reactors employed in the aforementioned research articles. In addition to that, the commercialized process keeps 7-8% coke over the catalyst (by adjusting the regeneration process) to enhance light olefin selectivity and reduce C_4^+ olefins. Considering the various WHSVs used in different articles, a universal parameter termed catalyst processing ability was defined to simplify the comparison. To calculate processing ability, WHSV is multiplied by catalyst lifetime (time on stream while the conversion exceeds 90%), which gives the methanol weight that can be processed by 1 gram of catalyst. One can use this parameter to identify the superior catalyst among all synthesis procedures and promotion techniques that have been tried so far. Overall, it seems that our optimum mixed-template catalysts (TEAOH/DEA and TEAOH/TEA) possess the longest lifetime among their counterparts in the literature (Table S 4). MOR-TEAOH-directed samples last longer than other mixed-template catalysts but suffer from relatively lower light olefins selectivity. Nonetheless, considering the catalyst lifetime, WHSV, and number of BASs (roughly based on the strong acidic sites determined by NH₃-TPD tests), the number of methanol molecules that have been converted over each BAS before catalyst deactivation falls in the range of 400-900 mol_{MeOH}mol_{BAS} for long-lasting samples. More specifically, the active sites of TEAOH-1 illustrated cumulative activity of 460 $mol_{MeOH}mol_{BAS}^{-1}$ and TEA-1 showed 880 $mol_{MeOH}mol_{BAS}^{-1}$. It should be noted that even poor-performing catalysts, such as DEA and MOR-directed ones, had BAS activity of 50-60 $mol_{MeOH}mol_{BAS}^{-1}$. This demonstrates that BAS in SAPO-34 catalysts, despite its performance, still plays a catalytic role rather than a stoichiometric one.

4.5 Coke formation analysis

In terms of the TGR-MS results, by utilizing a highly permeable catalyst basket and passing the excess methanol around it, homogenous coke formation throughout the catalyst bed was achieved. This can almost simulate a fluidized bed reactor and be used to connect the product distribution with the homogenous coke content of the catalyst. This was validated by the observation of uniform gradual color change of the catalyst in the TGR basket during the test. In contrast, within a fixed bed reactor, the side of the catalyst bed facing the fresh reactant is darker and contains more

coke. The coke deposition in a fixed-bed reactor usually starts from the front side of the catalyst and moves forward until the entire catalyst bed has become deactivated (termed as the "breakthrough" point). Fig. 4-11 demonstrates the gradual coke formation over TEAOH/DEA-2 and DEA-1 catalysts (as a comparison between the great and poor-performing samples, respectively) in the thermogravimetric reactor. The initial decrease in catalyst weight that is due to moisture desorption (during the temperature rise from ambient to the reaction temperature of 425 °C) has been omitted to simplify the results, but it is visible over another catalyst, as seen in Fig. S 5.

The moisture content over different samples was in the range of 18-25 wt% (i.e., in terms of the weight percent of moisture over dry catalyst). The ones with higher surface area and pore volume contained higher moisture. The samples then remained at 425 °C for 1 h to stabilize the weight and after, the feeding commenced utilizing \sim 7% methanol in argon. Initially, 80-85% of methanol was converted while the rest passed around the catalyst basket unreacted. The products' distribution was the same as the ones recorded in the fixed-bed reactor using GC. Over time on stream, a gradual increase in ethylene selectivity as well as a decrease in heavy olefins production were observed (Fig. 4-11 c and d). This transpired until the catalyst's pores were completely blocked with coke, and as a result, DME plus an upsurge of unreacted methanol began to appear at the effluent of the reactor.



Fig. 4-11 TGR-MS analysis: coke formation measurement using TGA and products distribution acquisition by MS over (a) & (c) TEAOH/DEA-2 and (b) & (d) DEA-1 catalysts. Reaction condition: T = 425 °C, P = 0.2-0.35 barg, $WHSV = 1 g_{MeOH} g_{Cat}^{-1} h^{-1}$, and feed composition 7 mol% CH₃OH and 93 mol% Ar

The catalyst lifetime was found to be almost the same in both fixed-bed and thermogravimetric reactors after considering uncomplete methanol conversion in the latter (i.e., 13.7 h in the fixedbed reactor versus 13.6 h in the TGR). The final coke deposition in the TGR is slightly lower than that of the fixed bed reactor (23.5 wt% vs 25.8 wt% over TEAOH/DEA-2 and 6.9 wt% vs 7.9 wt% upon DEA-1 catalyst), as in the latter, the methanol flow had to pass through the catalyst bed and the catalyst capacity for conversion was completely exploited. The weight change of the catalyst within one minute reflects the instantaneous coke formation rate, which in turn can be converted to coke selectivity by dividing by the quantity of methanol that has been converted within that time interval. The resulting values have been depicted in Fig. 4-11 (a) and (b). An interesting point that has never been reported is the coke selectivity during the reaction. Over our optimum catalyst (i.e., TEAOH/DEA-2 sample, Fig. 4-11 a), the coke formation began with a spike. The coke selectivity then slightly diminished followed by a stabilization at ~1.7% and gradually rose thereafter, reaching a maximum of 5.1% within the final region of catalyst activity (before complete deactivation occurs). A recent study by Lin et. al, [262] reported the emergence of HCHO in the early stages of the reaction, and within the catalyst deactivation stage in higher quantities. While within the plateau of complete methanol conversion, HCHO was infinitesimal. They speculated that HCHO assists the formation of the hydrocarbon pool (HCP) species in the initial stage and the generation of poly cyclic aromatic hydrocarbons in the deactivation stage, ultimately accelerating both reaction initiation and deactivation. This completely agrees with our TGR-MS results where we recorded a spike of weight gain in the early stages of the reaction (due to the formation of the entrained species such as HCP autocatalytic intermediates), and high coke formation rate towards the advanced times on stream and close to deactivation (that is due to the formation of poly cyclic aromatic hydrocarbons or coke). The gentle increase in the coke selectivity or coke formation rate has been illustrated in Fig. 4-12.



Fig. 4-12 Coke evolution in the pores of the SAPO-34 catalyst. Left) in the beginning of the activity run. Right) in enhanced times on stream close to catalyst deactivation

This phenomenon can be explained by the fact that in the early stage of the reaction, the pores are fully open, which enables the heavy compounds to easily escape out of the catalyst cages. As the reaction proceeds, the pores of the catalyst, especially those located in the outer layers will be restricted by partial coke formation. As small molecules of methanol continue to penetrate in and light compounds exit out of catalyst particles, heavy products are inhibited from diffusing out because of pore restriction, which results in a decrease of heavy olefins selectivity. This causes large molecules to remain trapped inside the interior pores and leads to further growth of their

hydrocarbon chains leading to higher coke formation rates. Cyclization and aromatization of these long chains ultimately generate multi-ring aromatics that block the catalyst's pores completely. The highest light olefins production was recorded over the partially coked catalyst with a coke deposition of 14.9 wt% (coke /dry catalyst). Subsequently, when the coke deposition reached a value of 23 wt%, no hydrocarbon was produced other than DME. It is worth mentioning that the coke selectivity was 0.25-0.3 wt% when the catalyst was producing only DME at the equilibrium conversion, almost 1/15 of the average coke selectivity in the MTO reaction. This could be justified based on the fact that at this point, the majority of the catalyst active sites have been blocked, and hence, methanol molecules are only able to go through a singular dehydration step to form DME, rather than consecutive transformations to formulate heavier hydrocarbons and ultimately coke. Over DEA-1 (Fig. 4-11 b), as a representative of samples with a short lifetime, the coke selectivity profile similarly experienced a spike at the beginning of the reaction and then an increase to a maximum until the deactivation occurred. However, the major difference here was the fact that the initial coke formation rate was almost 80% of the maximum coke formation, while with respect to the catalysts experiencing a longer lifetime, the initial coke formation was only ~30% of the maximum value. This can be justified by the lack of macro- and mesopores (i.e., the absence of an external surface area) in the DEA-1 sample, which stimulated fast coke formation from the beginning of the reaction.

The same behavior was displayed by other catalysts with long catalytic lifetimes regardless of the synthesis procedure. The relevant graphs of the in-situ TGA tests over TEAOH-1, MOR-1, and TEAOH/TEA-2 have been presented in the supplementary data (Fig. S 5 and Fig. S 6). This contrasts with the results reported by [11] who have conducted in-situ measurements of coke formation. They reported the highest rate of coke formation at the beginning of the experiment, which continuously decreased until complete deactivation, due to the high *WHSV* that has been used. Referring back to Fig. S 6, the TEAOH/TEA-2 sample (with almost the same catalytic performance as TEAOH/DEA-2) displayed analogous coke selectivity values of 1.8, 4.8 and 0.4 % at initial activity, final activity (before complete deactivation) and at DME production stages, respectively. The total coke deposition until complete deactivation (i.e., solely DME production) was measured to be 22 wt% (coke/dry catalyst). For TEAOH-1 (Fig. S 5), the coke selectivity commenced at almost a similar value (~1.8 %), and experienced a high of 6.1 %, followed by a

depletion to 0.3 % in the DME production stage. In terms of the total coke precipitation (until deactivation), 18 wt% (coke/dry cat) was recorded. As previously discussed, the total coke deposition over samples with shorter lifetimes is lower but dividing this value by the lifetime gives a higher average coke formation selectivity. For instance, 7.9 wt% total coke deposition within 2.3 h catalyst lifetime resulted in a 6.8 % average coke selectivity over DEA-1 catalyst, compared to 4.0 % average coke selectivity (by 25.8 wt% ultimate coke deposition within 13.7 h catalyst lifetime) for TEAOH/DEA-2 sample.

The formation of the Brønsted acidic sites within the SAPO-34 lattice has been extensively investigated [263] and is now well understood. Substitution of a Si⁴⁺ atom for a P⁵⁺ atom in the AlPO₄ framework (so-called isolated silica formation Si (4Al)) causes a negative charge that is neutralized by the addition of a proton attached to the bridging oxygen (Al-OH-Si) and correspondingly forms a Brønsted acidic site. Simultaneous substitution of adjacent Al and P atoms with multiple Si atoms can result in silica islands. For these silica islands, the case is more complicated as the siliceous island can include different numbers of silicon atoms, which can be dictated by the catalyst topology and Si content. In the case of the most ordinary silica island, four P and one Al atom are replaced by five Si. The central silicon (Si (4Si)) has no associating proton while 3 protons accompany 3 of the 4 surrounding Si atoms (Si (1Si 3Al)). The larger siliceous islands can create other silica environments including Si (2Si 2Al) and Si (3Si 1Al). According to the ²⁹Si NMR spectrum, these five silicon environments (Si (nSi (4-n)Al), *n* ranging from 0 to 4) can generate five peaks centered at -90, -95, -100, -105, and -110 ppm (all with a precision of ± 1), respectively. As indicated in Fig. 4-13 a, the main signal emerged at -89.5 ppm corresponding to Si (4Al) with a small shoulder at -94.5 ppm, which can be assigned to Si (1Si 3Al). It asserts that although the silica contents of the synthesized catalysts are different (from 5 to 10 mol%, Si/(Si+Al+P)) because of the alteration in the template and the synthesis method that has been utilized, still, this range favors the formation of mainly isolated silica active sites (Si (4Al)). This originates from the low silica content of the synthesis gel (Si/Al = 0.15), and is well in agreement with the literature [104]. Signals at -78 and -88 ppm, which can be attributed to defected and extra framework silicon, are more significant in MOR-2 and DEA-2. That could be a cause of the fast deactivation observed for these two samples. The width of the main peak at -89.5 ppm can reflect the crystallinity of the silica within the catalyst. The lower the width of the peak, the higher the

crystallinity. Sharper peaks for TEAOH/DEA-2, TEAOH/TEA-2, TEA-2 and TEAOH-1 samples prove that they possess more crystalline Si compared to DEA-2 and MOR-2 catalysts, which is in alignment with XRD results.



Fig. 4-13 a) ²⁹Si NMR spectrum of the catalysts b) ¹³C NMR of the coke-deposited samples

¹³C NMR was employed to identify the hydrocarbon species that form as coke over the catalysts (Fig. 4-13 b). The partially coked TEAOH-1 sample was extracted from the reactor after 3 h on stream by immediate feed shutdown and quenching of the catalyst bed (via opening the electrical furnace door). This sample along with completely deactivated TEAOH-1 (retrieved after 12 h on stream and 1 h of flushing argon) were analyzed to investigate the coke evolution through the catalyst lifetime. Signals at 15-25 ppm are considered to be R-CH₃ or R-CH₂-R groups in the form
of alkyl groups attached to aromatics or carbons in olefinic linear chains. Peaks at 125-135 ppm are assigned to both alkylated and non-alkylated aromatics. Whereas the peak at 100-110 ppm can be attributed to C=C olefinic chains [264]. The large peaks at 15-25 ppm, over partially coked TEAOH-1 sample, are created by R-CH₃ or R-CH₂-R groups in both the linear alkenes and polyenes (evident by the peak at 100-110 ppm) and alkylated aromatics (evident by the peak at 125-135 ppm). A small peak at 50 ppm is indicative of adsorbed methanol. As the reaction proceeds, over deactivated TEAOH-1 sample, the peak at 100-110 ppm disappears, showing that the alkenes and polyenes undergo cyclization and aromatization reactions. Besides, the ratio of the peak at 125-135 ppm over the one at 15-25 ppm substantially increases, projecting the fact that the light aromatics have gone through further growth to form heavy multi-ring aromatics. This again agrees with the literature [262] that reported the progressive increase of unsaturation degree of hydrocarbons retained in catalyst, from olefin to polyene, cyclopentadiene, aromatics, and to polycyclic aromatic hydrocarbons (PAHs) during coke evolution. This finding completely confirms the coke growth scheme illustrated in Fig. 4-11. The ¹³C NMR spectrum of the deactivated TEAOH/TEA-2 and TEAOH/DEA-2 samples, as our optimum catalysts, is the same as the deactivated TEAOH-1 with slightly higher peak intensities due to higher coke content.

Coke species over some of the deactivated catalysts were identified via GC-MS method as indicated in Fig. 4-14. M-dichlorobenzene is distinguished by red ink, as the internal standard. Coke species extracted from TEAOH-1 and TEAOH/DEA-2 are almost identical verifying the ¹³C-NMR results (Fig. 4-13 b); both mainly consisted of methyl/ethyl naphthalene, anthracene, and pyrene whereas the intensity of the peaks related to TEAOH/DEA-2 sample is higher due to its higher coke content. The coke species from MOR-1 and DEA-2 are alike and much lighter than the coke compounds from TEAOH-1. This can support the fact that MOR-1 and DEA-2 samples deactivate easily (the pores get blocked and inaccessible) even with smaller coke species such as naphthalene and methylated naphthalene due to lack of intergrowth macro and mesopores. The coke compounds released from the TEA-1 sample consist of the same heavy species (anthracene and pyrene) as the ones extracted from TEAOH-1 but include a considerable portion of lighter aromatics such as poly alkylbenzene, naphthalene, and methylnaphthalene. This could originate from the sheet-like particles of TEA-1 catalyst with a thickness of a few hundred nanometers. The short diffusion pathway lowers the chance of further growth of entrained species. Moreover,

polycyclic aromatics are formed by the hydrogen transfer between primary olefins and hydrocarbon pool compounds (poly methylbenzene) over acidic sites, and low acidity, in the case of the TEA-1 sample, can attenuate these reactions and generate a lower quantity of heavy aromatics [115].



Fig. 4-14 GC-MS analysis of coke species formed over deactivated catalyst samples.

4.6 Conclusion

The template's role in the physicochemical properties of SAPO-34 was investigated using the four most popular templates (TEAOH, MOR, TEA, and DEA) in both single and mixed-template methods to reduce the consumption of costly TEAOH. Catalyst activity in methanol conversion to light olefins was examined at 425 °C and *WHSV* of 1 g_{MeOH} g_{Cat}⁻¹ h⁻¹. The TEA-based sample proved to be a good substitute for TEAOH in single template SAPO, and both TEAOH/DEA and TEAOH/TEA-based samples were successfully produced with the sole existence of the SAPO-34 phase and exhibited acceptable performance. Possessing a high external surface area (macro and mesopores) was recognized to be the dominant parameter affecting the catalyst's lifetime while having the optimum acidity and small particle size played minor roles. In-situ measurement of coke formation over SAPO-34 was also conducted in a thermogravimetric reactor and led to the proposal of a coke formation mechanism, which was confirmed by ¹³C-NMR spectroscopy and GC-MS techniques.

5 SAPO-34 synthesis by alkali post-treatment

5.1 Introduction

In this chapter, to overcome the catalyst's fast deactivation due to coke formation, we aimed to improve the catalyst mass transfer by synthesizing a hierarchical structure within the catalyst. Alkali posttreatment was employed to perforate the catalyst particles and introduce macro and mesopores in the catalyst's microporous structure. Here, diethylamine (DEA), a weak alkali, was utilized to better control the etching process and to avoid the destruction of the parent SAPO-34 framework. It seems acid or basic post-treatment alters the ratio of strong/weak acidic sites (more specifically, Brønsted to Lewis acidic sites), which may correspondingly affect the product distribution. However, there still exists a lack of studies fixated on the role of Brønsted and Lewis acidic sites (BAS and LAS) in the MTO reaction over the treated catalysts. Hence, we took a step further, and after precise measurement of the acidic site's density and the product distribution over the parent and treated catalysts, we uncovered the role of BAS and LAS in the MTO reaction by DFT modeling. With the aid of comprehensive catalyst characterization techniques, DFT modeling, and precise analysis of the products over parent and treated samples, we assessed the effect of etching on the catalyst physiochemical properties (with emphasis on the LAS to BAS ratio) and related them to the catalytic activity performance.

5.2 Catalyst characterization results

Fig. 5-1 presents the SEM images of the parent as well as the treated catalysts. The yielded particles had the typical cubic shape of SAPO-34 with a size of 3-5 μ m. While the parent catalyst shows a solid surface without any holes, the treated samples clearly have secondary meso- and macropores as a result of etching in the alkali environment. The catalyst treated with 0.5 M DEA has mesopores (20-50 nm) on all sides of the cubic particles. Further increase in the DEA concentration causes severe corrosion and etching, which resulted in larger voids. These cavities are attached to each other to ultimately make hollow particles as illustrated in Fig. 5-1 for samples 2.0 and 4.0 DEA/SAPO-34, respectively.



Fig. 5-1 SEM images of the parent and treated catalyst samples.

The X-Ray diffraction pattern of the reference SAPO-34, parent SAPO-34, and the treated sample with the highest concentration of DEA (4.0 molar DEA) can be seen in Fig. 5-2 (a). Both parent and treated samples exhibit characteristic diffraction peaks corresponding to the reference pattern of the chabazite structure. After DEA treatment, even in the harshest condition (highest DEA concentration), no new peak was perceived, showing that the SAPO-34 structure is stable and well preserved during the treatment. The crystallinity of the treated sample compared to the parent catalyst was also calculated based on the ratio of the areas under the crystalline diffraction peaks of each catalyst. Lower crystallinity with regards to the treated sample relative to the parent catalyst can be explained by the severe etching via an alkali solution of high concentration that can partially destroy the SAPO-34 framework. However, the crystal size (using the Scherrer equation, K=0.9) stays the same after DEA treatment, which is again indicative of the catalyst framework conservation after the treatment (Table 5-1). The crystal size (calculated from XRD) is completely different from the particles size (seen in SEM images). Each cubic particle of the SAPO-34 catalyst can contain hundreds of crystals.



Fig. 5-2 (a) XRD diffraction peaks. (PDF # 00-047-0617 for the reference SAPO-34). (b) N₂-adsorption/ desorption isotherms of the prepared catalysts.

Relating the bulk and surface chemical composition of the parent catalyst according to the ICP and SEM-EDX data (Table 5-1), it is evident that SAPO-34 has greater silica content in the particle's core than on the outer surface. Based on the ICP results, Si reduces slightly in the treated samples and this observation proves that Si is the most vulnerable element in an alkali environment. Since the core of the SAPO-34 particles is richer in Si than the outer layer, it would be easily attacked by DEA and as illustrated in the SEM images, the severely treated samples are hollow.

Sample name	I(molar	ICP test – bulk molar composition (%) ^a			SEM-EDX – surface molar composition (%) ^b			Crystallinity	
Sample name	Al	Р	Si	Al	Р	Si	(nm) ^c	(%) ^d	
Parent SAPO-34	42.9	42.0	15.1	47.5	41.7	10.8	69	100	
4.0 DEA/SAPO-34	42.9	42.9	14.2	47.4	42.1	10.5	69	83	
^a Precision: ± 0.1 %	^b Precis	sion: ± 0.2 %	° Pi	recision: ± ().5 nm	^d Precisi	on: \pm 3% based	l on repetition	

Table 5-1 Crystallinity, crystal size, and chemical composition (mol%) of the synthesized catalysts

Sample name	$\frac{S_{BET}}{(m^2 g^{-1})}$	$\begin{array}{c} S_{\text{Micro}^a} \\ (m^2 \ g^{-1}) \end{array}$	$\frac{S_{Meso+Macro}{}^a}{(m^2g^{-1})}$	VPore ^b (m ³ g ⁻¹)	Weak acid sites ^c (mmol _{NH3} g _{cat} ⁻¹) Peak Temp (°C) ^d	Strong acid sites ^c (mmol _{NH3} g _{cat} ⁻¹) Peak Temp (°C) ^d
SAPO-34	561	544	17	0.248	1.12 (154 °C)	0.63 (399 °C)
0.5 DEA/SAPO-34	544	524	20	0.239	1.13 (155 °C)	0.51 (398 °C)
1.0 DEA/SAPO-34	515	491	24	0.238	1.06 (145 °C)	0.42 (390 °C)
2.0 DEA/SAPO-34	444	292	152	0.216	1.01 (148 °C)	0.34 (380 °C)
4.0 DEA/SAPO-34	324	272	52	0.213	1.01 (150 ℃)	0.33 (385 °C)

Table 5-2 Physio-chemical properties of the samples using N₂ adsorption and NH₃-TPD techniques.

^a S_{BET} = BET total specific surface area obtained from adsorption data in the p/p_0 range from 0.06–0.3; all reported data are within ±5 m² g⁻¹ based on repeated analysis. S_{Micro} = micropore; S_{Meso+Macro} = meso + macropore surface areas. ^b V_{Pore} = pore volume was obtained at $p/p_0 = 0.9$. ^c Precision ± 2% relative ^d Precision ± 3°C

The nitrogen adsorption/desorption isotherms of the samples are depicted in Fig. 5-2 (b). As expected, the parent SAPO-34 follows a type I isotherm pattern [265], indicating a microporous structure; while the treated samples possess a combination of type I and IV isotherms, which confirms the coexistence of micro and mesopores in the catalyst structure. The ascent of the isotherms at a higher relative pressure ($p/p_0 > 0.8$) is due to capillary condensation in mesopores. This phenomenon is more pronounced as we increase the DEA concentration until 4.0 DEA/SAPO-34, which experiences a significant reduction in surface area ($324 \text{ m}^2 \text{ g}^{-1} \text{ vs.}$ 560 m² g⁻¹ for parent SAPO-34 in Table 5-2) due to the merging of mesopores and forming of hollow particles (as described in SEM images). The gradual loss of surface area for treated samples compared to the parent catalyst stems from the destruction of the microporous structure by alkali treatment. The treated samples with low DEA concentration still possess a high surface area (544 m² g⁻¹ for parent 0.5 DEA/SAPO-34) but decreases to 444 m² g⁻¹ and 324 m² g⁻¹ for 2.0 and 4.0 DEA/SAPO-34 samples, respectively. The contribution of the external surface area corresponding to secondary pores (macro- and mesopores) went up as the DEA concentration increased except for the 4.0 DEA/SAPO-34 sample, which agreed with the SEM observations.

Using NH₃-TPD, acidic alteration of the treated samples was evaluated relative to the parent catalyst. All the samples presented two main peaks: one at 145-155 °C, representing the weak acid sites (mostly attributed to extra-framework aluminum; Lewis acidic sites (LAS)) and one at 380-400 °C, indicative of strong acidic sites (largely assigned to Brønsted acidic sites (BAS)), (Fig. 5-3 (a) and Table 5-2). While the weak sites barely change with further treatment, the number of

strong acid sites reduces by half in the case of the 4.0 DEA/SAPO-34 sample. According to the ICP results (Table 5-1), parent SAPO-34 has a formula of $Al_{43}P_{42}Si_{15}O_{199.5}$ with a molecular weight of 6074 g mol⁻¹. As a result, 1 g of catalyst contains 2.5 mmol of Si. This means only a part of the silica atoms are accompanying protons and others are extra framework Si. This explains why with a small change in Si content over the treated sample (4.0 DEA/SAPO-34), half of the Brønsted acidic sites have been omitted.

To investigate the BAS and LAS on the catalysts, IR spectroscopy was conducted using CD₃CN as the probe molecule (Fig. 5-3 (b)). Since the acid site density over the treated samples depicted a meaningful trend (i.e., the more intense the DEA treatment, the lower the number of strong acidic sites), only parent SAPO-34 and the most severely treated sample (4.0 DEA/SAPO-34) were evaluated.

As depicted in Fig. 5-3 (b), all the samples show characteristic peaks related to the SAPO-34 framework in the range of 700-1700 cm⁻¹ [168,170,253,254]. The CD₃CN-saturated samples point out peaks at 2117, 2270, and 2314 cm⁻¹ that are attributed to the symmetric vibration of CD₃, C \equiv N interaction with BAS, and C=N interaction with LAS, respectively, while the blank sample has no peaks in the interval of 2100-2400 cm^{-1} [255,256]. The intensities of BAS and LAS-related peaks do not necessarily correlate with the abundance of such acidic sites. Based on the Lambert-Beer law [255,256], the C \equiv N stretching vibration, which is influenced by interaction with different acidic sites, has different extinction coefficients. On the contrary, the peaks related to similar acidic sites are comparable amongst the different samples and test temperatures. Relating the spectra of parent SAPO-34 and 4.0 DEA/SAPO-34 at 50 °C, the intensities of the Lewis-related peaks are almost the same, but the BAS-related peak over 4.0 DEA/SAPO-34 catalyst is around 54% of the one over the parent catalyst. This agrees well with the NH₃-TPD test results. With the gradual increase of temperature, the BAS-related peak stays intact up to 150 °C while the LAS peak almost disappears. The broad peak in the band region of 3100-3700 cm⁻¹ is due to adsorbed water that drops at elevated temperatures. Another observation was the transformation of the C=N adsorption band at 2270 cm⁻¹ (i.e., BAS-related peak) to two peaks at 2270 and 2286 cm⁻¹ at higher temperatures.



Fig. 5-3 (a) NH₃ temperature-programmed desorption curve, (b) Temperature-dependent DRIFT spectra after adsorption of deuterated acetonitrile (C₂D₃N) on parent SAPO-34 (black) and on 4.0DEA/SAPO-34 (blue). For comparison, DRIFT spectra of the blank 4.0DEA/SAPO-34 (grey).

5.3 Activity measurements

As outlined in the experimental section, products of the MTO reaction were separated through the GC column. Fig. S 9 illustrates the chromatograms of the reaction products analysis over parent SAPO-34 at three different times on stream, which correspond to the fresh catalyst, the half-lifetime of the catalyst, and the time after deactivation, respectively. This evolution of the products over time is in line with previously described literature [266,267] and follows the same behavior for all samples. Methanol conversion and selectivity to different products versus time on stream, over parent SAPO-34 and 0.5 DEA/SAPO-34 samples, have been presented in Fig. 5-4



Fig. 5-4 Methanol conversion and products' selectivity versus time on stream. (a & b) over parent SAPO-34 and (c & d) over 0.5 DEA/SAPO-34. Temperature 400 °C, atmospheric pressure, and at a *WHSV* of 1 $g_{MeOH} g_{Cat}^{-1} h^{-1}$.

With time on stream, gradual and continuous coke formation narrows the catalyst pores, favoring the production of smaller molecules (methane, ethylene, and ethane). For instance, ethylene selectivity experienced a rise (between the start of the activity test and the onset of catalyst deactivation) from ~28 to ~41% over both catalysts. Propane and propylene as medium-size molecules among the MTO products had completely different behavior. This suggests the fact that the production of these two species is being controlled by different mechanisms which outweigh the molecular-sieving effect. Propylene slightly increased over time on stream (by ~2%), whereas propane production shrank severely. The selectivity towards heavier compounds like C₄ and C₅⁺ olefins also reduced substantially over time. In line with the notion that coking until a certain amount can increase the selectivity towards light olefins, the highest light olefin selectivity (around

77-78%) was recorded on the partially coked catalysts. Following advanced times on stream, catalyst activity diminishes abruptly due to deactivation.

Even after catalyst deactivation (i.e., following a steep decrease in olefins production), DME as an intermediate was being produced at Methanol-DME equilibrium conversion corresponding to the reaction temperature. The only significant differences between these two catalysts in terms of activity performance are longer lifetime and higher alkane formation over 0.5 DEA/SAPO-34 in comparison to the parent SAPO-34. The catalyst lifetime was measured from the onset of the reaction until the methanol conversion decreased to 95%.

The overall selectivity of the products along with coke over each specific catalyst was acquired by taking an average of their values over the catalyst's lifetime. Fig. 5-5(a) presents the catalyst lifetime, light olefins selectivity (LOS), and coke selectivity on the parent catalyst, as well as the four treated samples, under the MTO process. Replication of the activity tests has displayed uncertainties of less than 0.3 h for lifetime and less than 0.4% for LOS. The 0.5DEA/SAPO-34 sample, thanks to the successful introduction of secondary pores and more facile mass transfer had a longer lifetime and lower coke formation rate in comparison to the parent SAPO-34 catalyst. However, the more intense the DEA post-treatment, the lower the catalyst lifetime, which can be attributed to the severe depletion of catalyst surface area and fewer Brønsted acid sites. An interesting observation was the partial loss of light olefin selectivity over the treated samples that escalated as the DEA treatment intensified. Initially, it was speculated that it had occurred as a result of higher production of heavier compounds due to secondary pores, but in reality, the selectivity towards heavier compounds remained almost equivalent to that of the parent catalyst. Thus, it seems that the secondary macro or mesopores facilitate the mass transfer and do not greatly participate in the determination of product distribution, but rather, it is dictated primarily by the micropores of SAPO-34. A closer look at the numerical values of product distribution in Table 5-3 reveals the cause of the reduction in light olefins selectivity. More alkane species (methane, ethane, and propane) was produced by 50% to 80% over the 0.5DEA/SAPO-34 and 4.0DEA/SAPO-34 samples respectively compared with the parent catalyst. Fig. 5-5(b) illustrates a typical temperature-programmed oxidation result for a spent SAPO-34 catalyst. Within the first 20 min

(up to 150 °C), about 1-3 wt% of moisture is removed. While the coke is burned between 400-600 °C.



Fig. 5-5 (a) Comparison of the catalyst lifetime (blue), light olefin selectivity (orange), and coke selectivity (grey) for the different catalysts tested (until 95% conversion) at 400 °C, atmospheric pressure, and *WHSV* of 1 $g_{MeOH} g_{Cat}^{-1}$ h⁻¹. (b) TPO-TGA analysis of deactivated SAPO-34.

Numerical values of coke deposition and temperatures of the maximum coke combustion curve have been presented in Table 5-4. The temperature corresponding to the trough of the coke combustion rate curve gradually increases as the DEA treatment intensity rises from sample to sample. This makes evident the direct relationship between the treatment intensity and the increase of coke species' molecular weight.

Catalyst	C1 ^a (mol%)	C2 ⁼ (mol%)	C2 (mol%)	C3 ⁼ (mol%)	C3 (mol%)	C4 ⁼ (mol%)	C5 ⁼ (mol%)	C6 ⁼ (mol%)	Coke ^b (mol%)
Parent SAPO-34	0.9	34.9	1.1	36.8	5.3	13.3	1.6	0.5	5.5
0.5 DEA/SAPO-34	1.4	35.0	1.8	34.5	8.6	12.0	1.9	0.3	4.5
1.0 DEA/SAPO-34	1.4	33.8	1.9	34.8	8.8	12.3	2.0	0.3	4.5
2.0 DEA/SAPO-34	1.5	33.9	2.0	34.3	9.3	12.0	2.1	0.4	4.6
4.0 DEA/SAPO-34	1.6	33.6	2.1	33.8	9.4	12.1	2.0	0.4	5.2

Table 5-3 The average selectivity (mol%) of products on the different catalyst samples

^a Average selectivity throughout the catalyst lifetime until conversion drops to 95% - calculated based on the equivalent portion of the methanol converted towards products. For low-value compounds like methane and ethane, the accuracy is ± 0.05 %, for more abundant ones like ethylene and propylene the precision is ± 0.2 %

^b Determined via TPO-TGA

Catalyst	Moisture (wt%)	Coke deposition (wt% dry)	Peak temperature (°C)
SAPO-34	3.1	18.9	559
0.5 DEA/SAPO-34	2.3	20.8	563
1.0 DEA/SAPO-34	2.2	20.3	569
2.0 DEA/SAPO-34	1.8	19.6	577
4.0 DEA/SAPO-34	1.5	19.3	578

Table 5-4 Coke content analysis of the deactivated catalysts using TGA-TPO

To identify the nature of the coke species, the GC-MS technique was employed (Fig. 5-6). Mdichlorobenzene was shown in red ink, as the internal standard. Coke species over the deactivated parent catalyst are generally lighter than the ones formed over 4.0DEA/SAPO-34. The heaviest coke compound on the former catalyst is methylated pyrene, whereas the latter contains heavier species such as benzo[a]pyrene. As a semi-quantitative analysis, the aggregate area under the peaks related to lighter coke species (referring to retention times smaller than 12 min i.e., compounds lighter than anthracene (3-ring aromatic)) constitutes 49.5% of all species formed over parent SAPO-34. This value is 30.5% with regard to 4.0 DEA/SAPO-34. Comparing the hydrogen-tocarbon ratio over the most abundant coke species (i.e., methylnaphthalene $C_{11}H_{10}$, anthracene $C_{14}H_{10}$, and pyrene $C_{16}H_{10}$), it is evident that multi-methylated light aromatics possess much higher H/C values than heavy multi-ring aromatics. This means that by having heavier coke species, more hydrogen atoms will be provided for alkane production within the reaction environment. These findings completely justify the higher alkane formation over treated samples (Table 5-3).



Fig. 5-6 GC-MS analysis of coke species formed over deactivated parent SAPO-34 and deactivated 4.0 DEA/SAPO-34 catalysts.

Although there is a consensus that the produced coke consists of aromatic compounds, not all research groups have reported the same species. Some research groups have declared pyrene as the heaviest compound [174], while Zhao *et al.* [175] analyzed the insoluble coke portion using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) and found much heavier aromatic compounds with carbon numbers as high as 55. In alignment with Zhao *et al.* [175], we noticed that a small portion of coke remained insoluble (as a small black sludge in the interface between the organic and aqueous phases) during the hexane extraction step. To include all the possible coke species formed, ¹³C-NMR was employed (Fig. 5-7). Signals at 15-25 ppm are considered to be R-CH3 or R-CH2-R groups in the form of alkyl groups attached to aromatics, whereas the peaks at 125-135 ppm are assigned to both alkylated and non-alkylated aromatics

[264]. While the low ppm range peak is almost the same for both catalysts, the higher ppm range peak is 57% bigger on the 4.0 DEA/SAPO-34 sample. This agrees with both GC-MS and TPO-TGA results, showing that heavier coke species with lower H/C ratio have preferentially formed over DEA-treated samples compared to the parent catalyst.



Fig. 5-7 Solid-state ¹³C-NMR analysis of coke species formed over deactivated parent SAPO-34 and deactivated 4.0 DEA/SAPO-34 catalysts.

5.4 DFT modelling

According to the CD₃CN-FTIR results (Fig. 5-3 (b)), the higher the intensity of the treatment, the higher the ratio of Lewis to Brønsted acidic sites. The greater tendency of the treated samples for faster aromatization and heavier coke species formation (proved by TGA-TPO, GC-MS, and ¹³C-NMR tests) may be caused by this higher ratio of LAS to BAS over these samples. Hence, the role of different active sites in the formation of olefins or aromatics (as coke) on SAPO-34 should be investigated by employing Density Functional Theory (DFT) calculations. Regarding the SAPO-34 catalyst, the Brønsted acidic site formation by substitution of a phosphorous atom with silicon is well understood, but the extra framework aluminum, known as the Lewis acidic site, needs to be analyzed further. As depicted in Fig. 5-8, starting with pure Al attached to a strong energetic stabilization of the aluminum complex, forming a tetrahedral molecular geometry. It is evident

from these results that hydroxylated aluminum is the resting state of the extra framework Lewis site.



Fig. 5-8 Gibbs Free energy profile at 400 °C and 1 bar of the formation of Al(OH)₂ from pure extra framework aluminum. Reactants are depicted in blue and products in brown. Reactants and products labeled in the diagram correspond to both pathways except when marked with *1, which only correspond to reactants and products of the H₂O pathway, or *2, which correspond to the CH₃OH pathway.

Now that both acidic sites have been well introduced, the realistic mechanistic pathways and their individual elementary steps, for both olefin and coke formation, should be investigated over LAS and BAS. Over the last few decades, the MTO reaction mechanism has been explored and continues to be studied. Despite extensive research, the elementary steps contributing to the generation of the first C-C coupling are still under debate. Some experimental evidence has ratified the hypothesis of DME being an intermediate [73,268,269], while others have suggested that olefins are being produced from a cluster of aromatic intermediates (mainly polyalkylbenzenes) in the so-called hydrocarbon pool (HCP) mechanism [52–61]. Other potential active intermediates

such as oxonium ylides [48–50], carbenes [270,271], carbonium ions [272–274], and free radicals [275–277] have been suggested by research groups as the outcome of their experimental tests such as isotope labeling technique.

To assess the ability of BAS to catalyze olefin formation, two possible reaction pathways of ethylene formation (the simplest olefin) were studied (supplementary data Fig. S 10) at 400 °C and a pressure of 1 bar: (1) MeOH insertion and protonation ($CH_3OH_2^+$) and (2) MeOH insertion and methylation (H⁺-DME). Overall, based on the activation energy barriers, it can be inferred that the DME pathway is preferred over the MeOH formation pathway (due to the lower value of the most energy-demanding step). To confidently assert the most feasible MTO reaction mechanism, one should undertake a comprehensive DFT- based study of all the proposed mechanisms and perform a comparative analysis. The most viable route should be further approved via precise experimental techniques. However, no matter which mechanism is involved in olefin formation, the reality is that methanol adsorption on the active site, forming an active methyl group, is the essential step. Accordingly, the methyl adsorption was simulated over both BAS and LAS. Comparing a Brønsted (ZOH) with a Lewis site (ZOAl(OH)₂), the activation energy on the Lewis site is much higher (by \sim 2 eV), as observed in Fig. 5-9. As discussed before, the resting state of the LAS is assumed to be ZOAl(OH)₂. Removing hydroxyls from pure aluminum may enhance its reactivity but only due to being undercoordinated, and promoting such configuration would bring an enormous energetic cost (Fig. 5-9).



Fig. 5-9 Gibbs Free energy profile of the initiation step in the ethylene formation on Brønsted (blue) and Lewis (brown) active sites. Illustrations of each active site are shown below the diagram.

5.5 Discussion

The presented results indicate that Lewis sites do not participate directly in the olefin formation, since the methylation reaction energy barrier is higher on LAS compared to BAS. On the other hand, as reported [59,67], coke formation commences with hexene and its subsequent cyclization to form cyclohexene. This is followed by a repetition of deprotonation, hydride transfer reactions, and alkylation steps resulting in the formation of polyalkylaromatics, which are the primary precursors of coke species (i.e., heavy multi-ring aromatics). A study undertaken by Gao and coworkers [278] has demonstrated that dehydrogenation and C-C coupling are the most energy-demanding steps in the MTO reaction through the HCP mechanism. Aligned with our finding, they

suggested LAS cannot directly contribute to C-C coupling and olefin formation is taking place over BAS. They further discovered that the effective barrier for the dehydrogenation step (for 1, 3-dimethylcyclohexene dehydrogenation to form m-xylene) is lower over LAS compared to the BAS via the carbenium mechanism. The group considered m-xylene to be an active intermediate for olefin formation through the HCP mechanism concept (through either the side chain mechanism [56,63,64] or the expansion-contraction mechanism [56–58,66,69] with the presence of BAS) and suggested LAS are beneficial to olefin production in general. However, from a wider viewpoint, dehydrogenation resulting in aromatization, which is facilitated by LAS, can result in an increased coke formation rate. Their findings along with our DFT calculations can be interpreted, in our case, that higher LAS/BAS ratios can cause faster aromatization and heavier aromatic species formation (coke formed) over treated samples, which is completely in agreement with both the product distribution results obtained from activity tests and the TGA-TPO analysis.

It seems two opposite and competing effects are induced by alkali treatment. The first consists of better mass transfer due to the introduction of macro/mesopores (hierarchical structure) which results in the prolonging of the catalyst's lifetime. However, simultaneously, the second effect involves the increase of the LAS/BAS ratio, which in turn decreases the olefin formation while boosting aromatization. This results in the generation of heavier coke species, enhanced alkane formation, alongside reduced LOS over treated samples. With regards to the 0.5DEA/SAPO-34 sample, the positive effect was prevailing and led to a longer lifetime and slightly lower LOS, while in the case of 4.0 DEA/SAPO-34, the negative effect was dominant, triggering improved alkane formation, shorter lifetime, and much lower LOS.

As a benchmark, Table S 5 has compared the activity performance of the optimum catalyst in the present work with catalysts developed in the literature, using different treatment procedures mentioned before (in the introduction). Light olefins selectivity has not been presented in the table, as some articles have overlooked the coke contribution and reported unrealistic values of 85-95%, while the light olefins selectivity of the commercially established process by UOP/Hydro is within the range of 75-80% (carbon-based) with almost 3% coke and 1% CO_x formation [279]. Considering the various WHSVs used in different articles, a universal parameter termed catalyst processing ability was defined to simplify the comparison. To calculate processing ability, *WHSV*

is multiplied by catalyst lifetime, which gives the methanol weight that can be processed by 1 gram of catalyst while the conversion exceeds 95%. One can use this parameter to identify the superior catalyst among all synthesis procedures and promotion techniques that have been tried so far. Overall, it seems that shortening the diffusion pathway by synthesizing the nano-sized catalyst using any of the seed-assist, post-synthesis milling, and recrystallization, microwave-assisted hydrothermal or ultrasonic mixing methods demonstrated the most substantial improvements relative to other techniques that attempt to create a hierarchical structure to improve the mass transfer. With that being said, a more just evaluation of the technique employed to improve catalyst performance can be carried out by comparison of the treated sample with the respective parent catalyst produced in the same study, since different groups have used different templates and synthesis procedures for the parent catalyst. In this regard, the seed-assist, post-synthesis milling, recrystallization, and microwave-assisted hydrothermal methods excel with almost 4 times larger methanol processing ability compared to their parent catalysts.

5.6 Conclusion

Alkali post-treatment was employed as an efficient route for the introduction of secondary mesopores and improvement of mass transfer. Mild-treated samples exhibited ~50% longer lifetime; however, with precise product analysis, slightly lower light olefins selectivity (due to higher alkane formation) relative to the parent catalyst was uncovered. TGA-TPO, followed by GC-MS and ¹³C-NMR tests, revealed the formation of heavier coke species (with a lower H/C ratio content) over the treated samples that can provide extra hydrogen for higher alkane production. Heavier coke formation over treated samples was hypothesized to be related to the alteration in active sites. According to the CD₃CN-FTIR test, it was noticed that Lewis acidic sites remained intact while the Brønsted acidity was depleted after alkali treatment. Our Density Functional Theory (DFT) calculations, complemented by recent findings, revealed that methanol adsorption and C-C coupling are more favorable over Brønsted sites (leading to olefin formation) while Lewis acidic sites facilitate dehydrogenation and aromatization (resulting in enhanced coke generation). Hence, a meaningful connection and worthwhile plot were depicted between heavier coke species formation, higher alkane production, and lower light olefins selectivity with greater Lewis/Brønsted acidic site ratio over treated catalysts.

6 SAPO-34 synthesis on γ-Al₂O₃ microspheres for fluidizedbed application

6.1 Introduction

In former studies [182,280,281], kaolin and α -Al₂O₃ microspheres have been utilized as the support for catalyst preparation applicable to the fluidized-bed reactors. By utilizing kaolin microspheres (having equimolar Si and Al elements), controlling the silica incorporation into the SAPO-34 framework, which determines the acidic strength and has a crucial effect on the catalyst performance, is challenging. α -Al₂O₃ microspheres (abbreviated as MS), on the other hand, have low surface area and reactivity, which results in low SAPO-34 loading and poor adhesion. In our third subproject, we will attempt to mount SAPO-34 over γ -Al₂O₃ in high-weight content. γ -Al₂O₃ has a higher surface area than α -Al₂O₃ and kaolin (190 m² g⁻¹ compared to 1 and 35 m² g⁻¹, respectively) and has been widely tested for methanol conversion to dimethyl ether (DME), a known intermediate in the MTO reaction [183]. Furthermore, a novel fabrication technique using microwave heating will be employed. Microwave-assisted SAPO-34 synthesis due to homogeneous heating and enhanced nucleation compared to conventional heating via oven has proved to shorten crystallization time and yield smaller particles [184,185]. Spray-dried SAPO-34 will also be prepared and studied comprehensively to truly assess the consequences of SiO₂ addition on the physicochemical properties of SAPO-34.

6.2 Results and discussion

Aluminum oxide is an amphoteric substance, which means it can react with both acids and bases. At room temperature, no matter how much acid was added to the γ -Al₂O₃ spheres, the surface of the spheres partially reacted with acid and incorporated 3-4 mol% of phosphorus. By trying various temperatures, we found that at over 90 °C, aluminum oxide starts to react with phosphorous creating AlPO₄. Long residence in this condition deforms the spheres and merges them into larger agglomerates. That's why rapid heating by microwave with short residence time was employed.

Inspired by Wu *et al.* [282], first, we formed AlPO₄-34 by the addition of the template within this stage and later replaced phosphorous with silica to introduce Brønsted acidic sites.

Fig. 6-1 confirms the formation of pure SAPO-34 phase while employing TEAOH as the diffraction peaks completely match with those of the reference SAPO-34 diffractogram. However, on the TEA-SAPO sample, the emergence of a new peak at $2\theta = 7.4^{\circ}$ reveals the partial formation of the other SAPO competing phase (i.e., SAPO-5). On the other hand, aluminum oxide is mostly amorphous and displays minor peaks at 67° , 46.2° , and 37.4° in descending order which corresponds to plane indexes of 440, 400, and 311, respectively [283]. The successful formation of the SAPO phase is evident on both TEAOH-SAPO/ γ -Al₂O₃ MS (MS denotes microsphere) and TEA-SAPO/ γ -Al₂O₃ MS samples, while γ -Al₂O₃-related peaks are subtle due to much lower intensity compared to SAPO-related ones (3 orders of magnitude smaller). Besides, the intensity of the SAPO-5 identification peak at 7.4° over TEA-SAPO/ γ -Al₂O₃ MS has risen compared to the TEA-SAPO catalyst, which infers SAPO-5 content has increased within TEA-SAPO/ γ -Al₂O₃ MS.

SAPO-34 synthesis on γ -Al₂O₃ microspheres for fluidized-bed application



Fig. 6-1 X-ray Diffraction pattern for the prepared catalysts along with the corresponding references: SAPO-34 (PDF # 00-047-0617), and SAPO-5 (PDF # 00-047-0619). TEA and TEAOH denote the different template, while γ -Al₂O₃ MS denotes the alumina microsphere.

SEM images (Fig. 6-2) of both TEAOH-SAPO and TEA-SAPO samples illustrate the formation of crystalline SAPO particles with sizes $1-5 \mu m$. No amorphous or irregularly-shaped particles are presented that can indicate high yield in SAPO synthesis. TEAOH as the structure-directing agent has formed uniform cubic particles while TEA application has yielded a mix of cubic and sheet-like particles.



Fig. 6-2 SEM images of as-synthesized parent SAPO catalysts using different templates.

SEM images (Fig. 6-3) of SAPO-mounted γ -Al₂O₃ spheres show the creation of SAPO crystals on the outer shell of the microspheres. TEAOH and TEA-directed samples maintained their morphologies (cubic shape and sheet-like structure, respectively) but emerged in smaller sizes due to the application of microwave-assisted hydrothermal in a much shorter period than conventional heating. TEAOH-SAPO/ γ -Al₂O₃ MS seems to be more resistant to erosion and has better adhesion than the TEA-SAPO/ γ -Al₂O₃ MS sample.



Fig. 6-3 SEM images of bare and SAPO-mounted y-Al₂O₃ microspheres. TEA and TEAOH denote the different templates, while y-Al₂O₃ MS denotes the alumina microsphere.

The nitrogen adsorption/desorption isotherms of the samples are depicted in Fig. 6-4 and the corresponding values have been presented in Table 6-1. Both TEAOH-SAPO and TEA-SAPO samples follow the type I isotherm pattern [265] indicating a microporous structure. This

microspheres for fluidized-bed application

constitutes high adsorption at low relative pressures ($p/p_0 < 0.01$) and then almost a plateau until it reaches saturation pressure. Further nitrogen uptake at higher relative pressures ($p/p_0 > 0.8$) is due to capillary condensation in mesopores which is more profound over TEA-SAPO since it has higher meso/macropores. On the contrary, SiO₂ powder (as the binder used for spray drying of SAPO-34) and γ -Al₂O₃ contain mostly meso/macropores and their isotherm is similar to that of type IV. As it was expected, TEAOH-SAPO/ γ -Al₂O₃ MS, TEA-SAPO/ γ -Al₂O₃ MS, and SD-TEAOH-SAPO samples inherited the characteristics of their ingredients and possessed a combination of type I and IV isotherms, which confirms the coexistence of micro and mesopores in the composite catalyst structure. The SD-TEAOH-SAPO catalyst lost around 17% of its micropores, as anticipated, due to blockage by the binder (i.e., SiO₂) addition. Another valuable interpretation of the nitrogen adsorption/desorption test is to estimate the SAPO content (wt %) in the SAPO mounted on γ -Al₂O₃ microspheres since SAPO has almost the sole contribution in micropore surface area or micropore volume in the final composite catalyst. The application of the formulas below resulted in similar values.

$$x_{(SAPO-34)} = \frac{[S_{micro(composite)} - S_{micro(Y-Al_2O_3 MS)}]}{[S_{micro(SAPO-34)} - S_{micro(Y-Al_2O_3 MS)}]}, \quad x_{(SAPO-34)} = \frac{[V_{micro(composite)} - V_{micro(Y-Al_2O_3 MS)}]}{[V_{micro(SAPO-34)} - V_{micro(Y-Al_2O_3 MS)}]}$$

Accordingly, the TEAOH-SAPO/ γ -Al₂O₃ MS sample was comprised of 44 wt% SAPO phase and TEA-SAPO/ γ -Al₂O₃ MS catalyst encompassed around 31 wt% These values are impressive relative to the SAPO loading achieved in literature (i.e., 9 wt.% on kaolin microspheres [179], 22 wt.% on kaolin microspheres [280], and 6.4 wt.% on α -Al₂O₃ spheres [281]).



Fig. 6-4 N₂-adsorption/desorption isotherms of the prepared catalysts along with SiO₂ powder and γ -Al₂O₃ MS for comparison. TEA and TEAOH denote the different templates, while γ -Al₂O₃ MS denotes the alumina microsphere, and SD denotes the spray drying.

In terms of acidity, the ammonia desorption profile is presented in Fig. 6-5 and the corresponding numerical values can be accessed through Table 6-1. SiO₂ and γ -Al₂O₃ MS have negligible acidic sites compared to the SAPO catalysts (Fig. 6-5). The acidity of the composite catalysts in Table 6-1 has been prorated based on the SAPO content. Accordingly, it can be concluded that SAPO formed over γ -Al₂O₃ MS maintained the strong acidic sites and in the case of TEAOH-SAPO/ γ -Al₂O₃ MS sample, the weak sites improved compared to the parent catalyst. This is a good sign, that indicates, SAPO formed over γ -Al₂O₃ MS does not differ from parent SAPO. Regarding the spray-dried SAPO sample, considering the SAPO content (i.e., 50 wt%), NH₃-TPD results showed that the strong acid sites have depleted by 35% compared to the parent SAPO. This is in alignment with the reduction in micropore surface area reduction due to blockage by binder. Another interesting observation was that despite utilizing similar gel composition, TEA-directed samples possessed a lower number of both weak and strong acidic sites. This was further investigated by surface elemental composition analysis using the SEM-EDX technique.



Fig. 6-5 NH₃ temperature-programmed desorption curve. TEA and TEAOH denote the different templates, while γ -Al₂O₃ MS denotes the alumina microsphere and SD denotes spray drying.

Fig. 6-6 displayed the SEM images of spray-dried catalyst and SAPO-mounted γ -Al₂O₃ microspheres along with relevant EDX map logs and tabulated elemental compositions. Si content in TEA-SAPO/ γ -Al₂O₃ MS is lower than that of TEAOH-SAPO/ γ -Al₂O₃ MS catalyst (5.5 versus 8.8 mol%, respectively). This approves our hypothesis about the change in Si incorporation rate as a result of template alteration and supports the NH₃-TPD results. The elemental maps of the outer shell of γ -Al₂O₃ microspheres mirror each other, confirming the coexistence of Al, P, and Si in the SAPO framework. In contrast, the Si map over the spray-dried sample is opposite to the Al and P maps, since the Si within the framework of SAPO cubes is negligible compared to the Si added as the binder and fills the spaces between SAPO particles. The adhesion of the SAPO outer shell to the γ -Al₂O₃ microspheres and its resistance to the abrasion and erosion for the two SAPO-mounted catalysts along with the spray-dried one was examined using a sieve shaker. Bare γ -Al₂O₃ MS lost less than 0.3 wt% of its weight after 100 h of attrition test, while TEAOH-SAPO/ γ -Al₂O₃

MS and TEA-SAPO/ γ -Al₂O₃ lost 0.7 and 2.1 wt%, respectively. The spray-dried catalyst was vulnerable to the attrition test and experienced 8.9 wt% weight reduction after 100 h of the test.



Fig. 6-6 SEM-EDX analysis of spray-dried SAPO-34 catalyst along with SAPO-mounted γ-Al2O3 microspheres for fluidized-bed application. TEA and TEAOH denote the different templates, while γ-Al₂O₃ MS denotes the alumina microsphere and SD denotes spray drying.

Sample name	$\begin{array}{c} {S_{BET}} \ ^{a} \\ (S_{Micro} + \\ S_{Meso+Macro}) \\ (m^{2} \ g^{-1}) \end{array}$	$\begin{array}{c} V_{Micro+} \\ V_{Meso+Macro^{b}} \\ (cm^3g^{-1}) \end{array}$	Weak acid sites ^c (mmol _{NH3} g_{cat}^{-1}) at peak temp (${}^{0}C$) ^d	Strong acid sites ^c (mmol _{NH3} g _{cat} ⁻¹) at peak temp (°C) ^d
TEAOH-SAPO	533 (529 + 4)	0.242 + 0.080	0.97 at (160 °C)	0.79 at (413 °C)
TEA-SAPO	567 (552 + 15)	0.251 + 0.042	0.73 at (155 °C)	0.63 at (385 °C)
y-Al ₂ O ₃ MS	189 (8 + 181)	0.002 + 0.516	0.14 at (150 °C)	0.0
\mathbf{SiO}_2	150 (0 + 150)	0.000 + 0.209	0.05 at (145 °C)	0.11 at (500 °C)
TEAOH-SAPO/y-Al ₂ O ₃ MS ^e	332 (236 + 95)	0.108 + 0.143	1.12 at (160°C)	0.81 at (405 °C)
TEA-SAPO/y-Al ₂ O ₃ MS ^e	290 (172 + 118)	0.079 + 0.185	0.74 at (145 °C)	0.63 at (385 °C)
SD-TEAOH-SAPO ^e	313 (221 + 92)	0.100 + 0.167	0.63 at (170 °C)	0.25 at (380 °C)

Table 6-1 Physicochemical properties of the samples using N2 adsorption and NH3-TPD techniques.

^a S_{BET} = BET total specific surface area obtained from adsorption data in the p/p_0 range from 0.06–0.3; all reported data are within ±1% based on repeated analysis. S_{Micro} = micropore surface area; $S_{Meso+Macro}$ = meso + macropore surface areas. ^b $V_{Meso+Macro}$ = BJH cumulative volume of the pores between 10-970 Å radius. V_{Micro} = t-plot micropore volume ^c Precision ± 2% relative ^d Precision ± 5°C ^e the acidity of the composite catalysts has been prorated based on the SAPO content

Finally, the activity tests were conducted to investigate the catalytic performance of the prepared catalysts. Fig. 6-7 depicts the methanol conversion and the product's evolution over TEAOH-SAPO and TEA-SAPO samples as a function of time on stream. The products' distribution trends were similar on both catalysts. As gradual coke formation narrowed the pores of the catalyst, the

production of smaller molecules (methane, ethylene, and ethane) enhanced, and the yield of heavier compounds (C_3^+) diminished. This continued until the pores got completely blocked by large coke species (heavy multiring aromatics) and consequently, the methanol conversion dropped abruptly with DME emergence in the products. TEA-SAPO lasted longer than the TEAOH-SAPO sample (15.3 h versus 9.5 h, respectively) due to smaller particles (shorter mass transfer path), higher surface area, and milder acidity. However, the light olefins selectivity was lower due to the higher formation rate of heavy compounds (Table 6-2) that could originate from the existence of large-pore SAPO-5 (having pores with the size of 7.42 Å versus 3.72 Å in the case of SAPO-34) in TEA-SAPO sample.



Fig. 6-7 Methanol conversion and products' selectivity by time on stream over (A&C) TEAOH-SAPO, and (B&D) TEA-SAPO. Temperature 400 °C, atmospheric pressure, and at a *WHSV* of 1 $g_{MeOH} g_{SAPO}^{-1} h^{-1}$

Moving forward, Fig. 6-8 has compared the as-synthesized SAPO catalysts with composite samples that have been prepared for fluidized-bed application. For all the samples, LOS was within the acceptable range (78 ± 0.5 %mol) and the decision-making metric seemed to be the catalyst

lifetime under reaction conditions. Starting with the spray-dried sample, inferior performance was recorded compared to the parent catalyst (6.9 h versus 9.5 h, respectively) as was expected due to loss in the number of active sites and micropore surface area. On the opposite, SAPO-mounted γ -Al₂O₃ MS samples illustrated superior performance compared to their parent SAPO counterparts. This can be attributed to the successful formation of SAPO on the γ -Al₂O₃ outer surface and the application of microwave-assisted hydrothermal that had caused the formation of smaller SAPO crystals. TEA-SAPO/ γ -Al₂O₃ MS and TEAOH-SAPO/ γ -Al₂O₃ MS lasted for 21.7 h and 10.5 h on stream, while their related parent samples were active for 15.3 h and 9.5 h, respectively. Another observation was the reduction in ethylene formation along with an increase in propylene production over SAPO/ γ -Al₂O₃ MS samples compared to the parent catalysts. LOS, however, was comparable and did not change considerably.



Fig. 6-8 (A) Methanol conversion (filled marker) and Light olefins selectivity (hollow marker) versus time on stream (B) Catalyst lifetime and average LOS within the catalyst lifetime. Temperature 400 °C, atmospheric pressure, and at a WHSV of 1 g_{MeOH} g_{SAPO}⁻¹ h⁻¹. TEA and TEAOH denote the different templates, while γ-Al₂O₃ MS denotes the alumina microsphere and SD denotes spray drying.

To provide a perspective of what has been already achieved in literature, Wang et al. [179] reported almost 2 h of lifetime for parent catalyst using mixed-template (TEA and TEAOH) synthesis technique and 14 h of lifetime for SAPO-34 formed on kaolin microspheres at 450 °C, and WHSV of 1 $g_{MeOH} g_{SAPO}^{-1} h^{-1}$. Another group [280] obtained less than an hour lifetime over

TEA-directed SAPO-34 on kaolin at 450 °C, and WHSV of 1.47 $g_{MeOH} g_{SAPO}^{-1} h^{-1}$. Hence, the catalysts prepared in the present study stand in a better position in terms of catalytic performance compared to the former studies.

			-	-	-					
	Catalust	Methane	Ethylene	Ethane	Propylene	Propane	C ₄ Olefins	C ₅ Olefins	C ₆ Olefins	DME
Catalyst	Catalyst	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)
	TEAOH-SAPO	0.9	39.2	0.9	39.2	3.6	13.0	2.4	0.4	0.4
	TEA-SAPO	1.1	37.1	0.6	40.2	1.2	14.2	4.0	1.2	0.4
	TEAOH-SAPO/y- Al ₂ O ₃ MS	1.1	37.8	1.1	39.8	4.4	13.1	2.1	0.3	0.3
	TEA-SAPO/γ-Al ₂ O ₃ MS	1.3	33.7	0.5	43.7	1.0	15.5	3.3	0.6	0.4
	SD-TEAOH-SAPO	0.9	37.8	0.9	40.3	4.2	13.0	2.2	0.3	0.4

Table 6-2 The average selectivity (mol%) of products on the different catalyst samples

^{an} Average selectivity throughout the catalyst lifetime until conversion drops to 90% - calculated based on the equivalent portion of the methanol converted towards products. For low-value compounds like methane and ethane, the precision is $\pm 0.05\%$, for more abundant ones like ethylene and propylene the precision is $\pm 0.2\%$.

6.3 Conclusion

Although intense research has been allocated for the improvement of SAPO-34 to mitigate its fast deactivation, the catalyst final shaping for fluidized-bed application has rarely been studied. The conventional spray drying method (by using 50 wt% SiO₂ as the binder) downgraded the properties of the parent catalyst (i.e., caused 35% loss in active sites and 17% reduction in micropore surface area) and displayed an almost 30% shorter lifetime. Hence, a novel technique for in-situ mounting of SAPO over the outer shell of γ -Al₂O₃ microspheres was developed. SAPO loadings of 31 and 44 wt% with different morphologies (cubic and sheet-like particles) were achieved using two different templates. Both SAPO-mounted γ -Al₂O₃ catalysts illustrated longer lifetimes in reaction with acceptable light olefin selectivity compared to their parent SAPO counterparts. These catalysts also went through attrition tests and indicated better resistance than the spray-dried sample.

7 SAPO-34 promotion by in-situ metal incorporation

7.1 Introduction

Metal modification of SAPO-34 (abbreviated as Me-SAPO-34) has been studied in the hope of prolonging catalyst lifetime and boosting light olefins selectivity. To the best of our knowledge, so far, the following metals have been tested in this respect: Co, Ni, Fe, La, Ce, Y, K, Ag, Ca, Cu, W, Mg, Mn, Ge, Zn, Ti, and Zr [155–172]. A majority of the research groups have inferred that metal-promoted SAPO-34 displays superior performance with respect to lifetime and LOS [155,156,158,162,170,172]. On the contrary, some articles have partially backed up the idea of metal-incorporated catalysts performing worse than the parent [158,161,165,168]. One study [161] reported that the metal-modified catalysts possessed lifetimes shorter (for Co-SAPO-34) and similar (in the case of Ni-SAPO-34) to the parent catalyst (without considerable changes in light olefins selectivity). Another study [158] explored the effect of Fe-incorporated SAPO-34 and found that the selectivity towards C₂ and C₃ olefins (under optimal conditions) was notably small due to substantial methane formation, in comparison to the parent catalyst. Deterioration of catalytic performance by secondary metal addition has also been reported using the impregnation technique. Co-, Ni- and Zn-impregnated SAPO-34 catalysts in one study [168] demonstrated a significantly shortened lifetime relative to the parent catalyst with worse or comparable LOS. This inferior performance due to metal addition has also been observed in other circumstances, such as La- and Y- impregnated [157] and physically-blended ZnO modified samples [166].

Overall, by observing the results of the conducted research in metal modification of SAPO-34, clear contradictions can be spotted. Even while employing similar metals, opposing catalytic performances have been reported. For instance, in the case of Ni-incorporated SAPO-34, there have been reports of significantly improved [160], unchanged [161], and slightly worsened [168] light olefins selectivity (relative to the parent catalyst). Due to the discrepancies in the literature about whether the secondary metal promotion of SAPO-34 catalyst has a positive or negative effect on the catalyst performance, this chapter seeks to clarify the link between metal promotion and the catalytic activity of SAPO-34. Hence, this study looks to examine a wider range of metal-incorporated catalysts than typically seen in the literature. By utilizing seven of the metals that have already been evaluated (Mg, Ca, Mn, Fe, Ni, W, Ce), alongside thirteen additional metals

that have not been investigated (Li, V, Zr, Mo, Ga, In, Sn, Tl, Pb, Ru, Nd, Sm, Gd), we aim to offer a thorough comparison of the similarities and distinctions of metals of diverse periodic groups (with correspondence to their performance). Metals were chosen because they have shown proper catalytic activity in other processes with similar elementary reaction steps (such as C-C coupling and C-H bond cleavage) as the ones that happen in the MTO reaction. For instance, Li and Mg are active in the oxidative coupling of methane [284], Ru and Ni are used in CO₂ hydrogenation [285], and Mo in direct methane conversion to aromatics and olefins [286]. In addition, In, Tl, Sn, and Pb, being from the same groups as Al and Si, were chosen as they may have a higher potential to incorporate into the SAPO-34 structure by replacing Al and Si atoms.

Metal content in the synthesis gel (i.e., the ratio of Me/Al₂O₃) was decided to be 0.05 as the most common quantity used in the literature [156,158,160,169,172]. Furthermore, we will take a step further by co-feeding hydrogen to metal-promoted SAPO-34. Hence, the possible synergistic effects of metal promotion and hydrogen can be examined that may in theory selectively crack heavy hydrocarbons, leading to a boost in LOS and a longer catalyst lifetime. In contrast to the previous hydrogen co-feeding attempt [230] at high pressure, which resulted in substantial LOS depletion, we will instead utilize ambient pressure conditions- a more economically and commercially favorable approach.

7.2 Results and discussion

Co-feeding of hydrogen with methanol may cause two opposing effects on the MTO reaction. The beneficial effect is to trigger the cracking and ring-opening reactions of multiring aromatics (known as coke or coke precursors) through hydrogenation which leads to a lower coke formation rate. The unfavorable effect, o n the other hand, is the direct hydrogenation of olefins to paraffins that prompts the depletion in olefins selectivity. Olefins hydrogenation over Brønsted acidic sites of the zeolite has been investigated before [287]. Aromatics hydrogenation or cracking catalyzed by zeolite was also approved by another group [288], which recorded a 40 wt.% reduction in coke content after hydrogen treatment of deactivated SAPO-34 catalyst at 450 °C. Higher hydrogen partial pressure significantly increases the rate of both hydrogenation reactions. To maintain the high light olefin selectivity, we conducted the tests at ambient pressure. Catalyst lifetime, methanol conversion, and light olefins selectivity of the SAPO-34 catalyst fed with different molar ratios of

H₂/MeOH (0.0, 1.5, 3.0, and 6.0) have been depicted in Fig. 7-1 (a&b). Generally, catalyst lifetime progressed by hydrogen co-feeding because of a drop in the coke formation rate. SAPO-34 fed by H₂/MeOH=1.5 lasted 27 % longer compared to the one fed by pure methanol. This progress in lifetime was 29 and 40% for H₂/MeOH ratios of 3.0 and 6.0. Average light olefins selectivity within the catalyst lifetime also enhanced from 81.2 to 82.2, 82.3, and 82.6 mol% corresponding to H₂/MeOH molar ratios of 0.0, 1.5, 3.0, and 6.0, respectively. Higher average light olefin selectivity in the presence of hydrogen is due to the longer catalyst lifetime. The LOS with or without hydrogen is almost the same at the beginning of the reaction (approving the fact that alkene hydrogenation is not happening at ambient pressure) (See Fig. 7-1 a). However, in the presence of hydrogen, the coke formation rate is lower which lengthens the catalyst lifetime, and since the partially coked catalyst has higher LOS, the overall light olefins selectivity (average throughout the catalyst lifetime) is higher with H_2 co-feeding. Overall, it can be said that progress in catalyst lifetime and LOS is more substantial after the addition of H₂ to the feed (H₂/MeOH=1.5) and further increase of hydrogen does not significantly improve these parameters. Besides, high H₂/MeOH ratios are not practical and economically feasible. Hence H₂/MeOH ratios of 0 and 1.5 (the optimal value) were chosen and applied for activity tests of the metal-promoted SAPO-34 catalysts.



Fig. 7-1 Activity results by changing the H₂/MeOH molar ratios in the feed (a) Methanol conversion (filled marker) and Light olefins selectivity (hollow marker) versus time on stream (b) Catalyst lifetime and average LOS within the catalyst lifetime. Temperature 450 °C, atmospheric pressure, and at a WHSV of 1 g_{MeOH} g_{Cat}⁻¹ h⁻¹.

The average product distribution of the tests conducted under various H_2 /MeOH ratios has also been tabulated (Table 7-1). As the hydrogen in the feed increases, the selectivity to methane,

ethylene, ethane, and propylene rises, while propane and heavier olefins are produced in smaller quantities.

	-	•		-	-	-					
the feed. temperature 450 °C, atmospheric pressure, and at a WHSV of 1 $g_{MeOH} g_{Cat}^{-1} h^{-1}$.											
H ₂ /MeOH	Methane	Ethylene	Ethane	Propylene	Propane	C ₄ Olefins	C_5 Olefins	C ₆ Olefins			
(mol/mol)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)			
0.0	1.4	44.4	1.1	36.8	2.8	11.0	2.3	0.3			
1.5	1.4	45.0	1.2	37.1	2.4	10.5	2.1	0.2			
3.0	1.5	45.1	1.2	37.1	2.3	10.4	2.1	0.2			
6.0	1.6	45.5	1.2	37.2	2.3	10.0	2.0	0.2			

Table 7-1 The average selectivity (mol%) ^a of products while changing H_2 to methanol molar ratio in

^a Average selectivity throughout the catalyst lifetime until conversion drops to 90% - calculated based on the equivalent portion of the methanol converted towards products. For low-value compounds like methane and ethane, the precision is ± 0.05 , for more abundant ones like ethylene and propylene the precision is ± 0.15 absolute.

The catalyst lifetime and average light olefins selectivity over metal-promoted catalysts, with and without hydrogen in the feed, have been depicted in Fig. 7-2. Those tests under hydrogen atmosphere have been distinguished by "H₂" preceding the catalyst name. Overall, higher LOS and longer lifetime were observed over all the samples in the presence of hydrogen compared to their counterparts with pure methanol as the feed. This can again support the findings in the first section of this study regarding the hydrogen co-feeding effect. The catalysts have been arranged in descending order from the best to the worst lifetime. The LOS was in the range of 78.3 to 82.3 mol% with pure methanol as the feed and in the range of 79.4 to 83.0 mol% in the hydrogen atmosphere. Even the worst-performing samples (i.e., Ni and Ru-promoted SAPO catalysts), with almost half the lifetime of the parent catalyst, still have acceptable LOS. This can be justified since although some pores of the parent catalyst have been blocked by inefficient metal promotion, the rest would function similarly to the parent catalyst. Subsequently, the lifetime would be shorter, but the LOS is almost within the acceptable range. This is analogous to performing the MTO reaction under a higher WHSV (since some portion of the catalyst is not accessible). Indium and molybdenum-promoted catalysts illustrated slightly longer lifetime (10-15%) and similar LOS relative to the parent catalyst. Moreover, SAPO-34 promoted with Sm, W, Sn, and Zr performed similarly to the parent SAPO-34 catalyst. Addition of other metals to SAPO-34 resulted in deteriorated performance with V, Tl, Ni, Ru and Pb at the bottom of the chart.



Fig. 7-2 Average light olefins selectivity and catalyst lifetime in the MTO reaction over bare and Metal-promoted SAPO-34 with and without H₂ co-feed. H₂/MeOH molar ratios of 0.0 and 1.5, temperature 450 °C, atmospheric pressure, and *WHSV* of 1 $g_{MeOH} g_{Cat}^{-1} h^{-1}$.

According to the Hydrocarbon Pool mechanism (HP), the most accepted mechanism for the MTO reaction amongst scholars, the formation of coke species initiates from molecular rearrangement, ring expansion and aromatization of HP intermediates such as multi methyl benzene and naphthalene [67,71]. The necessary hydrogen transfer reaction between such intermediates and surface-associated methoxy groups leads to the formation of heavy multiring aromatics (such as anthracene and pyrene, known as coke) alongside methane [67,71]. Hence, the formation rate of methane or similarly, other light alkanes, can be indicative of the pace of coke creation. This hypothesis applies fairly to our promoted catalysts. According to Table 7-2, In, Mo, Sm, W, Sn and Zr-SAPO-34 samples with long lifetimes were less selective to methane formation than Ni and V-promoted samples that possessed short lifetimes. Tl and Ru-promoted samples, on the other hand, produced moderate amounts of methane but they were more selective towards propane, hence justifying their fast deactivation.
	N 4	F (1, 1	D /1	D 1	D	C_4	C ₅	C
Catalyst	Methane	Ethylene	Ethane	Propylene	Propane	Olefins	Olefins	Olefins
	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)
SAPO-34	1.4	44.4	1.1	36.8	2.8	11.0	2.3	0.3
H ₂ SAPO-34	1.4	45.0	1.2	37.1	2.4	10.5	2.1	0.2
In-SAPO-34	1.3	44.1	1.2	36.3	3.4	10.9	2.1	0.3
H ₂ In-SAPO-34	1.4	45.7	1.0	36.3	2.5	10.4	2.1	0.2
Mo-SAPO-34	1.3	44.0	1.0	37.2	2.8	11.1	2.1	0.3
H ₂ Mo-SAPO-34	1.3	44.0	0.8	38.0	2.2	10.9	2.1	0.2
Sm-SAPO-34	1.1	44.1	1.1	37.2	3.1	10.8	2.0	0.3
H ₂ Sm-SAPO-34	1.4	43.2	0.9	37.5	3.0	11.4	2.2	0.3
W-SAPO-34	1.2	45.4	1.1	36.8	2.8	10.0	1.8	0.3
H ₂ W-SAPO-34	1.3	45.5	0.9	37.3	2.5	9.9	1.8	0.2
Sn-SAPO-34	1.2	44.7	1.1	36.9	3.2	10.5	1.9	0.3
H ₂ Sn-SAPO-34	1.2	45.6	1.1	37.1	2.7	10.2	1.9	0.2
Zr-SAPO-34	1.2	44.7	1.3	36.7	3.4	10.3	1.8	0.3
H ₂ Zr-SAPO-34	1.3	45.3	1.1	37.0	3.0	10.1	1.8	0.2
Nd-SAPO-34	1.1	44.1	1.1	37.3	3.1	10.8	2.0	0.3
H ₂ Nd-SAPO-34	1.2	44.5	1.0	37.7	2.7	10.4	1.8	0.3
Ga-SAPO-34	1.4	46.0	1.1	35.9	2.8	10.0	1.9	0.3
H ₂ Ga-SAPO-34	1.7	46.8	0.9	36.2	1.9	9.9	2.0	0.2
Fe-SAPO-34	1.8	43.4	1.1	36.7	3.0	11.2	2.2	0.3
H ₂ Fe-SAPO-34	1.8	44.1	1.0	37.3	2.1	10.7	2.2	0.3
Gd-SAPO-34	1.2	41.7	1.1	38.0	3.7	11.5	2.2	0.3
H ₂ Gd-SAPO-34	1.2	42.6	1.0	38.3	3.1	11.0	2.0	0.3
Mg-SAPO-34	1.8	44.9	1.2	36.2	2.8	10.4	2.1	0.3
H ₂ Mg-SAPO-34	1.8	45.2	0.9	36.8	2.3	10.1	2.2	0.2
Ca-SAPO-34	1.2	43.5	1.1	37.3	3.3	11.1	2.0	0.3
H ₂ Ca-SAPO-34	1.2	44.1	1.0	37.6	2.9	10.6	2.0	0.2
Li-SAPO-34	1.2	42.3	1.1	38.2	3.7	11.1	1.9	0.2
H ₂ Li-SAPO-34	1.4	42.9	0.9	38.9	3.4	10.5	1.8	0.2
Mn-SAPO-34	1.6	43.6	1.3	35.5	3.9	11.0	2.2	0.3
H ₂ Mn-SAPO-34	1.6	43.5	1.0	36.5	3.4	11.2	2.2	0.3
Ce-SAPO-34	1.2	40.9	1.1	37.7	4.0	12.0	2.4	0.4
H ₂ Ce-SAPO-34	1.3	41.5	1.0	37.9	3.5	11.6	2.4	0.3
V-SAPO-34	1.9	42.7	1.3	36.3	4.2	10.9	2.0	0.3
H ₂ V-SAPO-34	2.0	42.7	1.2	36.8	3.8	10.7	2.0	0.3
TI-SAPO-34	1.3	40.7	1.3	37.6	4.3	11.6	2.2	0.3
H ₂ Tl-SAPO-34	1.2	40.7	1.1	38.7	3.8	11.7	2.3	0.3
Ni-SAPO-34	1.8	44.9	1.1	35.8	3.1	10.7	2.1	0.3
H ₂ Ni-SAPO-34	2.0	45.0	1.1	36.3	2.6	10.1	2.1	0.3
Ru-SAPO-34	1.0	41.6	1.3	37.3	4.9	11.1	2.0	0.3
H ₂ Ru-SAPO-34	1.6	42.5	1.2	37.4	4.2	10.4	2.0	0.2
Pb-SAPO-34	1.2	39.6	1.4	36.5	4.8	12.2	2.6	0.4
H ₂ Pb-SAPO-34	1.5	40.2	1.3	38.4	3.9	11.7	2.4	0.4

Table 7-2 The average selectivity (mol%) of products over metal-promoted catalysts with and without hydrogen co-feed. H₂/MeOH molar ratios of 0.0 and 1.5, temperature 450 °C, and at a *WHSV* of 1 $g_{MeOH} g_{Cat}^{-1} h^{-1}$.

^a Average selectivity throughout the catalyst lifetime until conversion drops to 90% - For low-value compounds like methane and ethane, the precision is ± 0.05 , for more abundant ones like ethylene and propylene the precision is ± 0.15 absolute.

Fig. 7-3 depicts the SEM images of some of the metal-incorporated catalysts along with SEM-EDX analysis of the surface molar composition of particles having different morphologies. A backscattered electron (BSE) detector was employed to distinguish secondary-metal-enriched particles from the SAPO-34 crystals. This is because heavier elements (i.e., elements possessing a greater number of protons/Z-number) are able to generate more BSEs, and in turn appear brighter, relative to lighter elements [204]. The addition of the 20 metals used in the present study in the middle of the gel preparation steps of SAPO-34 zeolite resulted in 4 different cases regarding metal incorporation and crystallinity based on SEM and SEM-EDX results. These 4 categories can be enumerated as 1- complete incorporation of the secondary metal into SAPO-34 structure with no sign of amorphous or new crystalline phase, 2- SAPO-34 cubic particles with low metal loading (0-1 mol%) and formation of different SAPO-34 shapes with higher metal content (3-6 mol%), 3-SAPO-34 cubic particles with low metal loading (0-2 mol%) and creation of amorphous phases with high metal content (3-15 mol%), 4- secondary metal failing to incorporate into the SAPO-34 framework but emerging as an amorphous phase with substantial metal content (9-45 mol%). Obviously, based on the nature of the metal (valency number), some of the metals were not able to enter the SAPO-34 framework such as alkali and alkaline earth metals (groups 1 and 2 of the periodic table). In the case of successful metal incorporation, SEM-EDX results asserted that the secondary metals mostly substituted for aluminum and silicon of the SAPO-34 framework. This can justify the reduction in the number of acidic sites over the majority of the metal-promoted catalysts as presented in Table 7-3. Some metal-promoted samples, however, have gained acidic site density such as Zr, In, and Sn-SAPO-34, whereas others remained unchanged (Gd, W, V, and Nd-SAPO-34) compared to the parent catalyst. Ru and Ce addition caused the emergence of a third peak in the NH₃-desorption plot that indicated the generation of a completely new acidic site. The surface area (Table 7-3) was improved in the case of Zr, In, and Sn-promoted samples, due to smaller particles caused by faster nucleation as a result of metal addition. However, for most of the samples, the surface area was akin to the parent catalyst. As further presented in Table 7-3, the crystallinity was calculated based on the X-ray diffraction tests and all the metal-promoted catalysts showed significant loss of crystallinity relative to the SAPO-34 unpromoted catalyst. This can be ascribed as the dominant reason for poor catalytic performance of the majority of the metalpromoted samples. The X-ray diffraction patterns of the metal-promoted samples are indicated in



Fig. S 11 whereas no sign of secondary metals could be detected, and the diffractions were similar to that of the parent SAPO-34 with diminished intensity due to loss in crystallinity.

Fig. 7-3 SEM Images of metal-promoted catalysts along with the SEM-EDX results

Sample name	$\frac{S_{BET}}{(m^2 g^{-1})}$	V^{b} (cm ³ g ⁻¹)	Weak acid sites ^c (mmol _{NH3} g _{cat} ⁻¹) at peak temperature (^o C) ^d	Strong acid sites ^c (mmol _{NH3} g _{cat} ⁻¹) at peak temperature (°C) ^d	Crystallinity (%)
SAPO-34	533	0.250	1.13 (183 ⁰C)	0.89 (418 °C)	100
In-SAPO-34	626	0.286	1.29 (182 °C)	1.03 (425 °C)	81.1
Mo-SAPO-34	512	0.234	1.05 (180 °C)	0.69 (415 °C)	80.6
Sm-SAPO-34	521	0.238	1.21 (185 ℃)	0.71 (437 °C)	74.8
W-SAPO-34	549	0.250	1.07 (179 °C)	0.89 (415 °C)	67.5
Sn-SAPO-34	597	0.273	1.29 (184 °C)	1.00 (425 °C)	82.0
Zr-SAPO-34	631	0.288	1.35 (183 °C)	1.07 (420 °C)	85.0
Nd-SAPO-34	519	0.237	1.12 (179 °C)	0.82 (422 °C)	63.8
Ga-SAPO-34	510	0.247	1.14 (179 ⁰C)	0.81 (416 °C)	70.0
Fe-SAPO-34	519	0.249	1.05 (175 °C)	0.66 (401 °C)	76.2
Gd-SAPO-34	533	0.244	1.13 (178 ⁰C)	0.88 (422 °C)	60.9
Mg-SAPO-34	526	0.240	1.07 (179 °C)	0.72 (401 °C)	76.3
Ca-SAPO-34	497	0.227	1.05 (177 °C)	0.77 (413 °C)	59.9
Mn-SAPO-34	551	0.252	1.14 (173 °C)	0.81 (401 °C)	63.6
Ce-SAPO-34	550	0.251	1.09 (182 °C)	0.93(428 °C),0.04(545 °C)	57.8
Li-SAPO-34	496	0.227	1.07 (180 °C)	0.67 (407 °C)	68.3
V-SAPO-34	573	0.262	1.15 (179 °C)	0.83 (416 °C)	78.3
Tl-SAPO-34	509	0.233	1.07 (176 °C)	0.72 (415 °C)	58.5
Ni-SAPO-34	530	0.242	1.07 (176 °C)	0.76 (405 °C)	76.4
Ru-SAPO-34	423	0.194	1.04(177 °C),0.13(255 °C)	0.55 (368 °C)	59.5
Pb-SAPO-34	474	0.217	1.03 (175 °C)	0.67 (415 °C)	44.8

Table 7-3 Physicochemical properties of the samples using N₂ adsorption and NH₃-TPD techniques.

^a S_{BET} = BET total specific surface area obtained from adsorption data in the p/p_0 range from 0.06–0.3. all reported data are within ±1% based on repeated analysis. ^b V = single point adsorption total pore volume of the pores with radius of less than 967 Å at p/p_0 of 0.9900. ^c Accuracy ± 1% relative ^d Accuracy ± 5°C ^e the acidity of the composite catalysts has been prorated based on the SAPO content

7.3 Conclusion

Hydrogen co-feeding with methanol (H₂/MeOH molar ratio of 1.5) at ambient pressure extended the catalyst lifetime by 27% due to hydrogenation and cracking of the coke precursors and slightly improved the light olefins selectivity (81.2 to 82.2 mol%). Further hydrogen addition did not demonstrate a significant improvement and was not economically feasible either. All metal-promoted SAPO-34 samples behaved similarly with enhanced lifetime and LOS in the presence of hydrogen. In and Mo-promoted catalysts illustrated slightly longer lifetimes (10-15%) and similar LOS relative to the parent catalyst. SAPO-34 promoted with Sm, W, Sn, and Zr performed similarly to the parent SAPO-34 catalyst. The addition of other metals to SAPO-34 worsened its

performance with the inferior being V-, Tl-, Ni- and Ru-promoted samples. SEM images along with SEM-EDX analysis indicated that metal incorporation into the framework was accomplished for some metals, while others resulted in partial incorporation or failed to get into the SAPO structure and emerged as amorphous phases. Although in some cases, the surface area of the metal-promoted samples increased due to enhanced nucleation rate and smaller particle formation, in the majority of the promoted samples, the surface area was comparable to the parent catalysts or diminished due to pore blockage. All the samples experienced a significant loss in crystallinity from 15 to 55% reduction relative to the parent catalyst. Overall, based on our results, by applying the optimum silica content in the parent catalyst, the addition of the secondary metal cannot be beneficial and, in most cases, would worsen the catalytic performance.

8 A comprehensive scholarly discussion of all the findings

8.1 Effect of template alteration on SAPO-34 properties

TEAOH, MOR, TEA, and DEA, i.e., the most popular templates for SAPO-34 production, were assessed under similar synthesis conditions. Among single-template samples, all catalysts except the one prepared with TEAOH showed impurities in the form of either SAPO-5 or SAPO-11. Regarding the single-template method, TEA seems to be the best substitute for TEAOH with slightly lower LOS (74% compared with 76%, but 50% longer lifetime for the TEA-based sample). The other two templates (DEA and MOR) displayed poor performance by rapid catalyst deactivation and low LOS. Furthermore, in the case of mixed-temple samples, both TEAOH/DEA and TEAOH/TEA samples succeeded in eradicating the phase impurities and possessed only SAPO-34. They illustrated an almost 20% longer lifetime and slightly higher LOS relative to the TEAOH-directed sample. MOR-TEAOH sample, on the other hand, retained the SAPO-5 impurity and could not compete with the other samples with reference to LOS. Two different orders of mixing for precursor addition during catalyst gel synthesis were applied and it was concluded that as long as the final gel pH is being kept at the optimum range (8.0-8.5 for TEA-involved samples, 6.5-7.5 for the rest of the catalysts), the mixing order of the precursor does not affect the catalyst characteristics. The impact of silica dissolving into the template was explored for the first time, and it was recognized that it can improve the nucleation and reduce the particle size substantially. The sole influence of catalyst particle size was also revealed (as other affecting catalyst parameters such as surface area and acidity were kept constant), and it was inferred that reducing the particle size roughly from 3-7 to 0.2-1.3 µm can improve the catalyst lifetime by 10%. As the principal finding, the reason for a longer catalytic lifetime was found to be the possession of an external surface area, while optimum acidity, high total surface area, and small particle size are the other less important factors. Macro and mesopores, termed as external surface area, can improve mass transfer despite partial blockage of pores by coke formation and keep the interior active sites accessible to the reactant. This will help the catalyst endure longer and maintain the activity even at higher coke deposition amounts. As an example, DEA and MOR-directed samples deactivated after 7-8 wt% coke deposition while TEAOH/DEA and TEAOH/TEA samples held the activity up to 24-26 wt% coke content. Finally, in-situ measurement of coke formation using a thermogravimetric reactor was conducted using realistic reaction conditions for the first time. The results revealed a slow coke formation rate at the beginning of the activity test followed by a fast coke production (2-3 times faster) at an advanced time on stream. This indicates the importance of diffusion constraints on catalyst lifetime and coke formation rate. It is speculated that partially coked pores in the outer surface of the catalyst particles restrict heavier compounds from diffusing out, which in turn results in further growth of the hydrocarbon chain and more intense coke formation. Based on ¹³C-NMR spectroscopy over partially and fully coked catalysts, it is evident that coke in the early stages of TOS consists of both light alkylated aromatics, linear olefins, and polyenes, while coke in advanced stages comprises primarily multi-ring aromatics. Hence, overall, the mechanism of coke formation, which was initially hypothesized based on TGR results, was ultimately validated via the ¹³C-NMR analysis. The results provide a comprehensive insight into methanol to light olefin reaction over SAPO-34 catalysts prepared with different templates. They are relevant as well as serve as a basis to understand and optimize the SAPO catalyst further.

8.2 SAPO-34 synthesis by alkali post-treatment

To overcome the catalyst's fast deactivation due to coke formation, we developed a post-synthesis approach leading to hierarchical particles of SAPO-34 while retaining its crystalline structure. Utilizing alkali post-treatment, a significant reduction in Brønsted acidic sites over treated samples was observed as DEA preferentially extracts the Si species out of the SAPO-34 structure (according to the CD₃CN-FTIR technique). In terms of activity results, the mildly treated sample (0.5DEA/SAPO-34) showed a superior catalyst lifetime compared to the parent SAPO-34. However, the severely treated sample (4.0DEA/SAPO-34) displayed a worse performance due to intense surface area reduction and loss of active sites. In addition to that, different product distributions over parent and treated samples were acquired; treated samples had lower light olefins selectivity as a result of increased alkane production. This phenomenon was justified by TGA-TPO, GC-MS, and ¹³C-NMR tests, displaying the formation of heavier coke species over treated samples that contain a lower hydrogen per carbon ratio. This implies that a higher amount of hydrogen will be released during coke formation to facilitate the simultaneous occurrence of alkane production. Furthermore, DFT calculations were employed to investigate the role of

Brønsted and Lewis acidic sites in olefin and coke formation. Based on the Gibbs Free energy profile and activation energy barriers (corresponding to the elementary steps of the reactions) calculated in the present study and complemented by the work done by Gao *et al* [289], it was found that C-C coupling or olefin formation is only feasible over Brønsted acidic sites, while the dehydrogenation and aromatization is facilitated by Lewis acidic sites. This can clearly justify the faster aromatization and heavier aromatic formation over treated samples possessing higher LAS/BAS ratios compared with the parent SAPO-34 catalyst.

8.3 SAPO-34 synthesis on y-Al₂O₃ microspheres for fluidized-bed application

Employing the conventional spray drying technique to shape the agglomerates of SAPO-34, which is used for the fluidized-bed application, encountered major drawbacks. Agglomerates consisting of 50 wt% SiO₂ as the binder, experienced around 17% loss in micropore surface area, 35 % reduction in active sites, and consequently performed weakly in methanol conversion to light olefins reaction (with almost 30% shorter lifetime). Hence, a new technique was developed to mount SAPO-34 in situ over y-Al₂O₃ microspheres with high loading while maintaining the characteristics of the SAPO-34 parent catalyst. The method consisted of AlPO₄-34 formation on the outer shell of y-Al₂O₃ microspheres with rapid microwave heating followed by Si incorporation at 200 °C through the microwave-assisted hydrothermal step. TEAOH and TEA were separately utilized as structure-directing agents and resulted in crystals with different morphologies (cubic and sheet-like particles, respectively). SAPO loading of 44 and 31 wt% was measured over SAPOmounted y-Al₂O₃ microspheres using TEAOH and TEA, respectively. These catalysts also showed comparable light olefin selectivity and even enhanced catalytic lifetime compared to their parent counterparts. With the aid of the proposed synthesis method, a suitable catalyst designated for the fluidized-bed reactors with high SAPO-34 loading and good physical properties (having a good adhesion of SAPO-34 to the support and the abrasion-resistance structure) can be produced. This method does not sacrifice the physicochemical properties of the SAPO-34 catalyst under the shaping process.

8.4 SAPO-34 promotion by in-situ metal incorporation

Overall, some articles have claimed that the addition of secondary metal precursors enhances the nucleation, resulting in smaller crystals that have better mass transfer characteristics and can last longer within the reaction [163]. Alternatively, the introduction of new mesopores into the structure due to secondary metal addition has also been claimed to be one of the underlying factors for superior catalytic performance [159], although the mechanism for the formation of these mesopores has not been clarified. Apart from that, the majority of metal-promoted articles [155,156,158,160,162] stated that lowering the quantity of Brønsted acidic sites via substitution of Si (as opposed to the other SAPO elements) by the added metal hinders the evolution of coke precursor formation reactions while retaining the acidity level sufficient for the dehydration steps to light olefins. Hence, this results in decreased production of alkanes (specifically methane) and multi-ring aromatic species (the precursors of coke), leading to a delay in pore blockage in which the diffusion of species can continue to transpire (i.e., prolonged catalytic activity). Despite the consensus amongst these articles in support of this rationale, there still lies some ambiguities that need to be addressed. Firstly, these articles are quick to suggest that the decrease in acidity acts as the primary justification, when this alteration can be achieved by an easier approach: reducing the silica content in the starting gel. This should in turn question the need to use secondary metals entirely since they seem to increase costs unnecessarily when a more economic approach may be utilized instead. It should be noted that research groups have previously investigated the effect of silica content alterations on catalytic performance [106,107] and arrived at the conclusion that the optimal SiO₂/Al₂O₃ ratio, concerning catalyst lifetime, lies between 0.2 to 0.3. Those groups [158,162,169,171] who have reported a 2 to 5 times extended lifetime of the metal-promoted catalyst compared to the parent one, have started with a SiO₂/Al₂O₃ ratio of 0.6, which is not optimum. On the contrary, the studies [165] that commenced with an optimum Si content in the parent synthesis gel reported slightly enhanced, like, or even worse performance of the metalpromoted catalyst relative to the parent sample. Secondly, metal modification usually results in worsening of physicochemical properties, such as a loss in both surface area and crystallinity, which can further suppress the idea that metal promotion can yield enhanced results.

The promotion of metal with regards to the SAPO framework may in some way affect Brønsted acidic sites and/ or influence the mechanistic route taken (by altering the activation energy barriers

of elementary steps). The formation of the Brønsted acidic sites within the parent SAPO-34 lattice has been extensively investigated [263] and is now well understood. Substitution of a Si⁴⁺ atom for a P⁵⁺ atom in the AlPO₄ framework (so-called isolated silica formation Si (4Al)) causes a negative charge that is neutralized by the addition of a proton attached to the bridging oxygen (Al-OH-Si) and correspondingly forms a Brønsted acidic site. Simultaneous substitution of adjacent Al and P atoms with multiple Si atoms can result in silica islands. For these silica islands, the case is more complicated as the siliceous island can include different numbers of silicon atoms, which can be dictated by the catalyst topology and Si content. In the case of the most ordinary silica island, four P and one Al atom are replaced by five Si. The central silicon (Si (4Si)) has no associating proton while 3 protons accompany 3 of the 4 surrounding Si atoms (Si (1Si 3Al)). The larger siliceous islands can create other silica environments including Si (2Si 2Al) and Si (3Si 1Al). The acidity of the proton attached to the bridging oxygen (Si-OH-Al) can be highly affected by the electronegativity of the first and second shells of neighboring molecules. The higher the electronegativity of the surrounding atoms, the stronger the acidity of the Brønsted site. Therefore, if the secondary metal substituted for silica and still maintained the bridging hydroxyl group (Brønsted site), the strength of the acidic site will be determined based on the electronegativity of the metal added. If the secondary metal replaced the aluminum neighboring the Brønsted site, once again the strength of the acidic site based on the new atomic arrangement should be measured. There may even lie the possibility of metal atoms acting as new active sites themselves in addition to Brønsted acidic sites. However, regardless of the mechanism of the metal incorporation, which may alter the existing acidic sites or create new acidic sites, the amount of the metal added should be comparable with the Si content, otherwise, the effect of metal promotion may not be detectable. Nonetheless, a majority of the articles have tried a much lower metal quantity (0.05 Me/Al₂O₃) relative to their silicon content $(0.3-0.6 \text{ Si}/\text{Al}_2\text{O}_3)$. Higher metal loadings, on the other hand, have illustrated substantial negative effects on the catalyst surface area and crystallinity. In addition, the positive or negative influence of the new acid sites, as a result of metal incorporation, on the catalyst's performance can't be uncovered unless their role in the reaction mechanism and all the elementary steps involved are studied exclusively. This area of research, which could involve tools such as density functional theory (DFT) modeling or other more exhaustive characterization devices, seems to still be open for further exploration.

We studied a wide range of metals from different groups of the periodic table (alkali and alkaline earth metals, transition metals, rare earth metals, and basic metals). In and Mo-promoted catalysts illustrated slightly longer lifetimes (10-15%) and similar LOS relative to the parent catalyst. SAPO-34 promoted with Sm, W, Sn, and Zr performed similarly as the parent SAPO-34 catalyst. The addition of other metals to SAPO-34 worsened its performance with V, Tl, Ni, and Ru at the bottom of the chart. SEM images along with SEM-EDX analysis indicated that metal incorporation into the framework was accomplished for some metals while others resulted in partial incorporation or failed to get into the SAPO structure and emerged as amorphous phases. Although in some cases, the surface area of the metal-promoted samples increased due to enhanced nucleation rate and smaller particle formation, in the majority of the samples the surface area was comparable to the parent catalysts or dropped due to pore blockage. All the samples experienced a significant loss in crystallinity from 15 to 55% reduction relative to the parent catalyst, Overall, based on our results, by applying the optimum silica content in the parent catalyst, the addition of the secondary metal cannot be beneficial and, in most cases, would worsen the catalytic performance.

8.5 Final conclusion and summary

In summary, all of the objectives that had been assigned at the beginning of the project were achieved. A microreactor setup was designed and constructed to simulate the MTO reactor. The SAPO-34 catalyst was prepared according to our developed synthesis procedure and by providing the optimum reaction conditions, similar products as the commercialized process were gained. After a comprehensive literature review, 4 subprojects were defined to address the knowledge gaps in the MTO process context. Then, a comprehensive experimental and analysis plan was arranged and implemented to understand the fundamental relationship between synthesis procedures, catalyst properties, activity performance, and the deactivation pathway. Some techniques such as alkali-treatment and template alteration were proposed to improve the catalyst properties. The coke evolution mechanism and the roles of Lewis and Brønsted acidic sites over the SAPO-34 catalyst were investigated and explained. A new procedure for Fluidized-bed catalyst preparation was introduced. Metal promotion of the SAPO-34 catalyst was examined using a variety of metals and it was revealed that secondary metals do not have a beneficial effect on SAPO-34 performance. The results of these 4 subprojects were narrated in 4 manuscripts for publication. Our findings not

only serve the interests of the research sector but also can be employed to improve the economy of the MTO process for sustainable light olefin production.

8.6 Future work

8.6.1 Limitations of mechanistic studies

Although much progress has been made towards uncovering the mechanisms of the methanol conversion to olefins reaction, the individual steps amongst a majority of these mechanisms are somewhat vague and do not normally possess the detail needed to be termed as elementary steps. Furthermore, a majority of the mechanisms presented have been generalized for different types of zeolites (such as mordenite, H-ZSM-5, and SAPO-34), which may not be accurate considering differences in acidity, topology, and pore sizes. In reality, these factors that distinguish one zeolite catalyst from another could largely affect the activation energies of elementary steps, and in turn, influence the mechanistic route adopted. Research to explain how some zeolites may favor one path over another is quite limited and has only recently emerged [66]. With DFT calculations of van der Waals dispersive corrections, the group [66] concluded that the 'side chain mechanism' acts as the major reaction pathway over H-SAPO-34, whereas the H-ZSM-5 catalyst was shown to favor the paring route instead. Moreover, according to the HCP mechanism, polyalkylaromatics, which are deemed the active intermediates for light olefin production, are themselves being produced from light olefins, which seems counterintuitive. To the best of our knowledge, there still exists a lack of comprehensive studies that compare the elementary steps and energy activation barriers of initial light olefin production and desorption with that of further olefin reformation to create polyalkylaromatics and subsequent light olefins.

8.6.2 Metal promoted SAPO-34

By observing the results of the conducted research in metal modification of SAPO-34, clear contradictions can be spotted. Even while employing similar metals, opposing catalytic performances have been reported. For instance, even in the case of a specific metal application (Ni-incorporated SAPO-34), there have been reports of significantly improved [160], unchanged [161], and slightly worsened [168] light olefins selectivity (relative to the parent catalyst). This

demands a comprehensive molecular study on the role of secondary metal incorporation on the Brønsted acidic sites and further investigation of the effect of this change on the catalyst activity. Moreover, the state of the secondary metals during the MTO reaction (staying as oxides or transforming into reduced form or carbide) can be explored. With this regard, in-situ X-ray adsorption spectroscopy or XPS analysis of the catalyst before and after the activity test can be helpful.

8.6.3 Assess the acidity strength of the proton associated with the isolated and island Si in the SAPO-34 framework.

There is a consensus amongst researchers [115] that the acidic sites (protons attached to the bridging oxygen) associated with silica island are much stronger than the one that accompanies isolated silica and consequently, catalysts possessing higher silica islands are prone to faster deactivation. Comparing the first and second shells of neighboring atoms for the isolated silica (**Si** (4Al)(8P)) and the silica island (**Si** (1Si 3Al)(3Si 5P)), the first neighboring shell of silica island is more electronegative (due to the presence of one Si instead of one Al), compared to that of the isolated silica. This is how Barthomeuf [263] inferred that silica islands are more acidic than isolated silicas, overlooking the fact that the second neighboring shell is less electronegative due to the presence of three P atoms. To correctly assess the strength of the acidic sites, an aggregate effect of the first and second shells should be considered. This can be done by simulating the ammonia adsorption/desorption on the mentioned acidic sites using Density Functional Theory (DFT). Furthermore, no matter which acidic site is stronger, its positive or negative effect on the catalyst performance cannot be discussed unless the full mechanistic study is done by comparing the activation energy barriers for each elementary step of either olefin formation or coke creation.

9 Originality

9.1 Novelties regarding template alteration and coke formation analysis (chapter 4)

- Although mixed-template SAPO-34 synthesis had been tried, due to discrepancies and lack of meaningful trends in former studies, we attempted to find the principal reason behind the superior performance of mixed-template catalysts.
- For the first time, the four most popular templates (TEAOH, TEA, DEA, and MOR) were used in a single study to conduct a comprehensive investigation on the synthesis of single and mixed-template SAPO-34
- The optimum single and mixed template catalysts were introduced based on superior activity performance.
- The importance of the final gel pH in SAPO-34 synthesis was uncovered, and the optimum values depending on each template were reported, which was a novel initiative in this work.
- For the first time, the impact of silica dissolving into the template was explored, and it was recognized that it can improve nucleation and reduce catalyst particle size substantially.
- The sole influence of catalyst particle size on its activity performance was also revealed (as other affecting catalyst parameters such as surface area and acidity were kept constant), and it was inferred that reducing the particle size from 6 to 1 micron can improve the catalyst lifetime by 10%.
- As the principal finding, the dominant affecting parameter for a longer catalyst lifetime was found to be the possession of an external surface area, while optimum acidity and high total surface area and small particles were other less important factors.
- Live measurement of coke formation using a thermogravimetric reactor mass spectrometer (TGR-MS) was conducted using realistic reaction conditions for the first time. The results revealed a slow coke formation rate at the beginning of the activity test followed by rapid coke production (2-3 times faster) at advanced times on stream.

Originality

 The coke formation mechanism, which was initially hypothesized based on TGR results, was ultimately validated via the GC-MS and ¹³C-NMR analysis of partially and fully coked catalysts.

9.2 Novelties regarding alkali treatment and BAS/LAS role (chapter 5)

- For the first time, the consequences of acidic site alteration due to alkali treatment were investigated.
- By precise analysis of the products, different product distributions over parent and treated samples were spotted; treated samples had lower light olefins selectivity because of increased alkane production.
- This phenomenon was justified by TGA-TPO, GC-MS, and ¹³C-NMR tests, displaying the formation of heavier coke species over treated samples that contain a lower hydrogen per carbon ratio. This implies that a higher amount of hydrogen will be released during coke formation to facilitate the simultaneous occurrence of alkane production.
- Furthermore, for the first time, DFT calculations were employed to investigate the role of Brønsted and Lewis acidic sites in olefin and coke formation. Based on the Gibbs Free energy profile and activation energy barriers (corresponding to the elementary steps of the reactions) calculated in the present study and complemented by the work done by Gao *et al* [289], it was found that C-C coupling or olefin formation is only feasible over Brønsted acidic sites, while the dehydrogenation and aromatization is facilitated by Lewis acidic sites. This can clearly justify the faster aromatization and heavier aromatic formation over treated samples possessing higher LAS/BAS ratios compared with the parent SAPO-34 catalyst.

9.3 Novelties regarding catalyst synthesis for fluidized-bed application (chapter 6)

- The conventional spray drying technique was evaluated as a benchmark for composite catalysts suitable for fluidized bed application. Agglomorates consisting of 50 wt% SiO₂ as the binder, experienced around 17% loss in micropore surface area, 35 % reduction in active sites, and consequently performed weakly in methanol conversion to light olefins reaction (with almost 30% shorter lifetime).
- For the first time, SAPO-34 was mounted on γ-Al₂O₃ microspheres due to alumina's high surface area and stability in the reaction conditions.
- High loading of SAPO-34 (30-40 wt.%) with good adhesion to the support was achieved using a new technique.
- The method consisted of AlPO₄-34 formation on the outer shell of γ-Al₂O₃ microspheres with rapid microwave heating followed by Si incorporation at 200 °C through the microwave-assisted hydrothermal step.
- The new composite catalysts showed comparable light olefin selectivity and even enhanced catalytic lifetime compared to their parent counterparts.

9.4 Novelties regarding in-situ metal incorporated SAPO-34 (chapter 7)

- For the first time, hydrogen co-feeding with methanol at ambient pressure was tested and its effect on catalyst lifetime and light olefin selectivity was investigated.
- H₂/MeOH molar ratio of 1.5 in the feed (at ambient pressure) extended the catalyst lifetime by 27% due to hydrogenation and cracking of the coke precursors and slightly improved the light olefins selectivity (81. 2 to 82.2 mol%).

- A thorough assessment of the secondary metal addition on SAPO-34 performance was conducted by utilizing 20 metals from different groups of the periodic table (thirteen metals have not been tested before).
- In some cases, the surface area of the metal-promoted samples increased due to enhanced nucleation rate and smaller particle formation. However, in the majority of the promoted samples, the surface area was comparable to the parent catalysts or diminished due to pore blockage.
- All the metal-promoted SAPO-34 samples experienced a significant loss in crystallinity from 15 to 55% reduction relative to the parent catalyst.
- Overall, for the first time, it was revealed that by applying the optimum silica content in the parent catalyst, the addition of the secondary metal cannot be beneficial and, in most cases, would worsen the catalytic performance.

Contribution of the authors

Conceptualization, investigation, development of the methodology, data curation, analysis, visualization, validation, and writing the original draft of the present dissertation was accomplished by **Roham Ghavipour** as partial fulfillment of the requirements of his Ph.D. degree.

DFT calculations regarding the role of BAS and LAS of SAPO-34 catalyst in the MTO reaction presented in Chapter 5 were done by our collaborators **Dr. Samira Siahrostami & Dr. Tiago J. Goncalves** from the Department of Chemistry, University of Calgary.

Ralph Al Hussami, an undergrad student employed under the SURE program, was trained by Roham Ghavipour on all characterization techniques, performing the catalyst synthesis and activity tests, and interpreting the results. He helped us conduct some of the experiments and proofread the manuscripts.

Ranjan Roy, the technician of the analytical lab in the Chemical Engineering Department, assisted in performing the GC-MS analysis of the coke and CD₃CN-DRIFT tests.

Dr. **Kirill Levin**, a research associate in the Chemistry Department, conducted the ¹³C and ²⁹Si solid-state NMR tests.

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Nomenclature

Latin symbols

$\Delta H_{\rm i}$	kJ·mol ⁻¹	heat of adsorption of species <i>i</i>
$\Delta H_{\rm R}^0$	kJ·mol ⁻¹	heat of reaction
$\varDelta H_{\rm f,i}{}^0$	kJ·mol ⁻¹	heat of formation of species <i>i</i>
$M_{ m i}$	kg·mol ⁻¹	molar weight of species <i>i</i>
т	kg	mass
S	$m^2 \cdot g^{-1}$	specific surface area
Т	K or °C	temperature
Wi	-	mass fraction of species i
Xi	-	molar fraction of species <i>i</i>

Greek symbols

δ	m	thickness	(delta)
Е	-	void fraction or porosity	(epsilon)
η	-	efficiency	(eta)
Vij	-	stoichiometric factor of species i in reaction j	(nu)
ρ	kg·m ⁻³	density	(rho)

Subscripts and superscripts

ads	adsorbed
av	average
cat	catalyst
N	norm condition $T = 273.15$ K and $p = 1.0$ bar

tot total

MeOH Methanol

Abbreviation

DFT	density functional theory
DRIFTS	diffuse reflectance infrared Fourier transform spectroscopy
EDS	energy-dispersive X-ray spectroscopy
FBR	fixed bed reactor
FID	flame ionization detector
FTIR	Fourier transform infrared
GC	gas chromatography
GHSV	gas hourly space velocity
ICP	inductively coupled plasma
IR	infrared
LOS	light olefins selectivity
MAS	magic angle spinning (in NMR)
MS	mass spectrometry
MS	microsphere
MTO	methanol conversion to light olefins
SEM	scanning electron microscopy
SD	spray dried
SS-NMR	solid-state nuclear magnetic resonance
STEM	scanning transmission electron microscopy
TCD	thermal conductivity detector
Temp	temperature
TGA	thermogravimetric analysis
TI	temperature indicator
TIC	temperature indicator controller
TPD	temperature-programmed desorption
TPO	temperature-programmed oxidation
XRD	X-ray diffraction

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Metal	Comment/ Synthesis technique	Methanol Processing ability ^a (g _{MeOH} /g _{cat})	Average light olefins selectivity (mol %)	Gel formula (molar) (Al ₂ O ₃ / P ₂ O ₅ / SiO ₂ / T/ H ₂ O/ Me)	Catalyst formula (mol%) Al _x P _x Si _x M _x	Reaction Conditions	Ref
_	Parent SAPO-34	7.9	N/A	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.4 SiO ₂ / 1 TEAOH/ 1 MOR/ 60 H ₂ O	$Al_{0.485}P_{0.405}Si_{0.108}$	_	
-	Hierarchical SAPO-34	10.4	N/A	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.4 SiO ₂ / 1 TEAOH/ 1 MOR/ 60 H ₂ O	$Al_{0.474}P_{0.423}Si_{0.101}$	WHSV =	
Со	Hierarchical + In-situ metal incorporation	15.8	N/A	$\begin{array}{c} 1 \ Al_2O_3/ \ 1 \ P_2O_5/ \\ 0.4 \ SiO_2/ \ 1 \ TEAOH/ \\ 1 \ MOR/ \ 60 \ H_2O/ \ 0.08 \ Co \end{array}$	$\begin{array}{c}Al_{0.480}P_{0.426}Si_{0.079}\\Co_{0.014}\end{array}$	5.00 h ⁻¹ Reaction T: 400 °C	[155]
	Hierarchical + Impregnation	13.3	N/A	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.4 SiO ₂ / 1 TEAOH/ 1 MOR/ 60 H ₂ O	$\begin{array}{c}Al_{0.481}P_{0.409}Si_{0.093}\\Co_{0.016}\end{array}$	MeOH: 19 mol% Water:	[155]
Ni	Hierarchical + In-situ metal incorporation	14.2	N/A	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.4 SiO ₂ / 1 TEAOH/ 1 MOR/ 60 H ₂ O/ 0.08 Ni	$\begin{array}{c}Al_{0.482}P_{0.421}Si_{0.087}\\Ni_{0.009}\end{array}$	81 mol%	
	Hierarchical + Impregnation	8.3	N/A	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.4 SiO ₂ / 1 TEAOH/ 1 MOR/ 60 H ₂ O	$\begin{array}{c} Al_{0.489} P_{0.405} Si_{0.090} \\ Ni_{0.015} \end{array}$	-	
_	Parent SAPO-34	8.0	N/A	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.4 SiO ₂ / 1.1 TEAOH/ 0.9 MOR/ 60 H ₂ O	$Al_{0.481}P_{0.407}Si_{0.112}$		
Fe	In-situ metal incorporation	9.0	N/A	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.4 SiO ₂ / 1.1 TEAOH/ 0.9 MOR/ 60 H ₂ O/ 0.05 Fe	$\begin{array}{c} Al_{0.467}P_{0.386}Si_{0.139} \\ Fe_{0.008} \end{array}$	-	
Со	In-situ metal incorporation	11.0	N/A	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.4 SiO ₂ / 1.1 TEAOH/ 0.9 MOR/ 60 H ₂ O/ 0.05 Co	$\begin{array}{c} Al_{0.468} P_{0.385} Si_{0.135} \\ Co_{0.012} \end{array}$	$WHSV = 2.46 \text{ h}^{-1}$ Reaction T:	
Ni	In-situ metal incorporation	10.0	N/A	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.4 SiO ₂ / 1.1 TEAOH/ 0.9 MOR/ 60 H ₂ O/ 0.05 Ni	$\begin{array}{c} Al_{0.478}P_{0.381}Si_{0.138}\\ Ni_{0.003} \end{array}$	MeOH: 19 mol% Water:	[156]
La	In-situ metal incorporation	15.0	N/A	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.4 SiO ₂ / 1.1 TEAOH/ 0.9 MOR/ 60 H ₂ O/ 0.05 La	$\begin{array}{c} Al_{0.470}P_{0.378}Si_{0.137} \\ La_{0.015} \end{array}$	- 81 110176	
Ce	In-situ metal incorporation	17.0	N/A	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.4 SiO ₂ / 1.1 TEAOH/ 0.9 MOR/ 60 H ₂ O/ 0.05 Ce	$\begin{array}{c} Al_{0.472}P_{0.380}Si_{0.132}\\ Ce_{0.016}\end{array}$	-	
_	Parent SAPO-34	4.9	81.0	N/A	$Al_{0.448}P_{0.352}Si_{0.200}$		
La	3 wt% La loading, solid- state ion exchange	5.6	84.5	N/A	N/A	$WHSV = 2.10$ h^{-1} Reaction T:	
	Liquid phase ion exchange	4.6	81.2	N/A	La _{0.002}	450 °C MeOH:	[157]
Y	3 wt% Y loading, solid- state ion exchange	5.8	85.0	N/A	N/A	25 mol% Water: 75 mol%	
	Liquid phase ion exchange	4.7	81.9	N/A	Y _{0.003}		

Table S 1 Summary of the key parameters and results from metal promoted SAPO-34 studies.

Metal	Comment/ Synthesis technique	Methanol Processing ability ^a (g _{MeOH} /g _{cat})	Average light olefins selectivity (mol %)	Gel formula (molar) (Al ₂ O ₃ / P ₂ O ₅ / SiO ₂ / T/ H ₂ O/ Me)	Catalyst formula (mol%) Al _x P _x Si _x M _x	Reaction Conditions	Ref
_	Parent SAPO-34	12.0	85.0	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.6 SiO ₂ / 9 DEA/ 110 H ₂ O	$Al_{0.460}P_{0.364}Si_{0.176}$	WHSV = 6.00	
Fe	In-situ metal incorporation	36.0	10.0	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.6 SiO ₂ / 9 DEA/ 110 H ₂ O/ 0.05 Fe ₂ O ₃	$\begin{array}{c} Al_{0.335}P_{0.325}Si_{0.114} \\ Fe_{0.227}^{\gamma} \end{array}$	h^{-1} Reaction T: 450 °C	[158]
K	Ion exchange - wet impregnation	60.0	90.0	N/A	N/A	MeOH: 30 mol% Water:	[150]
Ag	Ion exchange - wet impregnation	17.0	91.0	N/A	N/A	/0 mol%	
_	Parent SAPO-34	7.3	40.3	1 Al ₂ O ₃ / 1.15 P ₂ O ₅ / 0.55 SiO ₂ / 2 TEAOH/ 110 H ₂ O	Al _{0.526} P _{0.357} Si _{0.117}	WHSV = 4.85	
Ca	In-situ metal incorporation	9.7	58.7	1 Al ₂ O ₃ / 1.15 P ₂ O ₅ / 0.55 SiO ₂ / 2 TEAOH/ 110 H ₂ O/ 0.007 CaO _x	$\begin{array}{c} Al_{0.544}P_{0.308}Si_{0.141}\\ Ca_{0.007} \end{array}$	Reaction T: 350 °C	[150]
Cu	In-situ metal incorporation	8.9	49.0	1 Al ₂ O ₃ / 1.15 P ₂ O ₅ / 0.55 SiO ₂ / 2 TEAOH/ 110 H ₂ O/ 0.007 CuO _x	$\begin{array}{c}Al_{0.541}P_{0.341}Si_{0.116}\\Cu_{0.002}\end{array}$	5 mol% Helium:	[139]
W	In-situ metal incorporation	5.7	40.9	1 Al ₂ O ₃ / 1.15 P ₂ O ₅ / 0.55 SiO ₂ / 2 TEAOH/ 110 H ₂ O/ 0.007 WO _x	$\begin{array}{c} Al_{0.537} P_{0.326} Si_{0.130} \\ W_{0.007} \end{array}$	- 95 mor/6	
_	Parent SAPO-34	N/A	1.8	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.6 SiO ₂ / 1 TEAOH/ 1 MOR/ 60 H ₂ O	$Al_{0.58}P_{0.29}Si_{0.12}$	$WHSV = 8.70 \text{ h}^{-1}$	
Ni	In-situ metal incorporation	N/A	7.8	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.6 SiO ₂ / 1 TEAOH/ 1 MOR/ 60 H ₂ O/ 0.05 NiO	$\begin{array}{c} Al_{0.50}P_{0.31}Si_{0.19}\\ Ni_{0.005} \end{array}$	Reaction T: 400 °C MeOH:	[160]
Mg	In-situ metal incorporation	N/A	4.0	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.6 SiO ₂ / 1 TEAOH/ 1 MOR/ 60 H ₂ O/ 0.05 MgO	$\begin{array}{c} Al_{0.36}P_{0.44}Si_{0.20}\\ Mg_{0.006} \end{array}$	19 mol% Water: 81 mol%	
_	Parent SAPO-34	15.8	85.0	1 Al ₂ O ₃ / 1 P ₂ O ₅ /0.30 SiO ₂ /2.0 TEAOH/50 H ₂ O	N/A		
Со	In-situ metal incorporation (Method 1)	11.0	87.0	1 Al ₂ O ₃ / 1 P ₂ O ₅ /0.30 SiO ₂ /2.0 TEAOH/50 H ₂ O/ 0.007 CoO	Co _{0.003}	$WHSV = 0.48 \text{ h}^{-1}$	
Mn	In-situ metal incorporation (Method 1)	25.0	86.0	1 Al ₂ O ₃ / 1 P ₂ O ₅ /0.30 SiO ₂ /2.0 TEAOH/50 H ₂ O/ 0.005 MnO	Mn _{0.003}	- Reaction T: 400 °C MeOH:	[161]
	In-situ metal incorporation (Method 1)	9.6	85.0	1 Al ₂ O ₃ / 1 P ₂ O ₅ /0.30 SiO ₂ /2.0 TEAOH/50 H ₂ O/ 0.007 NiO	Ni incorporation ~ 0	- 5 mol% Nitrogen: 95 mol%	
N1	In-situ metal incorporation (Method 2)	17.3	85.0	1 Al ₂ O ₃ / 1 P ₂ O ₅ /0.10 SiO ₂ /2.0 TEAOH/50 H ₂ O/ 0.01 NiO	Ni _{0.003}	-	
_	Parent SAPO-34	119.1	90.0	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.6 SiO ₂ / 2 TEAOH/ 70 H ₂ O	$Al_{0.381}P_{0.477}Si_{0.142}$	$WHSV = 14.3 \text{ h}^{-1}$	
Ce	Impregnation (Optimal: 0.5 wt% CeO ₂ loading)	214.5	91.0	$\begin{array}{c} 1 \ Al_2O_3 \! / \ 1 \ P_2O_5 \! / \ 0.6 \\ SiO_2 \! / \ 2 \ TEAOH \! / \ 70 \ H_2O \\ \ / \ 0.012 \ CeO_2 \end{array}$	$\begin{array}{c} Al_{0.380} P_{0.480} Si_{0.137} \\ Ce_{0.002} \end{array}$	400 °C MeOH: 30 mol% Water: 70 mol%	[162]

Table S1 continued

Metal	Comment/ Synthesis technique	Methanol Processing ability ^a (g _{MeOH} /g _{cat})	Average light olefins selectivity (mol %)	Gel formula (molar) (Al ₂ O ₃ / P ₂ O ₅ / SiO ₂ / T/ H ₂ O/ Me)	Catalyst formula (mol%) Al _x P _x Si _x M _x	Reaction Conditions	Ref
_	Parent SAPO-34	N/A	82.0	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.2 SiO ₂ / 0.7 TEAOH/ 1.1 DEA/ 50 H ₂ O	$Al_{0.501} P_{0.425} Si_{0.074}$	$WHSV = 3.5 h^{-1}$ Reaction T:	
Ge	In-situ metal incorporation (Optimal: 0.1 mol GeO ₂ loading)	N/A	84.0	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.1 SiO ₂ / 0.7 TEAOH/ 1.1 DEA/ 50 H ₂ O/ 0.1 GeO ₂	$\begin{array}{c} Al_{0.503}P_{0.436}Si_{0.048}\\ Ge_{0.013} \end{array}$	450 °C MeOH: 27 mol% Water: 73 mol%	[163]
_	Parent SAPO-34	15.3	80.1	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.4 SiO ₂ / 2 TEAOH/ 70 H ₂ O	N/A	$WHSV = 4.0 h^{-1}$ Reaction T: 450 °C MeOH: 36 mol%	[164]
AgPW	In-situ metal incorporation	32.7	92.3	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.4 SiO ₂ / 2 TEAOH/ 70 H ₂ O / 0.010 AgPW	AgPW _{0.009}	Water: 64 mol%	
-	Parent SAPO-34	7.0	N/A	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.3 SiO ₂ / 1 TEAOH/ 50 H ₂ O	$Al_{0.503}P_{0.347}Si_{0.151}$	WHSV =	
Fe	In-situ metal incorporation	4.5	N/A	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.3 SiO ₂ / 2 TEAOH/ 50 H ₂ O/ 0.075 FeO	$\begin{array}{c} Al_{0.509}P_{0.351}Si_{0.137} \\ Fe_{0.002} \end{array}$	1.00 h^{-1} Reaction T: $425 ^{\circ}\text{C}$	
Co	In-situ metal incorporation	8.0	N/A	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.3 SiO ₂ / 2 TEAOH/ 50 H ₂ O/ 0.075 CoO	$\begin{array}{c} Al_{0.506}P_{0.329}Si_{0.162}\\ Co_{0.004} \end{array}$	MeOH: 15 mol%	[165]
Ni	In-situ metal incorporation	5.0	N/A	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.3 SiO ₂ / 2 TEAOH/ 50 H ₂ O/ 0.075 NiO	$\begin{array}{c}Al_{0.494}P_{0.361}Si_{0.143}\\Ni_{0.001}\end{array}$	85 mol%	
_	Hierarchical SAPO-34	16.7	82.3	1 Al ₂ O ₃ / 0.8 P ₂ O ₅ / 0.4 SiO ₂ / 2.0 TEAOH/ 50 H ₂ O	N/A		
	Physical mixing (Interpellet)	15.0	82.4	1 Al ₂ O ₃ / 0.8 P ₂ O ₅ / 0.4 SiO ₂ / 2.0 TEAOH/ 50 H ₂ O/ 0.11 ZnO	N/A	$WHSV = 10.0 \text{ h}^{-1}$ Reaction T:	
ZnO	Physical mixing (Intrapellet- AL i.e., not calcined mixture)	9.2	84.0	1 Al ₂ O ₃ / 0.8 P ₂ O ₅ / 0.4 SiO ₂ / 2.0 TEAOH/ 50 H ₂ O/ 0.11 ZnO	N/A	500 °C MeOH: 85 mol% Nitrogen:	[166]
	Physical mixing (Intrapellet-HY i.e., calcined mixture)	8.4	83.7	1 Al ₂ O ₃ / 0.8 P ₂ O ₅ / 0.4 SiO ₂ / 2.0 TEAOH/ 50 H ₂ O/ 0.11 ZnO	N/A	15 mol%	
_	Parent H-SAPO- 34-L (sample with relatively large crystals)	11.7	65.0	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.3 SiO ₂ / 2.0 TEAOH/ 52 H ₂ O	$Al_{0.52} P_{0.34} Si_{0.14}$	WHSV = 10.0 h ⁻¹ Reaction T:	
Ti	In-situ metal incorporation (Optimal: TiO ₂ loading in 0.006 relative molar ratio)	30.0	78.0	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.3 SiO ₂ / 2.0 TEAOH/ 52 H ₂ O/ 0.006 TiO ₂	$\begin{array}{c} Al_{0.56} P_{0.31} Si_{0.13} \\ Ti_{0.00034} \end{array}$	400 °C MeOH: 77 mol% Nitrogen: 23 mol%	[167]
_	Parent SAPO-34	5.5	77.0	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.6 SiO ₂ / 3 TEA/ 50 H ₂ O	$Al_{0.470}P_{0.351}Si_{0.178}$	$WHSV = 2.0 \text{ h}^{-1}$ Reaction T: 425 °C	
Zn	In-situ metal incorporation	8.5	80.0	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.6 SiO ₂ / 3 TEA/ 50 H ₂ O/ 0.04 Zn(NO ₃) ₂ · 6H ₂ O	$\begin{array}{c} Al_{0.448}P_{0.339}Si_{0.198}\\ Zn_{0.015} \end{array}$	MeOH: 50 mol% Water: 50 mol%	[172]

Table	S 1	continued
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Metal	Comment/ Synthesis technique	Methanol Processing ability* (g _{MeOH} /g _{cat})	Average light olefins selectivity** (mol %)	Gel formula (molar) (Al ₂ O ₃ / P ₂ O ₅ / SiO ₂ / T/ H ₂ O/ Me) ^a	$\begin{array}{c} Catalyst formula \\ (molar) \\ Al_a P_b Si_c M_d \end{array}$	Reaction Conditions	Ref
-	Parent SAPO-34	9.5	80.5	N/A	N/A		
G	Wet Impregnation	7.0	76.7	N/A	Co _{0.0176}		
Co	Template- assisted method	10.0	81.3	N/A	Co _{0.0024}	WHSV = 2.0 h ⁻¹ Reaction T:	
	Wet Impregnation	7.5	78.2	N/A	Ni _{0.0175}	400 °C MeOH:	[168]
N1	Template- assisted method	11.0	80.4	N/A	Ni _{0.0028}	35.7 mol% Nitrogen:	
7	Wet Impregnation	6.5	82.5	N/A	Zn _{0.0178}	04.5 1101/0	
Zn	Template- assisted method	9.5	77.5	N/A	Zn _{0.0050}		
Ni	In-situ metal incorporation	2.5	88.0	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.6 SiO ₂ / 1 DEA/ 70 H ₂ O/ 0.05 NiO	$ \begin{array}{c} Al_{0.470}P_{0.380}Si_{0.130} \\ Ni_{0.02}{}^{\gamma} \end{array} $	$WHSV = 0.4 \text{ h}^{-1}$	
Mn	In-situ metal incorporation	4.2	94.0	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.6 SiO ₂ / 1 DEA/ 70 H ₂ O/ 0.05 MnO	$\begin{array}{c} Al_{0.480}P_{0.390}Si_{0.120} \\ Mni_{0.01}^{\gamma} \end{array}$	Reaction T: 400 °C MeOH: 30 mol%	[169]
Mn & Ni	In-situ metal incorporation (bimetallic)	2.5	85.0	1 Al ₂ O ₃ / 1 P ₂ O ₅ / 0.6 SiO ₂ / 1 DEA/ 70 H ₂ O/ 0.05 NiO/ 0.05 MnO	$ \begin{array}{c} Al_{0.380}P_{0.420}Si_{0.170} \\ Ni_{0.02}Mni_{0.01}^{\gamma} \end{array} $	Water: 70 mol%	
_	Parent SAPO-34	8.3	60.0	N/A	$Al_{0.411}P_{0.485}Si_{0.105}$	$WHSV = 1.0 \text{ h}^{-1}$ Reaction T: 350 °C	
Со	In-situ metal incorporation, milling and recrystallization (Optimal: 0.003 mol in relative molar ratio)	11.8	65.0	N/A	$\begin{array}{c} Al_{0.472}P_{0.415}Si_{0.086}\\ Co_{0.027} \end{array}$	MeOH: 83.5 mol% Water: 16.5 mol%	[170]
_	Parent SAPO-34	12.3	79.0	1 Al ₂ O ₃ / 0.8 P ₂ O ₅ / 0.6 SiO ₂ / 2.5 MOR/ 80 H ₂ O	$Al_{0.43}P_{0.43}Si_{0.14}$	$WHSV = 2.0 \text{ h}^{-1}$	
t-ZrO ₂ (Tetrago	Physical blending method	28.4	82.0	N/A	Al _{0.41} P _{0.41} Si _{0.18}	Reaction T: 380 °C MeOH: 50 mo1%	[171]
nal- phase zirconia)	Hydro-thermal surface coating modification method	37.3	82.0	N/A	$Al_{0.42}P_{0.40}Si_{0.18}$	Water: 50 mol%	

Table S1 continued

^a Methanol processing ability = $WHSV (g_{MeOH} / (g_{cat}h)) \times (time taken to go to 90\% MeOH conversion) (h)$



Fig. S 1 SEM images of SAPO-34 samples prepared by different silica addition methods. Left: silica added separately. Right: silica added to the template.



Fig. S 2 SEM image of TEAOH-1 β catalyst and use of ImageJ software to analyze the particle size distribution.



Fig. S 3 particle size analysis of the prepared catalysts using ImageJ software.



Fig. S 4 NH₃-TPD for (a) single and (b) mixed template samples

Catalyst	Weight reduction due to	Weight reduction due to	Coke deposition
	moisture desorption (%wt)	coke combustion (%wt)	(%wt, coke/dry cat)
ΤΕΑΟΗ-1β	3.9	16.9	21.3
TEAOH-1	3.6	16.9	21.3
TEAOH-2	1.2	16.8	20.5
MOR-1	3.2	6.8	7.6
MOR-2	3.6	6.9	7.7
DEA-1	9.6	6.6	7.9
DEA-2	6.7	6.7	7.7
TEA-1	2.8	16.1	19.9
TEA-2	6.1	16.5	21.3
TEAOH/MOR-1	5.7	15.3	19.4
TEAOH/MOR-2	5.4	17.4	22.5
TEAOH/DEA-1	4.0	18.7	24.2
TEAOH/DEA-2	3.8	19.7	25.8
TEAOH/TEA-1	4.1	19.9	26.2
TEAOH/TEA-2	1.2	20.3	25.9

Table S 2 Coke deposition on different catalysts after complete deactivation using the TGA-TPO test

Note: These coke contents are until the time that the only methanol conversion product was DME.

Sample calculation for average coke selectivity:

- ✓ In term of TEAOH-1 sample, coke deposition is 18.7% coke/dry cat weight (until conversion drops to 90%)
- ✓ Catalyst lifetime is 10.9 h, average methanol conversion within catalyst lifetime is 99.50%
- ✓ Considering the aromatic nature of the coke, we assume the coke formula to be C_nH_n which means the carbon content of coke is 12/13
- ✓ WHSV of methanol is 1 $g_{MeOH} g_{Cat}^{-1} h^{-1}$ and carbon content of methanol is 12/32

Average coke selectivity =
$$\frac{\frac{18.7 \text{ g coke}}{100 \text{ g Cat}} \times \frac{12}{13}}{\frac{1 \text{ g MeOH}}{1 \text{ gCat} \times h} \times 10.9 \text{ h} \times 0.995 \text{ Ave Conv} \times \frac{12}{32}} = 4.24 \%$$

Sample name	S _{BET} ^a (m ² g ⁻¹)	S _{Micro} ^b (m ² g ⁻¹)	SMeso+Macro b (m ² g ⁻¹)	Single point BJH total pore volume ^d (cm ³ g _{cat} ⁻¹)	t-plot micropore volume (cm ³ g _{cat} ⁻¹)	BJH adsorption cumulative macro and mesopore volume ^e (cm ³ g _{cat} ⁻¹)
ΤΕΑΟΗ-1β	533	519	14	0.253	0.202	0.051
TEAOH-1	549	532	17	0.278	0.213	0.063
TEAOH-2	524	503	21	0.296	0.214	0.082
MOR-1	534	534	$\sim 0^{\text{ f}}$	0.248	0.248	0.001
MOR-2	561	561	$\sim 0^{\text{ f}}$	0.256	0.256	0.002
DEA-1	565	565	$\sim 0^{\text{ f}}$	0.258	0.258	0.002
DEA-2	511	511	~ 0 ^f	0.237	0.237	0.001
TEA-1	567	552	15	0.330	0.252	0.077
TEA-2	575	558	17	0.335	0.248	0.085
TEAOH/MOR-1	600	589	11	0.280	0.204	0.077
TEAOH/MOR-2	618	607	11	0.299	0.216	0.079
TEAOH/DEA-1	641	632	9	0.330	0.281	0.046
TEAOH/DEA-2	652	640	12	0.349	0.292	0.056
TEAOH/TEA-1	595	586	9	0.319	0.267	0.051
TEAOH/TEA-2	597	585	12	0.320	0.267	0.050
TEAOH/DEA-2 deactivated	19	8	11	0.056	0.003	0.055
TEAOH/TEA-1 deactivated	14	5	9	0.052	0.002	0.052

Table S 3 Surface area and pore volume analysis using BJH and t-plot models.

^a $S_{BET} = BET$ total specific surface area obtained from adsorption data in the p/p₀ range from 0.06–0.2; all reported data are within ±4 m²/g based on repeated analysis.

 b S_{Micro} = micropore; S_{Meso+Macro} = meso + macropore surface areas.

 d Single point adsorption total pore volume of pores less than 967.3 Å corresponding to $\,p/p_0\, of~0.990$

^e BJH cumulative adsorption volume of pores with radius between 10 and 967 Å

f negligible amount

Catalyst processing	Lifetime (min)**	Template	Bulk Si content XRF or ICP	Gel formula Al2O3/P2O5/SiO2/	Reaction Temp (°C)	WHSV (h ⁻¹)	Feed dilution	Ref
ability	()		mol%	T/H ₂ O	- F (-)		(mol%)	
$(\mathbf{g}_{MeOH} \mathbf{g}_{cat}^{-1})^*$			(Si/(Si+P+Al))	(molar)			. ,	
15.0	900	MOR-	16.9	1/1/0.6/1.5+0.5/52	450	1	He 92%	[290]
		TEAOH						
9.0	540	MOR-	17.5	1/1/0.6/1+1/52	450	1	He 92%	[290]
		TEAOH						
3.8	230	MOR	14.6	1/1/0.6/2/52	450	1	He 92%	[290]
6.0	360	TEAOH	10.6	1/1/0.6/2/53	425	1	N2 80%	[291]
10.0	600	DEA-	16.8	1/1/0.6/1+1/53	425	1	N2 80%	[291]
		TEAOH						
2.5	150	DEA	11	1/1/0.6/2/53	425	1	N2 80%	[291]
3.0	180	TEA	10.1	1/1/0.3/2/65	450	1	H ₂ O 60%	[292]
7.5	450	TEA-	8.9	1/1/0.3/1.8+0.2/65	450	1	H ₂ O 60%	[292]
		TEAOH						
5.0	300	TEA-	11.0	1/1/0.3/1.4+0.6/65	450	1	H ₂ O 60%	[292]
		TEAOH						
3.0	180	TEAOH	10.9	1/1/0.3/2/65	450	1	H ₂ O 60%	[292]
0.6	30	TEA	13.8	1/0.8/0.6/3/50	400	1.2	$N_2 50\%$	[293]
7.8	390	TEAOH	17.4	1/1/0.6/1/30	400	1.2	$N_2 50\%$	[293]
2.0	100	TEAOH-	13.0	1/1/0.6/1+0.6/40	400	1.2	N ₂ 50%	[293]
		MA ^a						
3.0	150	DPA ^b	13.0	1/1/0.6/2/20	400	1.2	$N_2 50\%$	[293]
1.8	90	DEA	16.7	1/0.8/0.6/2/50	400	1.2	$N_2 50\%$	[293]
12.0	160	MOR	14	1/1/0.6/4/70	450	4.5	H ₂ O 80%	[294]
10.0	600	TEA	11	1/1/0.2/6/100	425	1	0%	[174]
8.3	500	TEA	13	1/1/0.4/6/100	425	1	0%	[174]
6.7	400	TEA	15	1/1/0.6/6/100	425	1	0%	[174]
5.0	300	TEA	18	1/1/0.8/6/100	425	1	0%	[174]
11	660	TEAOH	8.8	1/1/0.3/2/70	425	1	Ar 70%-	This
							H ₂ O 10%	work
16.1	960	TEA	6.0	1/1/0.3/3/70	425	1	Ar 70%-	This
							H ₂ O 10%	work
17.3	1040	MOR-	6.7	1/1/0.3/1.875+0.62	425	1	Ar 70%-	This
		TEAOH	_	5/70			H ₂ O 10%	work
13.7	820	DEA-	8.5	1/1/0.3/1.5+0.5/70	425	1	Ar 70%-	This
		TEAOH					H ₂ O 10%	work
14.1	850	TEA-	7.9	1/1/0.3/2.25+0.75/	425	1	Ar 70%-	This
		TEAOH		70			H ₂ O 10%	work

Table S 4 Catalytic performance of the SAPO-34 catalysts: comparison of the literature and our study

* Catalyst processing ability = $WHSV (g_{MeOH} g_{cat}^{-1} h^{-1})) \times$ (time taken to go down to 90% MeOH conversion (h))

** Lifetime was computed as the span from the reaction beginning until conversion drops to 90%.



Fig. S 5 TGA-MS analysis. (a) coke formation measurement using TGA and (b) products distribution acquisition by MS over TEAOH-1 sample



Fig. S 6 TGA-MS analysis. live coke formation measurement using TGA and products distribution acquisition by MS over: (a) & (c) TEAOH/TEA-2; (b) & (d) MOR-1



Fig. S 7 SAPO-34 treatment by 0.5 molar DEA solution using magnetic bar stirrer for 24 h (the sample has crushed due to long treatment and mechanical mixing)



Fig. S 8 SAPO-34 treatment by 10 molar DEA solution using an orbital shaker for 5 h (high DEA concentration has corroded the sample and created plate-shape particles along with amorphous phase)



Fig. S 9 GC chromatograms over parent SAPO-34 at different times on stream (over the fresh catalyst, partially coked catalyst-half lifetime, and after deactivation)



Fig. S 10 Gibbs Free energy profile at 400 °C and 1 bar, for the catalytic formation of ethylene. Methanol pathway, depicted in orange, has protonated methanol (CH₃OH₂⁺) as an intermediate, whereas DME pathway has protonated DME (H⁺-DME). Reactants are depicted in blue and products in red. Reactants and products labelled in the diagram correspond to both pathways except when marked with *, which only correspond to reactants and products of the DME pathway, in green.

To assess the ability of BAS in catalyzing olefin formation, the possible reaction mechanisms of ethylene formation (the simplest olefin) were studied (Fig. S 10) at 400 °C and a pressure of 1 bar through two routes: (1) MeOH insertion and protonation ($CH_3OH_2^+$, orange pathway) and (2) MeOH insertion and methylation (H^+ -DME, green pathway). The Brønsted active site ZOH, corresponds to the zeolite framework (Z), that includes the Si-substituted site, followed by the neighboring oxygen, and added proton (OH). The active site then interacts with a methanol

molecule (MeOH) by proton transfer, leading to the formation of a nucleophile (ZO⁻) that interacts with $CH_3OH_2^+$ by donating an electron and cleaving the C-O bond, forming a methylated active site (ZOCH₃) and water. In a similar way, ZOCH₃ reacts with a second MeOH by either proton transfer (orange pathway) or methyl transfer (H⁺-DME formation, in green). In the former, a proton from the zeolite-bound methyl is transferred to MeOH, eventually producing ZOCH₂CH₃ and water, with a barrier of 3.6 eV, whereas in the latter, CH₃ is transferred over to MeOH and then a proton is transferred back to the active site. An additional MeOH molecule will be necessary to form ZOCH₂CH₃, however, the barrier is decreased to 2.7 eV. The final reaction involves a concerted reaction step, where a proton from CH₃ is transferred over to another neighboring zeolite-bound oxygen, while CH₂ detaches from the zeolite forming ethylene that returns to the gas phase. Overall, it can be inferred that the DME pathway due to the lower value of the most energy-demanding step is preferred over the MeOH formation pathway.

Methanol Processing ability (gmeOH gCat ⁻¹)*	Template	Bulk Si content % (Si/Si+P+Al)	Gel formula Al ₂ O ₃ /P ₂ O ₅ /SiO ₂ / T/H ₂ O molar	Reaction T (ºC)	WHSV (g _{MeOH} g _{Cat} ⁻¹ h ⁻¹)	Feed dilution (mol%)	Employed technique	Ref
5.0 P	TEAOH (seeds) - TEA	16 P	1/1.2/0.8/2/50	400	2	0	Nano sized catalyst using seed-assist	[295]
20.0 T	(secondary catalyst)	10 T	1/1/0/1.75/27.5			-	method	
4.7 P	DEA (initial)-	NA P	1/1/0.8/2/50	450	4		Using post- synthesis milling	[20/2]
20.0 T	(secondary)	8.8 T	1/1/0/1.75/27.5	450	4	H ₂ O 60%	and recrystallization method	[296]
NA		NA P	1/1/0 2/1/2	400	1	U-0.50%	Solvent-free hydrothermal synthesis,	[207]
15.0 T	ТЕАОН	7.6 T	1/1/0.5/1/5	400	1	1120 0070	porosity due to stacked nanocrystals	[277]
9.6 P 18 0 T	- TEAOH	13 P	1/1/0.6/6/110	400	1.2	0	Nano sized catalyst	[184]
<u>11 3 P</u>		17.9 P	0 5/1/0 3/2/70				Nano sized catalyst	
18.0 T	- TEAOH	19.1 T	1/1/0.6/2/70	450	4.5	H ₂ O 20%	using Ultrasonic mixing	[298]
4.0 P	- Morph	18 P	1/1/0.6/3/80	400	2.	0	Hierarchical SAPO-34 using	[299]
16.7 T	morph	16 T	1,1,0.0,5,00	100	-	Ŭ	Organosilane surfactant	[277]
8.0 P	- DFA	NA P	1/1/0 5/2 3/150	450	3	He 80%	Hierarchical SAPO-34 using	[300]
17.5 T	DLA	14.9 T	1/1/0.3/2.3/130	450	5	110 0070	Organosilane surfactant	[500]
2.2 P	Morph-	12 P			_		hierarchical SAPO-	
5.3 T	TEAOH	14 T	1/1/0.6/1.5+0.5/60	470	1	He 90%	34 using carbon nano tubes	[301]
4.7 P	_	16.9 P					Hierarchical SAPO-34 using	
3.3 T	Morpholine	16.1 T	1/1/0.8/2.1/57	400	2	N ₂ 70%	post-treatment with HF-NH ₄ F mixed aqueous solutions	[302]

Table S 5 Summary of the previous modification methods on SAPO-34 catalyst and their activity performa	nces
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* Methanol processing ability = $WHSV (g_{MeOH} g_{cat}^{-1} h^{-1})) \times$ (time taken to go down to 95% MeOH conversion (h))

* Until 95% methanol conversion , "P" stand for parent catalyst and "T" stands for treated or modified sample

Methanol		D -IL-C [*] ((Gel formula		WHOI?	E.J.		
Processing ability (g _{MeOH} g _{Cat} ⁻¹)*	Template	Sulk Si content % (Si/Si+P+Al)	Al ₂ O ₃ /P ₂ O ₅ /SiO ₂ / T/H ₂ O molar	Reaction T (°C)	WHSV (g _{MeOH} g _{Cat} ⁻¹ h ⁻¹)	Feed dilution (mol%)	Employed technique	Ref
8.3 P		9.9 P					Hierarchical SAPO-34	
8 2 T	- TEA	0.2 T	1/1.1/0.4/4.7/70	400	2	N2 70%	using post-treatment with HF-NH4F mixed	[302]
0.3 1		9.2 1					aqueous solutions	
25.0 P		10.1 P					Hierarchical SAPO-34	
16.7 T	TEAOH	5.9 T	- 1/2/1/4/138.8	450	4	N ₂ 50%	with HF-NH ₄ F mixed aqueous solutions	[302]
4.7 P		8.6 P	1/1/0 1/0 5/105	150	2	H O 5004	Introducing ordered	[202]
7.7 T	TEA	8.6 T	. 1/1/0.4/3.5/105	450	2	H ₂ O 50%	using NaHCO ₃	[303]
6.7 P	TEAOU	11 P	1/2/0 ////140	400	2	N. 700/	Nano sized catalyst	[204]
28.3 T	TEAUT	12 T	1/2/0.0/4/140	400	2	IN2 70%	using microwave	[304]
<u>10.8 P</u>	TEAOH	<u>13 P</u>	1/1/0.6/6/110	400	1.2	N ₂ 50%	Nano sized catalyst	[305]
15.6 T		5.7 T	1/1 2/0 6/2/40				using microwave	[]
6.0 P	TEAOH/	_ TEAOH/ 16 P seed	1/1.2/0.6/2/40 seed	400	2	NT A	Nano sized catalyst	[207]
21.7 T	TEA	10 T	1/1/0.4/4.7/70 outer layer	400	2	NA	using seeding	[306]
6.7 P 16.7 T	TEAOH	NA	1/1/0.5/2/65	400	4	N2 90%	Hierarchical SAPO-34 using Organosilane	[307]
6.0 P		21 P	1/1/0 //0 //0	400	1.0	N. 500/	Hierarchical SAPO-34 using	[200]
8.4 T	TEAOH	20 T	- 1/1/0.6/2/40	400	1.2	N ₂ 50%	hexadecyltrimethylam monium bromide (CTAB)	[308]
4.0 P	ТЕА	9 P	1/1/0 22/4/100	450	2	50% H ₂ O	Base-etching post	[200]
7.3 T	IEA	9 T	1/1/0.55/4/100	430	2	50% П2О	treatment	[309]
3.0 P	TEA	<u>9 P</u>	1/1/0.4/3/50	400	1	5% H ₂ O	Citric acid-etching	[310]
7.5 1		11.1					post treatment	
6.7 P	TEAOH	15.1 P	1/1/0.4/2/70	400	1	70% Ar	Alkali-etching post treatment	Thi stud
9.9 T		14.1 T						S S

Table S5 continued

* Methanol processing ability = $WHSV (g_{MeOH} g_{cat}^{-1} h^{-1})) \times$ (time taken to go down to 95% MeOH conversion (h))

* Until 95% methanol conversion, "P" stand for parent catalyst and "T" stands for treated or modified sample



Fig. S 11 X-ray Diffractions for the metal promoted samples along with parent SAPO-34 and the corresponding reference (SAPO-34 PDF # 00-047-0617).

Published contributions

Peer-reviewed journals

- M. Ghavipour, T.J. Goncalves, A. Hussami, R. Roy, J. Kopyscinski, Uncovering the role of Lewis and Brønsted acid sites in perforated SAPO-34 with an enhanced lifetime in methanol conversion to light olefins, New Journal of Chemistry. 47 (2023) 15907–15921.
- M. Ghavipour, R. A. Hussami, K. Levin, R. Roy, J. Kopyscinski, SAPO-34 catalyst: synthesis optimization by template alteration and in-situ coke evolution analysis in methanol conversion to light olefins, Industrial & Engineering Chemistry Research, 62, 44, (2023) 18362–18378.
- M. Ghavipour, J. Kopyscinski, Novel fabrication of high-content SAPO-34 mounted on γ-Al₂O₃ microspheres: a designated catalyst for fluidized-bed reactors of methanol conversion to light olefins, in preparation.
- M. Ghavipour, R. A. Hussami, J. Kopyscinski, *Can metal promotion of SAPO-34 genuinely improve its catalytic performance in methanol conversion to light olefins reaction?* in preparation.
- M. Ghavipour, R. A. Hussami, J. Kopyscinski, Sustainable light olefins production through methanol dehydration over SAPO-34: A review of the catalyst design, reaction mechanism and kinetics, in preparation.
- M. Shahryari, E. Pajootan, M. Ghavipour, J. Kopyscinski, *Non-Oxidative Methane Activation over Molybdenum and Tungsten Nitride Catalysts*. Chem Cat Chem, accepted.
- A. L. Moghaddam, M. Ghavipour, J. Kopyscinski, M. Hazlett, *Optimizing template and* crystallization time to synthesize super active KFI zeolite for stable dimethyl ether production as a low-emission energy carrier, in preparation.

Oral Presentations

- M. Ghavipour, J. Kopyscinski, *Elucidating the effect of the template on structure and activity of SAPO-34 catalyst in methanol conversion to light olefins*, the proceedings of the 26th Canadian Catalysis Symposium, Vancouver, May 2022.
- M. Ghavipour, J. Kopyscinski, *Hierarchical SAPO-34 could last longer in methanol conversion to light olefins by mitigating coke formation*, the proceedings of the 26th Canadian Catalysis Symposium, Vancouver, May 2022.
- M. Ghavipour, J. Kopyscinski, Novel fabrication of high-content SAPO-34 mounted on γ-Al₂O₃ microspheres: a designated catalyst for fluidized-bed reactors of methanol conversion to light olefins, the proceedings of 15th European congress on Catalysis, EuropaCAT2023, Czech Republic, Sep 2023.