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Aceppted manuscript Journal of Molecular Catalysis. A, Chemical MCAT 110606 https://doi.org/10.1016/j.mcat.2019.110606

Mechanistic insights of methane conversion to ethylene over gallium

oxide and gallium nitride using density functional theory

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Abstract

Density functional theory (DFT) was used to study the reaction mechanisms of direct nonoxidative methane (CH₄) coupling to ethylene (C₂H₄) on gallium–based catalysts, GaN ($1\overline{1}00$) and Ga₂O₃ (001) surfaces. The adsorption energies of the reactants, the potential intermediates, and the products were calculated on both surfaces. For each of the catalysts three mechanistic pathways have been proposed and discussed. Reaction energies and activation energy barriers for the reactions were calculated and compared. The dissociative adsorption of methane on both surfaces is exothermic. By comparing the activation barrier of the rate-limiting step on both surfaces, the results showed that the C–H bond cleavage of the CH₃* species have the highest activation barrier for both catalysts. The results also illustrate that mechanism I is the most feasible pathway among the GaN ($1\overline{1}00$) and Ga₂O₃ (001) surfaces for the ethylene formation. In the case of Ga₂O₃ (001) H₂O, CO, and CO₂ are formed as products creating an oxygen vacancy on the Ga₂O₃ (001) surface.

Keywords: DFT modeling; Gallium nitride catalyst; Gallium oxide catalyst; Non–oxidative methane dehydrogenation; Methane coupling to ethylene

1 Introduction

Methane is regarded as one of the cleanest fossil fuels. It is also used as a feedstock for the production of distillate fuels and chemicals. Methane (CH₄) is a light hydrocarbon and the main constituent of natural gas and shale gas. One of the grand challenges in catalysis is the conversion of methane into valuable chemicals such as olefins (ethylene), paraffins and aromatics (e.g., benzene) [1,2]. The direct non-oxidative conversion of methane to aromatics and olefins is found to be an atom-efficient route [3]. However, due to thermodynamic and kinetic constraints, this route is very challenging. The C–H bond in methane is very stable, and the activation requires high temperature (973–1373 K) and an efficient catalyst [4]. The activation of the C–H bond in methane is often found as the rate-determining step [5–9].

Guo et al. developed a single iron-site embedded in silica catalyst that produced ethylene, benzene, and naphthalene with peak selectivities of 48%, 28%, and 24%, respectively, at a methane conversion of 8% with apparently no coke formation [10]. They suggested that the lattice-confined iron site enable the CH₄ activation and form a methyl radical (*CH₃), which combines in the gas phase to C_2H_6 and then dehydrogenates to C_2H_4 . However, a temperature of ~2000 K is needed to synthesize the catalyst in the first place. Gerceker et a. showed that Pt-Sn zeolites were active towards methane coupling to ethylene with high selectivity (up to 90%, coke not included) but with low CH₄ conversion (<0.3%) and significant coking [11].

Gallium oxide has recently been shown to be a versatile catalyst for a wide range of reactions including propane dehydrogenation [12], nitrous oxide reduction [13], ethane dehydrogenation [14] and most recently C–H activation and methane non-oxidative aromatization [15]. Amongst the different polymorphs of gallium oxide (Ga₂O₃), only the monoclinic β –phase is stable at high

temperatures up to its melting point [16]. A few experimental studies have indicated that for the dehydrogenation of alkanes, the Ga₂O₃ based catalysts are highly active and selective [17–19].

Li et al. and Dutta et al. have shown the catalytic activity of commercially available gallium nitride (GaN) towards non-oxidative methane aromatization under batch and flow conditions, respectively [20–22].

Li et al. suggested that the first C–H bond activation occurs on the *m*–plane of GaN catalyst via the alkyl mechanism [20]. However, the detailed reaction mechanism from CH₄ to C₂H₄ and further to C₆H₆ on the GaN and Ga₂O₃ surfaces including surface intermediates are still unknown. Gallium–nitrogen and gallium–oxygen atom pairs are Lewis acid-base pairs that enable the dissociation of methane into an alkyl (CH₃) species and hydrogen (H) species following the alkyl pathway [20,23–25]. An alternative mechanism of methane activation known as the "carbenium" mechanism implies the hydride abstraction by gallium to form an alkyl (CH₃) species adsorbed on oxygen [23]. Computational modeling by Mayernick et al. indicated that methane activation on CeO₂(111), Pd_xCE_{1-x}O₂(111) and PdO(111) surfaces is limited by C–H bond activation [26]. Trinchero et al. found the same with Pd(111), Pd(100), Pd(211), Pd(321), Pt(111), Pt(100), Pt(211) and Pt(321) [27].

In the present study, DFT calculations are used to evaluate the GaN ($1\overline{1}00$) and Ga₂O₃ (001) surface for the non-oxidative CH₄ dehydrogenation and subsequent coupling to C₂H₄.

2 Experimental

 Ga_2O_3 and GaN catalysts were prepared following the evaporation induced self-assembly (EISA) technique. Briefly, Pluronic P-123 (Sigma Aldrich) was dissolved in anhydrous ethanol mixed with nitric acid and then added to a solution containing DI-water, ethanol, and gallium (III) nitrate

hydrate powder (99.9998 wt%, Thermo Fisher Scientific). After stirring for 5 h at 600 rpm, the sample was dried at 333 K for 48 h and then calcined at 923 K for 6 h to convert the galliumprecursor to Ga_2O_3 . The produced Ga_2O_3 powder was subsequently nitridated at 1023 K for 24 h with anhydrous ammonia to form GaN. Methane activation experiments over Ga_2O_3 and GaN were conducted in a packed-bed reactor at 973 K and 1 bar_{abs} with a CH₄-based gas hourly space velocity of 567 h⁻¹. Product gas was analyzed via a calibrated quadrupole mass spectrometer (Pfeiffer Omnistar GSD 301).

3 Computational methods and modeling

PWSCF codes that are contained in Quantum ESPRESSO package [28,29] were used for all types of calculations. Generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [30] was used to perform calculations along with ultrasoft pseudopotentials [31] for nuclei and core electrons.

The GaN $(1\bar{1}00)$ surface is represented by a four layers slab with a 2 x 3 cell and a vacuum of 10 Å was kept on sides of the slab. The bottom two layers were fixed in their bulk position, while the top two layers and the adsorbates could relax during geometry optimization. Adsorption was allowed only on one of the two exposed surfaces of gallium nitride. Saturation of the dangling bonds that connects the cut-out part of catalyst to the cluster with hydrogen atoms oriented towards the original occupied positions in the crystal was done. The kinetic energy cutoff value was kept at 30 Ry, and the charge density cutoff was kept 9 times to 270 Ry. Plane wave basis set was used with Kohn Sham orbital equations, and the spin polarization was considered. Fermi surface was treated with Methfessel and Paxon smearing width of 0.02 Ry [32]. The Brillouin zone for a unit cell was determined to be 16 x 16 x 16 and for the system was kept at 7 x 5 x 1. The electronic

configuration for the valence states are considered as: Ga: [Ar] $3d^{10}4s^24p^1$, N: [He] $2s^22p^3$. The cartesian force acting on each atom was kept at 10^{-3} Ry/Bohr and the convergence of total energy was kept at 10^{-5} Ry. The Quantum ESPRESSO GUI BURAI package [33] was used throughout for the calculations, and the visualization of chemical structures was done in XCrysDen graphics package [34,35].

For Ga₂O₃ (001), a 1 x 3 supercell was used with four layers with the bottom two layers fixed, and a 10 Å vacuum was set to avoid the interaction between the slabs. The Brillouin Zone integration for the k–mesh was determined to be 2 x 8 x 4 for the unit cell and 2 x 3 x 1 for the system. The electronic configuration for the valence states are considered as: Ga: [Ar] $3d^{10}4s^24p^1$, O: [He]2s²2p⁴. The kinetic energy cutoff was kept at 40 Ry, and spin polarization was considered. Other parameters were kept similar to that of gallium nitride. The distortion of oxygen atoms in gallium oxide [36] was eliminated by surface passivation with pseudo hydrogen atoms. To calculate the activation energy climbing-image nudged elastic band (CI-NEB) method [37,38] was used, which determines the minimum energy path (MEP) for all the elementary steps from CH₄ c to C₂H₄. The CI-NEB method determines the transition state as the image with the highest activation barrier. Transition state images were optimized using the quasi-Newton method, which determines the forces to find the saddle point.

Adsorption energies of the adsorbates were calculated based on the following equation:

$$E_{ad}(X) = E(slab - X) - [E(slab) + E(X)]$$
(E1)

Where $E_{ad}(X)$ is the adsorption energy of species X on 'slab'. E(slab–X) is the combined total energy of species X being adsorbed on the slab, E(Slab) and E(X) are the individual energies of slab and species X.

The dissociation energy of a compound was calculated using the following equation

$$E_{dis}(A-B) = \left[(E(slab - AB) - \left[(E(slab - A - B)) \right]$$
(E2)

Where $E_{dis}(A - B)$ is the dissociation energy between *A* and *B* adsorbed on the slab. E(slab - AB) is the total energy of species *AB* adsorbed on slab and E(slab - A - B) is the total energy of *A* and *B* adsorbed separately on the slab.

4 Results and discussion

4.1 Experiments

The total surface area of Ga₂O₃ and GaN catalyst were 19 and $12 \pm 4 \text{ m}^2 \text{ g}^{-1}$, respectively. Both catalysts had a bimodal pore size distribution with 8 and 32 nm for Ga₂O₃ and 9 and 23 nm for GaN. During the nitridation, the monoclinic β -Ga₂O₃ structure was converted to the wurtzite structure of GaN, with a reduction in surface area and pore size.

Both catalysts exhibited a similar CH₄ conversion behavior, with a maximum conversion of 5% at the beginning and rather fast decline to about 0.5% and 0.3% after 4 h on stream for Ga₂O₃ and GaN, respectively (Fig. 1A). Mass spectra analysis revealed that besides the formation of the desired products hydrogen (H₂) and ethylene (C₂H₄) small amounts of benzene (C₆H₆) was formed, see Fig. 1B–D. The turnover frequency of C₆H₆ was by a factor of 100 smaller. Furthermore, propylene and naphthalene were detected, which were ~1000 times smaller than ethylene (not shown). Over the Ga₂O₃ catalyst, undesired H₂O and CO₂ were produced within the first 20 min, which did not occur over GaN materials (Fig. 1E and F). Since, there was no other oxygen source in the inlet gas stream, the formation of H₂O and CO₂ can be explained by the reaction of CH₄ with the lattice oxygen of the Ga₂O₃ catalyst at the onset of the reaction (i.e., reduction of gallium oxide). Thus, the formation of H_2 , C_2H_4 and C_6H_6 was shifted towards a later time, with a maximum rate between 1–2 h. For GaN, the maximum rate of formation occurred within the first hour.



Fig. 1. (A) Methane conversion, turnover frequency of (B) hydrogen, (C) ethylene, (D) benzene, (E) water and (F) carbon dioxide as a function of reaction time during methane activation at 973 K and 1 bar_{abs}. GaN (orange symbols) and Ga₂O₃ (grey symbols).

The gas-phase selectivity for C_2H_4 was >98% for GaN over the whole reaction time, whereas for Ga_2O_3 selectivity values over 98% were only determined after the first hour.

Since H_2O and CO_2 were formed over the Ga_2O_3 catalyst, they were also included in the subsequent DFT modeling. Whereas for GaN, only the formation of C_2H_4 from CH_4 was considered.

4.2 Surface model

According to a previous study, the *m*-plane of gallium nitride was responsible for the methane adsorption [20]. Therefore, we modeled the $1\overline{1}00$ face of gallium nitride that consists of Ga and N atoms in equal numbers tetrahedrally coordinated amongst them as depicted in Fig. 2A and B. The *c*-plane of gallium nitride is a polar surface, which consists of either gallium or nitrogen atoms

representing piezoelectric polarization along the c-axis. The $1\overline{1}00$ lattice constants of GaN were calculated with a = 3.19 Å and b = 5.29 Å, which were consistent with experimental (a = 3.18 Å and b = 5.2 Å)[21] and theoretical values (a = 3.21 Å and b = 5.21 Å)[39].



Fig. 2. (A) Side and (B) top view of GaN (1100) surface, and (C) side and (D) top view of Ga₂O₃ (001) surface. Ga, N and O atoms are represented by blue, orange and red balls, respectively.

For Ga₂O₃, it has been observed that the 001 surface had higher catalytic activity than other faces [36]. Three in equivalent O sites (O(I), O(II) and O(III)) and two inequivalent Ga sites (Ga(I) and Ga(II)) exists as illustrated in Fig. 2C. The optimized lattice parameters of gallium oxide were a = 12.45 Å, b = 3.08 Å and c = 5.87 Å, which were in good agreement with the experimental (a = 12.22 Å, b = 3.04 Å, c = 5.8 Å)[40] and theoretical values (a = 12.23 Å, b = 3.04 Å, c = 5.8 Å)[41].

4.3 Adsorption energies and adsorbate structures during CH₄ conversion to C₂H₄ over GaN (1100) and Ga₂O₃ (001)

It is vital to characterize the adsorption of related species to understand the elementary steps in the ethylene formation. In this section, the adsorption of all possible species involved in the reaction are considered over different adsorption sites on the GaN ($1\overline{1}00$) and Ga₂O₃ (001).

4.3.1 GaN $(1\overline{1}00)$

For GaN ($1\overline{1}00$); seven stable surface intermediates are determined as illustrated in Fig. 3. The corresponding adsorption energies, as well as bond-distances, are summarized in Table 1.



Fig. 3. Side (top) and top views (bottom) of optimized structures of potential intermediates on the GaN (1100) surface. Ga, N, C and H atoms are represented by blue, orange, black and white balls. * denote an adsorbed species.

Species	Sites	Binding bonds	Bond distance (Å)	E_{ads} (eV)
$CH_{3}^{*} + H^{*}$	Ga-top/N-top	Ga1-C/N1-H	1.98/1.02	-7.45
CH_2*	hollow	N2-C/Ga1-C	1.52/2.18	-4.11
CH ₂ *	bridge	Ga ₁ -C/N ₁ -C	1.98/1.44	-4.60
$CH_2{}^*+CH_3{}^*+H{}^*$	bridge/Ga-top/N- top	$Ga_2 - C/N_2 - C/Ga_1 - C/N_1 - H$	1.98/1.49/1.98/1.01	-12.04
$2CH_2*$	bridge/hollow	$Ga_2 - C/N_2 - C/N_2 - C/Ga_1 - C$	1.98/1.49/1.51/2.03	-9.58
$2CH_2*$	hollow	N_4 -C/Ga_3-C/N_2-C/Ga_1-C	1.52/2.15/1.51/2.16	-8.18
2CH ₂ *	bridge	$Ga_3 - C/N_3 - C/Ga_1 - C/N_1 - C$	1.96/1.46/1.97/1.46	-9.18

Table 1. Stable adsorption sites, bond distances and adsorption energies of reactants, potential intermediates and products for methane to ethylene conversion on GaN ($1\overline{1}00$) surface.

CH₄*: CH₄ is a highly stable molecule and is weakly adsorbed on the Ga–top site of gallium nitride with the Ga–C distance of 3.014 Å. Li et al. found the Ga–C bond distance as 3.015 Å, which is very close to our value [20]. Due to the weak interaction of the CH₄ molecule with the gallium nitride surface, CH₄ closely keeps its gas phase structure with a C–H bond length of 1.09 Å and an HCH bond angle of 109.5°.

CH₃* + **H*:** As shown in Fig. 3A, CH₃* and H* are dissociated from CH₄ and adsorb on the Gatop and N-top sites, respectively. The adsorption energy of the adsorbed species is -7.45 eV (Table 1). The calculated Ga–C and N–H bond distances are 1.98 and 1.02 Å, respectively. The bond angle of HCH (Θ_{HCH}) of the CH₃ species adsorbed on Ga-top is 109.35°.

CH₂*: Two different adsorption configurations for CH_2 * species adsorption are possible (Fig. 3B and C). In the first configuration, the CH_2 * species adsorbs on the hollow site by forming a CH_2 * intermediate bridge between Ga and N atoms (Fig. 3B). The Ga–C and N–C calculated bond lengths are 2.18 and 1.52 Å with an adsorption energy of –4.11 eV.

The second configuration includes CH_2^* species adsorbed on the Ga and N bond bridge (Fig. 3C). The bond distances of Ga–C and N–C, in this case, are 1.98 and 1.44 Å, respectively, with a calculated adsorption energy of –4.6 eV, which is slightly higher compared to the first configuration. Previous studies of CH_2^* species adsorption on Ni(100) and Ni(211) determined adsorption energy of –4.32 and –4.12 eV, respectively [42]. This indicates that the CH_2^* species is more strongly adsorbed on the surface and the shorter bond lengths justifies that the adsorbate species held closely to the surface compared to the prior.

 $CH_{2}^{*} + CH_{3}^{*} + H^{*}$: The adsorption of CH_{2}^{*} , CH_{3}^{*} and H^{*} species at one time is an elementary step in ethylene formation. The CH_{2}^{*} species forms a bond bridge between gallium and nitrogen, while the CH_{3}^{*} species adsorbs on Ga–top site and H^{*} on N–top site as shown in Fig. 3D. The calculated adsorption energy for these intermediates is –12.04 eV and the corresponding bond lengths of Ga–C and N–C for CH_{2}^{*} species are 1.98 and 1.49 Å, and that for Ga–C and N–H for CH_{3}^{*} and H^{*} species are 1.98 and 1.01 Å.

2CH₂*: Three adsorption configurations of two CH₂* species co–adsorbed at one time can be obtained. These configurations are distinguished by the orientation of the CH₂* species on different sites. The first configuration consists of one of the CH₂* species forming a bond bridge between Ga and N atoms and the other CH₂* species forming a hollow bridge (Fig. 3E). The second configuration includes the two CH₂* intermediates co-adsorbed on the adjacent gallium and nitrogen hollow site forming a hollow bridge as shown in Fig. 3F. The third configuration includes the two CH₂* intermediates co-adsorbed on the adjacent bridge site forming a bond bridge (Fig. 3G). The calculated adsorption energies of these configurations are -9.58, -8.18 and -9.18 eV, respectively (Table 1).

4.3.2 Ga₂O₃(001)

For Ga_2O_3 (001) thirteen stable surface intermediates are determined as illustrated in Fig. 4. The corresponding adsorption energies, as well as bond-distances, are summarized in Table 2.



Fig. 4. Side (top) and top views (bottom) of optimized structures of potential intermediates on the Ga₂O₃ (001) surface. Ga, O, C and H atoms are represented by blue, red, black and white balls.

Species	Sites	Binding bonds	Bond distance (Å)	E_{ads} (eV)
$CH_{3}* + H*$	Ga-top/O-top	Ga ₂ -C/O ₁ -H	1.97/0.97	-8.20
CH_2*	O-top	O ₄ –C	1.29	-5.36
CH_2*	bridge	Ga ₂ -C/O ₂ -C	1.98/1.44	-4.91
CH_2*	hollow	Ga_2-C/O_1-C	2.15/1.42	-6.30
$CH_2*\!+\!H*\!+\!H*$	O-top/O-top/ O-top	$O_4 - C/O_1 - H/O_5 - H$	1.32/0.97/0.97	-12.54
$2CH_2*$	O-top/O-top	O7-C/O4-C	1.34/1.35	-10.50
$2CH_2*$	bridge/bridge	$O_6 - C/Ga_3 - C/O_2 - C/Ga_2 - C$	1.41/1.99/1.43/1.99	-9.66
$2CH_2*$	hollow/hollow	$Ga_3 - C/O_5 - C/Ga_2 - C/O_1 - C$	2.14/1.46/2.17/1.44	-11.82
CH*+H*	3-fold hollow/O-top	$O_2 - C/Ga_1 - C/Ga_2 - C/O_4 - H$	1.52/1.94/1.96/0.97	-17.75
CH*+H*	hollow/O-top	$Ga_2 - C/O_1 - C/O_5 - C/O - H$	2.11/1.46/1.47/0.97	-18.88
CH*+H*	bridge/O-top	$Ga_2 - C/O_1 - C/O_5 - H$	2.11/1.39/0.97	-19.18
C*	3-fold hollow	O ₂ -C/Ga ₁ -C/Ga ₂ -C	1.2/2.13/2.14	-13.72
C*	hollow	Ga1-C/Ga2-C/O1-C	2.15/2.15/1.25	-15.54

Table 2. Stable adsorption sites, key geometric parameters (Å) and adsorption energies of reactants,potential intermediates and products for methane to ethylene conversion on Ga_2O_3 (001) surface.

CH_{4*}: CH₄ being a very stable compound adsorbs weakly at a distance of 2.81 Å from the Ga atom without forming a chemical bond. At this distance, the C–H bond length is 1.09 Å with a bond angle of 109.5° for HCH, which is the same as in the CH₄ gas-phase molecule. The stretching of the C–H bond occurs when CH₄* is at 2.19 Å from Ga atom.

CH₃* + **H*:** CH₃* and H* species prefer to adsorb on the Ga-top and O-top site with Ga–C and O–H bond distances of 1.97 and 0.97 Å, respectively (Fig. 4A). The adsorption energy of -2.43 eV was calculated for the CH₃* species on the Ga-top site, which is similar to -2.4 eV of CH₃* on Pt(111) [43]. The adsorption energy of the co-adsorbed CH₃* and H* species is -8.2 eV, which is 0.75 eV higher than that on the GaN (1100) surface, indicating a stronger adsorption of the CH₃* and H* species on the Ga₂O₃ surface.

CH₂*: Three stable adsorption configuration for the CH₂* species were determined (Fig. 4B–D). The configurations are distinguished by different adsorption sites. CH₂* species adsorbs on the O-top site at bond length of 1.29 Å and adsorption energy of -5.36 eV (Fig. 4B). The second configuration involves a CH₂* species adsorbed on the Ga-O bridge site with O atom deformed from the surface (Fig. 4C). The calculated adsorption energy for this configuration involves a CH₂* species adsorbed on 1.29 Å and 1.44 Å. The last configuration involves a CH₂* species adsorbed on the Ga–C and O–C bond lengths of 1.98 and 1.44 Å. The last configuration involves a CH₂* species adsorbed on the Ga–O hollow site (Fig. 4D) with an adsorption energy of -6.3 eV, and Ga–C and O–C bond distances of 2.15 and 1.42 Å, respectively. Comparatively, the adsorbed CH₂* species at Ga–O hollow site has a stronger adsorption on the Ga₂O₃ (001) surface.

CH₂* + H* + H*: The CH₃* intermediate can dissociate into CH₂* and H* (Fig. 4E). The calculated adsorption energy for CH₂*, H* and H* species co-adsorbed on the Ga₂O₃ surface is – 12.54 eV with corresponding C–O, O₁–H and O₅–H bond lengths of 13.2, 0.97 and 0.97 Å.

2CH₂*: Three stable configurations can be obtained for two CH₂* species adsorbed on adjacent sites. These configurations are distinguished by the orientation of the CH₂* species on the Ga₂O₃(001) surface. The first stable configuration involves that two CH₂* species are adsorbed on O-top adjacent sites with C–O distances of 1.34 and 1.35 Å (Fig 4F). Compared to lone CH₂* species adsorbed at O-top site, the two CH₂* species co–adsorbed are slightly inclined towards the Ga atom. The calculated adsorption energy for this configuration is –10.51 eV. The second configuration involves the two CH₂* species adsorbed on an adjacent Ga-O bridge site with an adsorption energy of –9.66 eV (Fig. 4G). In the third configuration the two CH₂* species are adsorbed at adjacent Ga–O hollow sites with an adsorption energy of –11.82 eV (Fig. 4H).

CH*+H*: Three adsorption configuration for CH* species are observed and shown in Fig. 4I–K. The H* species are adsorbed on the O-top site in all three cases with an O–H bond distance of 0.97 Å. The CH* species adsorbs strongly on the 3-fold hollow site with carbon forming bonds (Ga₁– C = 1.94 Å and Ga₂–C = 1.96 Å) and an O–C bond with a distance of 1.52 Å. Another configuration involves a CH* species adsorbed on the Ga–O hollow site forming a bond with gallium at 2.11 Å and with two oxygen atoms at 1.46 and 1.47 Å (Fig. 4J). The last configuration is similar to the prior except the CH* species adsorbed on the Ga–O hollow site forms a bond only with one oxygen atom with a distance of 1.39 Å (Fig. 4K). The last configuration has the strongest adsorption with an energy of –19.18 eV, compared to –18.88 and –17.75 eV for the second and first configuration. The adsorption energy of CH* species alone is –12.04, –14.23, and –14.59 eV in the three configurations and that of H* species is –5.46 eV.

C*: Although C* species is observed on the catalyst surface, it can be termed as a bystander because of its high adsorption energy and it will unlikely be an unreactive intermediate. Two stable adsorption configurations for C* species, on the 3–fold hollow site and Ga–O hollow site are

observed (Fig.4 L and M) with adsorption energies of -13.72 and -15.54 eV, respectively. The bonds between gallium atoms and an oxygen atom are broken when the C* species are adsorbed on the 3-fold hollow site. For the first configuration, the bond distances between the two G–C bonds are 2.13 and 2.14 Å, and that for O–C is 1.2 Å at this configuration. For the second configuration, the C* species is adsorbed on the Ga–O hollow site with Ga–C bond distances of 2.15 Å and O–C of 1.25 Å.

4.4 Elementary steps over GaN

To explore the feasible reaction mechanisms for the dehydrogenation of methane with subsequent coupling to ethylene $(2 \text{ CH}_4 \rightarrow \text{C}_2\text{H}_4 + 2 \text{ H}_2)$ on GaN (1100) and Ga₂O₃ (001) surfaces, the activation barriers and reaction energies for all substantial elementary steps are calculated using the climbing–image nudged elastic band (CI–NEB) method. Table 3 summarizes the activation and reaction energies for all elementary steps on the GaN (1100) surface. Three different mechanisms for the formation of ethylene have been assumed and assessed. Figs. 5 to 7 depict the structures of the initial state (IS), transition state (TS), and final state (FS) for each elementary steps and mechanisms.

step	Elementary step	Activation barrier (E_a)	Reaction Energy (ΔE)
		eV	eV
R0	$CH_4(g) \rightarrow CH_4*$	_	-0.04
R1	$CH_4{}^* \rightarrow CH_3{}^* + H{}^*$	1.06	-1.02
R2-I	$CH_3{}^{\boldsymbol{*}} + H{}^{\boldsymbol{*}} \rightarrow CH_2{}^{\boldsymbol{*}} + H_2(g)$	4.68	3.92
R3-I	$2CH_2^* \rightarrow C_2H_4(g)$	4.51	-3.98
R2-II	$CH_3{}^{\boldsymbol{*}} + H{}^{\boldsymbol{*}} \rightarrow CH_2{}^{\boldsymbol{*}} + H_2(g)$	4.68	3.92
R3-II	$CH_4(g)+CH_2{}^{\boldsymbol{*}}\rightarrow CH_3{}^{\boldsymbol{*}}+CH_2{}^{\boldsymbol{*}}+H{}^{\boldsymbol{*}}$	1.50	-4.57
R4-II	$CH_3*+CH_2*+H* \rightarrow 2CH_2*+H_2(g)$	5.03	3.73
R5-II	$2CH_2^* \rightarrow C_2H_4(g)$	1.68	-1.74
R2-III	$CH_3{}^{\boldsymbol{*}} + H^{\boldsymbol{*}} \rightarrow CH_2{}^{\boldsymbol{*}} + H_2(g)$	5.40	3.97
R3-III	$2CH_2^* \rightarrow C_2H_4(g)$	9.39	-2.80

Table 3. Calculated activation barriers (E_a), and reaction energy (ΔE) of the elementary steps of the methane to ethylene conversion on GaN (1100).

4.4.1 Dissociative methane adsorption $CH_4(g) \rightarrow CH_3^* + H^*$

Initial state (IS), transition state (TS), and final state (FS) for the dissociative methane adsorption on GaN are depicted in Figs. 5 and S1 (supplementary information). A dissociation of CH₄ occurs, and the separated species CH₃* and H* are adsorbed on the Ga-top and N-top sites as per the alkyl mechanism [18, 25]. The gallium and nitrogen atoms of GaN represent a Lewis acid-base pair, which is able to cleave the C–H bond of methane [23]. The adsorption of CH₄ on Ga-top site (Fig. S1) is followed by the H in CH₄* being attracted towards the nitrogen atom and the C–H bond being stretched in adsorbed methane. The stretching of the C–H bond in methane is carried out once the methane and gallium distance reduces from 3.014 Å to 2.08 Å. The reaction R1 is exothermic with an energy of -1.02 eV. The activation energy barrier for R1 is 1.06 eV, which is ~0.9 eV lower than the activation energy barrier of methane dissociative adsorption on Pt(111)[43].



Fig. 5. Side (top) and top view (bottom) of the initial state (IS), transition state (TS) and final state (FS) involved in the dissociative methane adsorption on GaN (1100) surface.

4.4.2 Mechanism I

The formation of C_2H_4 in mechanism I is assumed to proceed via two CH_2^* species adsorbed on adjacent Ga–N hollow sites as depicted in Figs. 6 and S2–S3. The results are described below and summarized in Table 3 (R2-I and R3-I).



Fig. 6. Side (top) and top view (bottom) of the initial state (IS), transition state (TS) and final state (FS) involved in mechanism I on GaN (1100) surface.

R2-I: $CH_{3}^{*} + H^{*} \rightarrow CH_{2}^{*} + H_{2}(g)$

The H atom present in the CH_3^* species is attracted towards nitrogen atom on which an H* species is adsorbed. This induces the stretching of C–H bond in CH_3^* species and N–H bond of H* species adsorbed at N–top site as seen in R2-I of Figs. 6 and S2. The activation barrier is 4.68 eV, and the reaction energy is 3.92 eV. The final state of this elementary step is a CH_2^* species adsorbed on the Ga–N hollow site forming a bridge and H_2 molecule in the gas phase.

R3-I: 2CH₂* \rightarrow C₂H₄ (g)

Similar to the formation of a CH₂* species on the Ga–N hollow site, we considered another species of CH₂* being adsorbed on the adjacent Ga–N hollow site as shown in Figs. 6 and S3. The two CH₂* species turn towards each other to form C₂H₄ with an activation barrier of 4.51 eV. This step is a highly exothermic reaction (-3.98 eV). The desorption energy of C₂H₄ from GaN is -0.03 eV.

4.4.3 Mechanism II

In mechanism II, the formation of CH_2^* species on Ga–N hollow sites is assumed to be the same as in mechanism I, with the same energies as listed in Table 3 (R2 for mechanisms I and II). After the formation of CH_2^* in mechanism II, a second CH_4 molecule could adsorb on the same gallium atom. The top and side views of the IS, TS, and FS for each step of mechanism II are shown in Fig. 7, whereas all intermediate steps are shown in Figs. S4-S6. The calculated energies are summarized in Table 3 (R3-II, R4-II, and R5-II).



Fig. 7. Side (top) and top view (bottom) of the initial state (IS), transition state (TS) and final state (FS) involved in mechanism II on GaN (1100) surface

R3-II: CH₄ (g) + CH₂* \rightarrow CH₃* + CH₂* + H*

The formation of CH_2^* species on the Ga–N hollow bridge is shown in R2-I. Dissociative adsorption of a second CH_4 molecule results in the formation of CH_3^* and H^* species on Ga-top and N–top sites as shown in Figs. 7 and S4. The dissociative adsorption of methane molecule allows the CH_2^* species to spill over from the Ga–N hollow to a stable Ga–N bridge site, with a transition state of CH_2^* adsorbed on the nitrogen. This step has two activation barriers with a total of 1.5 eV for the stretching and breaking of the methane C–H bond over the Ga-top site. The reaction is highly exothermic with an energy of -4.57 eV.

R4-II: $CH_3^* + CH_2^* + H^* \rightarrow 2CH_2^* + H_2$ (g)

R4-II leads to the formation of two co-adsorbed CH_2^* species, one on gallium and nitrogen bond site, and the other over a Ga–N hollow site sharing the same gallium (Figs. 7 and S6). The stretching and breaking of the C–H bond in the CH_3^* species adsorbed on the Ga-top site and N– H bond leads to the formation of an H₂ molecule and CH_2^* species being adsorbed on the Ga–N hollow site. Our calculations estimate an activation barrier of 5.03 eV and a reaction energy of 3.73 eV.

R5-II: $2CH_2^* \rightarrow C_2H_4$

In the final step, the two co-adsorbed CH_2^* species form C_2H_4 with an activation barrier of 1.68 eV and a reaction energy of -1.74 eV. The activation barrier is much smaller than the value determined for mechanism I (1.68 vs. 4.51 eV, Table 3). The desorption energy of C_2H_4 from gallium nitride is calculated to be -0.11 eV.

4.4.4 Mechanism III

In mechanism III, the dissociative adsorption of CH_4 is followed by the formation of a CH_2^* species on the Ga–N bond site instead of on the hollow site as suggested in mechanisms I and II (Figs. 8 vs. 6). Furthermore, we considered another CH_2^* species being adsorbed on the adjacent Ga–N bond site. The IS, TS, and FS are displayed in Fig. 8, whereas Figs. S7 and S8 depict all intermediate steps.



Fig. 8. Side (top) and top view (bottom) of the initial state (IS), transition state (TS) and final state (FS) involved in mechanism III on GaN (1100) surface

R2-III: $CH_3^* + H^* \rightarrow CH_2^* + H_2(g)$

The C–H bond of the CH₃* species adsorbed on the Ga-top site is weakened as its hydrogen is attracted towards the H* occupied N-top site. The dissociation leads to an adsorbed CH₂* species over the gallium and nitrogen bond and an H₂ molecule as seen in Figs. 8 and S7. The activation barrier for this step is 5.40 eV, which is higher than for the CH₂* formation on the hollow site suggested in mechanism I (R2-I = 4.68 eV in Table 3). The reaction is endothermic with an energy of 3.97 eV that similar to 3.92 eV for mechanism I.

$\textbf{R3-III: 2CH}_2{}^{\star} \rightarrow \textbf{C}_2\textbf{H}_4\left(\textbf{g}\right)$

 C_2H_4 is formed by the two co-adsorbed CH_2^* species that first desorb from the gallium nitride surface at 3.75 Å and then react to C_2H_4 (Figs. 8 and S8) The calculated activation barrier for this step is rather large with 9.39 eV. The desorption energy of C_2H_4 from the surface is -0.08 eV and the reaction is exothermic with -2.8 eV.

4.4.5 Comparison of the mechanisms

Our calculations showed that the cleavage of the C–H bond in the CH₃* species adsorbed on Gatop site (i.e., R2-I) is the rate-limiting step in mechanism I. Whereas in mechanism II, the reaction R4-II (i.e., CH₃* + CH₂* + H* \rightarrow 2CH₂* + H₂) resulting in co-adsorption of two CH₂* species on the Ga–N hollow and Ga–N bridge site is the rate-limiting step with an activation barrier of 5.03 eV. CH₂* species can also be formed on the Ga–N bridge site via mechanism III; however, this required an activation energy of 5.40 eV, which is significantly higher than required on the Ga–N hollow sites (i.e., 4.68 eV) as suggested in mechanisms I and II. As for the formation of C₂H₄, activation barriers of 4.51, 1.68 and 9.39 eV were determined for mechanisms I, II and III, respectively. The analysis showed that the most likely pathway for CH₄ dehydrogenation to C₂H₄ follows the reaction pathway of mechanism I (Fig. 9, blue). This finding is in agreement with the experimental results that suggest a fast CH₄ dissociation and a rather slow CH₂* and subsequent C₂H₄ formation.



Fig. 9. Calculated activation energy profile of mechanism I (blue line), II (black line), and III (green line) for the non–oxidative methane coupling to ethylene on GaN $(1\overline{1}00)$ surface.

4.5 Elementary steps over Ga₂O₃

As mentioned above, the formation of H_2O , CO and CO_2 were included in the calculations. Tables 4 and 5 summarizes the activation and reaction energies for all elementary reactions on the Ga_2O_3 (001) surface. Figs. 10 to 12 portray the structures of the initial state (IS), transition state (TS) and final state (FS) for each elementary reaction. Figs. S9 to S30 in the supplementary material illustrates all intermediate steps.

4.5.1 Dissociative methane adsorption. $CH_4(g) \rightarrow CH_3^* + H^*$

In this study, three possible pathways for the dissociative methane adsorption were considered on Ga_2O_3 (001). The pathways were distinguished by the position of the adsorbed H atom after the cleavage of the first C–H bond as shown in Figs. 10 and S9–S11. The first step of CH₄ activation involves a weak adsorption on the Ga₂O₃ with carbon weakly bonded to Ga with a Ga–C bond length of 2.19 Å following the alkyl mechanism. After structure optimization, an H atom is being attracted towards O, which results in stretching and subsequently breaking the C–H bond. The activation barrier for dissociative methane adsorption on these three sites is summarized in Table 4.

	Flomontowy stop	Activation barrier (E_a)	Reaction Energy (ΔE)
Liementary step		eV	eV
R0	$CH_4(g) + * \to CH_4 *$	_	-0.05
R1-a	$CH_4* \rightarrow CH_3* + H*$	0.92	-2.35
R1-b	$CH_4{}^{\boldsymbol{*}} \rightarrow CH_3{}^{\boldsymbol{*}} + H{}^{\boldsymbol{*}}$	0.65	-2.10
R1-c	$CH_4{}^{\color{red}{*}} \rightarrow CH_3{}^{\color{red}{*}} + H{}^{\color{red}{*}}$	0.71	-1.15

Table 4. Calculated activation barriers (E_a), and reaction energy (ΔE) of the elementary steps of the dissociative methane adsorption on Ga₂O₃ (001).

The activation energies for the CH₄ dissociation on Ga_2O_3 (001) for R1-a, R1-b and R1-c are 0.92, 0.65, 0.71 eV, respectively. Thus, CH₄ dissociation is likely to happen by R1-b as the activation barrier is the lowest compared to the other two possibilities. The calculated energies for the CH₄ dissociation over Ga₂O₃ (001) are significantly lower than over GaN structure.



Fig. 10. Side (top) and top view (bottom) of the initial states (IS), transition states (TS) and final states (FS) involved in the dissociative methane adsorption on Ga₂O₃ (001) surface.

4.5.2 Mechanism I

After dissociative CH₄ adsorption on Ga_2O_3 (001) via R1-b mechanism, the CH₂* species is adsorbed at Ga–O hollow site in mechanism I. Two such CH₂* species adsorbed on adjacent Ga-O hollow bridges on Ga_2O_3 (001) lead to the formation of C₂H₄. Although the formation of H₂O, CO and CO_2 are undesired it is achieved by this pathway. The top and side views of the IS, TS, and FS for each step of mechanism I are shown in Fig. 10 and Table 5.

64	Elementary step	Activation barrier (E_a)	Reaction Energy (ΔE)	
Step		eV	eV	
R2a-I	$\mathrm{CH}_3{}^{\boldsymbol{*}} + \mathrm{H}^{\boldsymbol{*}} \rightarrow \mathrm{CH}_2{}^{\boldsymbol{*}} + \mathrm{H}_2(g)$	4.42	4.22	
R2b-I	$CH_3* + H^* \rightarrow CH_2* + H_2O(g)$	2.58	2.81	
R3a-I	$\mathrm{CH}_2{}^* + {}^* \to \mathrm{CH}{}^* + \mathrm{H}{}^*$	2.05	-1.30	
R3b-I	$\mathrm{CH}_2{}^* + {}^* \to \mathrm{CH}{}^* + \mathrm{H}{}^*$	1.64	1.45	
R4a-I	$CH^* + H^* \rightarrow C^* + H_2(g)$	2.55	1.74	
R4b-I	$CH^* + H^* \rightarrow CO_2(g) + 2H^*$	1.23	1.32	
R5-I	$C^* \rightarrow CO(g)$	2.05	2.18	
R6-I	$2CH_2^* \rightarrow C_2H_4(g)$	0.47	-1.11	
R2a-II	$\mathrm{CH}_3{}^* + \mathrm{H}^* \to \mathrm{CH}_2{}^* + \mathrm{H}_2(g)$	4.78	4.70	
R2b-II	$CH_3^* + H^* \rightarrow CH_2^* + 2H^*$	1.13	1.21	
R2c-II	$CH_3* + H^* \rightarrow CH_2* + H_2O(g)$	3.19	4.08	
R3-II	$\mathrm{CH}_2{}^* + {}^* \to \mathrm{CH}{}^* + \mathrm{H}{}^*$	0.44	-3.91	
R4-II	$2CH_2^* \rightarrow C_2H_4(g)$	0.19	-2.79	
R2a-III	$CH_3^* + H^* \rightarrow CH_2^* + H_2(g)$	4.77	5.56	
R2b-III	$CH_3^* + H^* \rightarrow CH_2^* + H_2O(g)$	4.38	4.06	
R3-III	$CH_2 * + * \rightarrow CH * + H *$	0.99	-3.92	
R4-III	$CH^* + H^* \rightarrow C^* + H_2(g)$	3.11	3.25	
R5-III	$C^* \rightarrow CO(g)$	1.02	-3.68	
R6-III	$2CH_2^* \rightarrow C_2H_4(g)$	1.68	-4.50	

Table 5. Calculated activation barriers (E_a), and reaction energy (ΔE) of the elementary steps in methane to ethylene conversion on Ga₂O₃ (001).



Fig. 11. Side (top) and top view (bottom) of the initial states (IS), transition states (TS) and final states (FS) of all elementary steps involved in mechanism I on Ga₂O₃ (001) surface.

R2a-I: CH₃* + H* \rightarrow CH₂* + H₂(g)

 CH_2* species can be formed via step R2a-I. The reaction is endothermic with 4.22 eV. The C–H bond of the adsorbed CH_3* species on the Ga-top site is cleaved as it is stretched towards the single H* adsorbed on the lattice oxygen. This results in the formation of CH_2* on Ga–O hollow sites and H_2 molecule, as shown in Fig. 11 and S12 with an activation barrier of 4.42 eV.

R2b-I: CH₃* + H* \rightarrow CH₂* + H₂O(g)

Instead of molecular H₂, H₂O can be formed. The oxygen atom O(I) from the catalyst surface Ga_2O_3 (001) gets involved in the formation of the product creating a vacancy in gallium oxide (Figs. 11 and S13). Our calculations showed that the activation barrier for this step is 2.58 eV, which is significantly lower than the step R2a-I with 4.42 eV. A reaction energy of 2.81 eV was determined. This is in agreement with the experimental results presented above (see Fig. 1 B and E).

R3a-I: $CH_2^* + * \rightarrow CH^* + H^*$

The conversion of CH_2^* species into CH^* and H^* species has an activation barrier of just 2.05 eV with a reaction energy of -1.3 eV. The most stable adsorption configuration for CH^* and H^* was found to be Ga–O hollow site and O-top site, respectively and is shown in Figs. 11 and S14.

R3b-I: CH₂*+ * \rightarrow CH* + H*:

The reactant and the product of R3b-I are the same as R3a-I, but the adsorption site for the products (CH*+H*) is different. The CH* species is adsorbed over the Ga–O hollow site forming bonds between Ga(I) atom and two O(I) atoms. Both the O(I) atoms bonded to the carbon atom of CH* species breaks the bonds between Ga(II) atoms as shown in Figs. 11 and S15. The activation energy is 1.64 eV, which is ~0.4 lower than R3a-I (Table 5). The reaction is endothermic with 1.45 eV.

R4a-I: CH* + H* \rightarrow C* + H₂(g)

The production of H_2 molecule from CH* and H* species in R4a-I results in the formation of C* between two adjacent Ga(I) atoms on the 3-fold hollow site as shown in Figs. 11 and S16. The O(I) atom is highly distorted forming a bonding with C* species and breaking its other bonds. The

elementary reaction is highly endothermic in nature with a reaction energy 1.74 eV. The activation barrier is 2.55 eV, which is similar to 2.54 eV on Pt(111)[44].

R4b-I: CH* + H* \rightarrow CO₂(g) + 2H*

The adsorption of CH* on the Ga–O hollow site appears similar to the HCOO* species which results in the formation of CO₂. The carbon atom in CH₂* species is adsorbed to two O(I) atoms as seen in Figs. 11 and S17. The formation of CO₂ results in two oxygen vacancies on the gallium oxide surface. The activation energy for R4b is 1.23 eV, which is significantly lower than for R4a (2.55 eV) and thus, more likely as confirmed by experiments. The formation of CO₂ is endothermic with 1.32 eV.

R5-I: $C^* \rightarrow CO^*$

Reaction R5-I might follow after reaction R4a-I. The strongly adsorbed C* species forms a strong bond with O(I) atom resulting in CO creating an oxygen vacancy (Figs. 11 and S18). The reaction is endothermic with an energy of 2.18 eV and an activation barrier of 2.05 eV. The higher reaction energy means that the reaction is reversible and less likely to happen.

$\textbf{R6-I: 2CH}_2* \rightarrow C_2H_4\left(g\right)$

R6-I results in the formation of the desired product C_2H_4 by combination of two CH_2^* species formed by reaction R2a-I on adjacent Ga–O hollow site (Figs. 11 and S19). The activation barrier for the formation of ethylene is just 0.47 eV, and the reaction is exothermic with –1.11 eV.

4.5.3 Mechanism II

In Mechanism II, the adsorption of CH_2^* species on O-top site is considered. Two CH_2^* species adsorbed on adjacent O(I) atom on Ga_2O_3 (001) lead to the formation of C_2H_4 . The formation of

 H_2O , CO and CO_2 are also observed in this mechanism. The top and side views of the IS, TS, and FS for each step of mechanism II are shown in Fig. 12 and Table 5.

R2a-II: CH₃* + H* \rightarrow CH₂* + H₂(g)

Similar to R2a in mechanism I, a CH_2^* surface intermediate and H_2 molecule are formed in R2a-II. However, the CH_2^* species is adsorbed at the O-top site after breaking the C–H bond of the Gatop adsorbed CH_3^* species (Figs. 12 and S20). The activation barrier is 4.78 eV and is slightly larger than for R2a in mechanism I in which the CH_2^* species is adsorbed on Ga–O hollow site (4.42 eV in Table 5). The reaction is highly endothermic with reaction energy 4.7 eV.

R2b-II: CH₃* + H* \rightarrow CH₂* + H* + H*

The reaction R2b-II results in the formation of CH_2^* species adsorbed on O-top site and two H* species adsorbed on O-top sites as shown in Figs. 12 and S21. The reaction is endothermic at 1.21 eV with an activation barrier of 1.13 eV, which is significantly lower than step R2a-II with a value of 4.78 eV.

R2c-II: $CH_3^* + H^* \rightarrow CH_2^* + H_2O(g)$

Similar to reaction R2b in mechanism I, H₂O can be produced. Oxygen vacancy is created as the O(I) atom is bonded with the two H atoms to form H₂O molecule as shown in Figs. 12 and S22. The activation barrier is 3.19 eV and higher than for R2b-II but lower compared to R2a-II (Table 5). This step is highly endothermic with reaction energy 4.08 eV, which is significantly higher than R2b-II.



Fig. 12. Side (top) and top view (bottom) of the initial states (IS), transition states (TS) and final states (FS) involved in the mechanism II on Ga₂O₃ (001) surface.

R3-II: $CH_2^* + * \rightarrow CH^* + H^*$

CH₂* adsorbed on the Ga-top site dissociates to CH* and H* species adsorbed on Ga–O hollow site and O-top sites, respectively (Figs. 12 and S23). The reaction is highly exothermic with –3.91 eV. An activation barrier of 0.44 eV has been determined, which is much lower than R3-I in mechanism I.

$\textbf{R4-II: 2CH}_2{}^* \rightarrow \textbf{C}_2\textbf{H}_4\left(\textbf{g}\right)$

 C_2H_4 is formed when two CH_2^* species are adsorbed on adjacent O-top sites (Figs. 12 and S24) following either reaction R2a-II, R2b-II or R2c-II. The activation barrier for this R4-II is 0.19 eV. The desorption energy of C_2H_4 from the Ga_2O_3 (001) surface is -0.07 eV and is highly exothermic with -2.79 eV.

4.5.4 Mechanism III

Mechanism III considers the CH₃* dissociation into CH₂* adsorbed on Ga–O bond sites and two such CH₂* species adsorbed on adjacent Ga–O bond sites are forming C₂H₄. Mechanism III also leads to the formation of CO and H₂O. The IS, TS, and FS of elementary reaction steps are displayed in Fig. 13.



Fig. 13. Side (top) and top view (bottom) of the initial states (IS), transition states (TS) and final states (FS) involved in the Mechanism III on Ga₂O₃ (001) surface.

R2a-III: $CH_3^* + H^* \rightarrow CH_2^* + H_2(g)$

 CH_3^* species in R2a-III leads to the formation of a CH_2^* species and H_2 molecule. The resulting CH_2^* species adsorbs at the Ga–O bond site and the O(II) atom is distorted as shown in Figs. 13 and S25. R2a-III is highly endothermic with 5.56 eV and an activation energy of 4.77 eV which is similar to R2a-I from mechanism I (see Table 5).

R2b-III: $CH_{3}^{*} + H^{*} \rightarrow CH_{2}^{*} + H_{2}O(g)$

R2b-III results in release of H_2O molecule and CH_2^* species adsorbed on the Ga–O bond site. The O(I) atom involved in the formation of H_2O created an oxygen vacancy as shown in Figs. 13 and S26. The activation barrier for R2b-III is 4.38 eV that is significantly lower than R2a-III, but higher than the reactions R2b-I from mechanism I and R2c-II from mechanism II in which H_2O is formed (Table 5). The reaction is endothermic with 4.06 eV.

$\textbf{R3-III: CH}_2* \rightarrow \textbf{CH}* + \textbf{H}*$

In this step, the C–H bond in CH_2^* is cleaved to form CH^* and H^* at the 3-fold hollow site and O-top site (Fig. 13 and S27). The reaction is highly exothermic with –3.92 eV and an activation barrier of 0.99 eV, which is higher than R3-II in mechanism II.

R4-III: $CH^* + H^* \rightarrow C^* + H_2(g)$

In R4-III, the formation of an H_2 molecule and C* species adsorbed at the 3-fold hollow site takes place. The activation energy is 3.11 eV, and the reaction is endothermic with 3.25 eV. The similar reaction R4-I in mechanism I had a lower activation energy of 2.55 eV.

R5-III: $C^* \rightarrow CO(g)$

R5-II results in the formation of a CO molecule creating an oxygen vacancy. The O(II) atoms form a bond with C* species adsorbed, leaving the $Ga_2O_3(001)$ surface distorted, as shown in Figs. 13 and S29. The activation energy for R5-III is 1.02 eV and about half of the similar reaction R5-I in mechanism I (Table 5). The reaction is highly exothermic with -3.68 eV.

R6-III: $2CH_2^* \rightarrow C_2H_4(g)$

When two CH_2^* species are adsorbed at Ga–O bond sites, C_2H_4 is formed by the coupling of the two species (Figs. 13 and S30). The activation barrier for the formation of C_2H_4 is 1.68 eV, and the reaction is exothermic with –4.5 eV. The desorption energy of C_2H_4 form Ga_2O_3 (001) surface is –0.14 eV.

4.5.5 Comparison of the mechanisms

Unlike GaN, Ga_2O_3 contains oxygen that can react with adsorbed hydrogen and carbon to form H_2O , CO, and CO_2 besides the desired C_2H_4 . Fig. 14 illustrates the activation energy profile for methane to ethylene conversion on gallium oxide for mechanisms I, II and III as stated in Table 5.



Fig. 14. Calculated activation energy profile of mechanism I (black), II (orange), and III (green) for the methane non–oxidative coupling to ethylene on Ga₂O₃ (001) surface.

The first step in this conversion involves the dissociative adsorption of methane, which requires an activation barrier of 0.65 eV where the CH₃* species is adsorbed on the Ga-top site and H* species is adsorbed on O-top site of O(I) atom. The cleavage of C–H bond from CH₃* species is found to be rate-limiting step with highest activation energy 4.42, 4.77 and 4.78 eV in mechanisms I, II and III, respectively. The rate-limiting step is found to be highly endothermic as for all three mechanisms with 4.22, 4.70 and 5.56 eV. The last step in ethylene formation is the coupling of two CH₂* species, which has an activation barrier of 0.47 and 0.19 eV for mechanism I and II. Whereas for mechanism III a much higher activation barrier of 1.68 eV is required. In general, this step is found to be highly exothermic for all three mechanisms.

 H_2O and CO_2 are undesired products, which are formed on the Ga_2O_3 surface when CH_4 is oxidized. H_2O creates a single oxygen atom vacancy on the Ga_2O_3 surface, whereas CO_2 creates

two oxygen vacancies. Fig. 15A and B show the pathways that lead to the formation of H_2O and CO_2 on the Ga_2O_3 surface, respectively. The rate-limiting step is the formation of water, which requires an activation energy of 2.58, 3.19 and 4.38 eV for mechanism I, II and III, respectively. In all the three mechanisms O(I) atom vacancy is created and are distinguished by the different site on which the CH_2^* species is adsorbed.



Fig. 15. Calculated activation energy profile for (A) H₂O and (B) CO₂ formation on Ga₂O₃(001).

Based on DFT modeling, only one pathway leads to the formation of carbon dioxide as shown in Fig. 15B. The rate-limiting step is the C–H bond cleavage in CH_3^* species similar to C_2H_4 and CO formation. The CH_2^* species is reduced to CH* adsorbed at the Ga–O hollow site and bonded with two O(I) atoms (Fig. S18). The CH_2^* species bonded with two O(I) atoms looks similar to the

HCOO species which is one of the intermediate steps in formation of carbon dioxide [45]. CO₂ is formed by creating two oxygen vacancies with activation barrier of 1.23 eV energy.

CO might also be produced on the Ga_2O_3 (001) surface via mechanisms I and III. The activation energy profiles are depicted in Fig. S32. The formation of CO results in an oxygen vacancy on the Ga_2O_3 surface which requires an activation energy of 2.05 eV for O(I) and 1.02 eV for O(II) for mechanism I and III, respectively.

5 Conclusions

In this work, DFT was used to study the mechanism of CH₄ dehydrogenation with subsequent coupling to C_2H_4 on GaN (1100) and Ga₂O₃ (001) surface. CH₄ can be activated on the *m*-plane of GaN structure with an activation energy of 1.06 eV. On the Ga₂O₃ (001) surface the activation barrier was smaller, with a value of 0.65 eV.

For GaN catalyst, CH_4 conversion via mechanism I is the preferred reaction path to form C_2H_4 , in which two CH_2^* species are adsorbed on adjacent Ga–N hollow sites. The rate-limiting step was found to be the cleavage of the C–H bond in the CH_3^* species adsorbed on Ga top site, which is in agreement with experimental results.

For the Ga_2O_3 catalyst, mechanism I has the lowest activation energy barrier for methane conversion to ethylene. A comparison between the two catalyst surfaces GaN (1100) and Ga_2O_3 (001) showed that the activation energy for the most favourable pathway is 4.68 eV and 4.42 eV, respectively, which is very close to each other.

The formation of H_2O , CO_2 , and CO was only possible via the involvement of lattice oxygen which created surface oxygen vacancies on Ga_2O_3 , with mechanism I as the preferred pathway.

Our calculations provide a better understanding of the catalytic processes from the microscopic perspective.

Associate content

DFT results include optimized structures of initial state and intermediate states of all elementary steps over GaN and Ga₂O₃ catalysts and as well activation energy profile for CO formation over Ga₂O₃.

Acknowledgment

The authors acknowledge the financial support from Fonds de recherche du Québec - Nature et

technologies (FRQNT, Team Grant PR-253397). This research was enabled in part by support

provided by Calcul Québec (calculquebec.ca) and Compute Canada (computecanada.ca).

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