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REDUCTION OF SULPHUR DIOXIDE OVER SUPPORTED MOLYBDENUM SULPHIDE CATALYSTS

by

David John Mulligan

A Thesis submitted to the Faculty of Graduate Studies and
Research in partial fulfillment of the requirements
of the degree of Doctor of Philosophy

November, 1992

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The shortened title of this thesis is as follows:

Reduction of SO_2 over supported molybdenum sulphide catalysts

ABSTRACT

The reduction of sulphur dioxide with methane using various supported molybdenum catalysts has been studied. Catalysts were prepared using either alumina or a silica-alumina support. For the alumina supported catalysts, the molybdenum loadings of 5, 10 or 15% were used. These catalysts were sulphided using 12% H_2S in argon or a mixture of SO_2 and CH_4 in argon. The 15% Mo/Al_2O_3 catalyst sulphided with H_2S was at least 1.5 times as active as the other alumina supported catalysts and had the highest yields of elemental sulphur and CO_2 and was 10 times as active as the silica-alumina supported catalyst with the same molybdenum loading. The addition of cobalt to the 15% Mo/Al_2O_3 catalyst decreased the activity by 20%. Alumina supported molybdenum catalysts sulphided using a mixture of 25% SO_2, 25% CH_4 and 50% Ar were more active, and had higher yields of sulphur and CO_2 than alumina itself. However, these catalysts were not as active as catalysts with a similar molybdenum loading which were sulphided using H_2S because the H_2S sulphided catalysts had a higher MoS_2 content. Kinetic experiments were carried out using the H_2S sulphided 15% Mo/Al_2O_3 catalyst. A rate expression was developed at the temperatures of 600, 625, and 650°C. The results indicate that the reaction is methane adsorption controlled.

RESUMÉ

La réduction du bioxyde de soufre à l'aide du méthane en utilisant différents catalyseurs à base de molybdène a été étudiée. Des supports d'alumine ou de silice-alumine furent utilisés pour la préparation des catalyseurs. Des charges en molybdène de 5, 10, ou 15% furent utilisées pour les catalyseurs sur supports d'alumine. Ces catalyseurs ont été sulfurés en utilisant 12% H_2S dans l'argon ou un mélange de SO_2 et de CH_4 dans l'argon. Le catalyseur contenant 15% de Mo/Al_2O_3 sulfuré avec du H_2S avait une activité au moins 1.5 fois supérieure aux autres catalyseurs à support d'alumine. Il avait de plus, les plus hauts rendements en soufre élémentaire et en CO_2, et était 10 fois plus actif que le catalyseurs à support de silice-alumine avec le même contenu de molybdène. L'addition de cobalt au catalyseur formé de 15% Mo/Al_2O_3 a pour effet de diminuer l'activité de 20%. Les catalyseurs au molybdène à support d'alumine sulfurés en utilisant un mélange de 15% SO_2, 25% CH_4, et 50% Ar étaient plus actif et avaient un plus haut rendement en soufre et en CO_2 que l'alumine. Ils n'étaient cependant pas aussi actifs en tant que catalyseurs avec un même contenu en molybdène sulfurés avec H_2S parce que les catalyseurs sulfurés au H_2S avaient un contenu de MoS_2 supérieur. Des expériences de cinétique ont été effectuées en utilisant le catalyseur 15% Mo/Al_2O_3 sulfuré au H_2S. Une expression pour le taux de réaction a été développée pour des températures de 600, 625, et 650°C. Les résultats indiquent que la réaction est contrôlée par l'absorption de méthane.

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To my Father

TABLE OF CONTENTS

PAGE

LIST OF FIGURES

LIST OF TABLES

LIST OF PLATES

NOMENCLATURE

A = pre-exponential factor (Equation 2.12)

A = total surface area of catalyst (m^2)

C = reactor exit concentration of methane

$C(i)_f$ = concentration of species i in feed (mol/cm^3)

C_b = bulk concentration of species i (Equation 7.2)

Co = reactor inlet concentration of methane

C_s = surface concentration of species i (Equation 7.2)

E = activation energy (Equation 2.12)

E = active site (Equation 7.4)

F(i) = exit molar flow rate of species i (mol/s)

$F(i)_o$ = inlet molar flow rate of species i (mol/s)

K = adsorption constant (Equation 7.7)

k = rate constant (Equation 7.7)

k_{-i} = rate constant for reverse reaction i

k_i = rate constant for forward reaction i

k_m = external mass transfer coefficient (Equation 7.2)

M = mass of catalyst (g)

n = number of tanks in series

P(i) = partial pressure of species i (atm)

Q_f = total volumetric feed rate (cm^3/s)

R = gas constant (1.987 cal/mol-K)

r(i) = rate of reaction of species i

s = sulphur selectivity (Equation 2.15)

T = temperature (K)

x = conversion of species i

$Y(CO_2)$ = carbon dioxide yield (%) (Equation 4.9)

$Y(S)$ = elemental sulphur yield (%) (Equation 4.8)

CHAPTER 1

INTRODUCTION

Sulphur dioxide is produced by industry in greater quantities than any other sulphur containing compound. It is produced either intentionally by the combustion of elemental sulphur or as a by-product of fossil fuel combustion and smelting operations. Sulphur dioxide is a very stable compound which can be used as a solvent, a disinfecting or bleaching agent, or as a preservative. It is, therefore, used in a wide variety of industries ranging from the production of pulp and paper to food processing. However, its greatest use is in the production of sulphuric acid which accounts for 98% of the total SO_2 used in industry. Despite its value to industry, sulphur dioxide, when produced as a by-product, is often emitted to the atmosphere where it contributes to the phenomenon known as "acid rain".

1.1 The Impact of Acid Rain on the Environment

Acid rain is defined as precipitation (rain, snow, etc.) which has a pH lower than 5.65. Rain and snow in the north-east United States and southern Quebec and Ontario has been shown to have a pH as low as 2.1 which is more acidic than vinegar (pH 2.4). On average, the pH of precipitation in these areas is around 4.0 (Goudie, 1986).

The increasing acidity of precipitation detrimentally affects the environment in a variety of ways. For example, acidification of bodies of water kills fish and allows other less desirable forms of life such as algae to proliferate. Acidification of soil leads to decreased productivity of farmland and forests because of accelerated leaching of essential nutrients. Plants and trees that are able to grow are often more susceptible to disease because protective coatings are removed from their leaves and stems. Plant and animal survival is also reduced because of the leaching of toxic minerals from rocks in the acidified water or soil. This can further affect the health of humans who consume contaminated food. Finally, acid rain is eroding and corroding buildings and many historic monuments and statues particularly those made from limestone and steel.

1.2 SO_2 Sources and Control Legislation

Because of the effects that acid rain has had on the environment, many investigations have been commissioned to study the processes involved and find solutions to the associated problems. As a result of these studies, it is known that both SO_2 and the oxides of nitrogen (NO_x) are involved. However, at the present time, approximately 60 to

70% of the problem is due to SO_2 emissions. Although some of the SO_2 in the atmosphere is from natural sources, over 90% is man-made (United Nations, 1984). As shown in Figure 1.1, SO_2 emissions have increased dramatically since the beginning of the industrial revolution. The primary sources of sulphur dioxide are listed in Table 1.1. Over 50% of the global emissions of SO_2 are due to the combustion of sulphur containing coal. This proportion will probably increase as the low sulphur coal supplies decrease and are substituted with cheaper, high sulphur coals.

The bulk of the remaining SO_2 emissions are due to the combustion of oil and lignite, and the smelting of various metal sulphide ores such as chalcopyrite, pyrite, pentlandite, and ZnS. In smelting operations, the ore is heated and burned in air. The general reaction is:

$$MeS_x + (3x/2)O_2 \longrightarrow MeO_x + xSO_2 \qquad (1.1)$$

In this case, the gaseous product can contain as much as 10-15% SO_2 compared with approximately 0.1-2% SO_2 found in the flue gases from fossil fuel burning power plants (Rochelle, (1983), Sander <u>et al</u>, (1984)).

In the last decade, governments have responded to the problems associated with acid rain by imposing regulations limiting the emissions of SO_2. The Canadian Clean Air Act of 1981 limits the emissions of SO_2 from power plants burning fossil fuels to 2.6×10^{-4} mg/J. Similarly, the

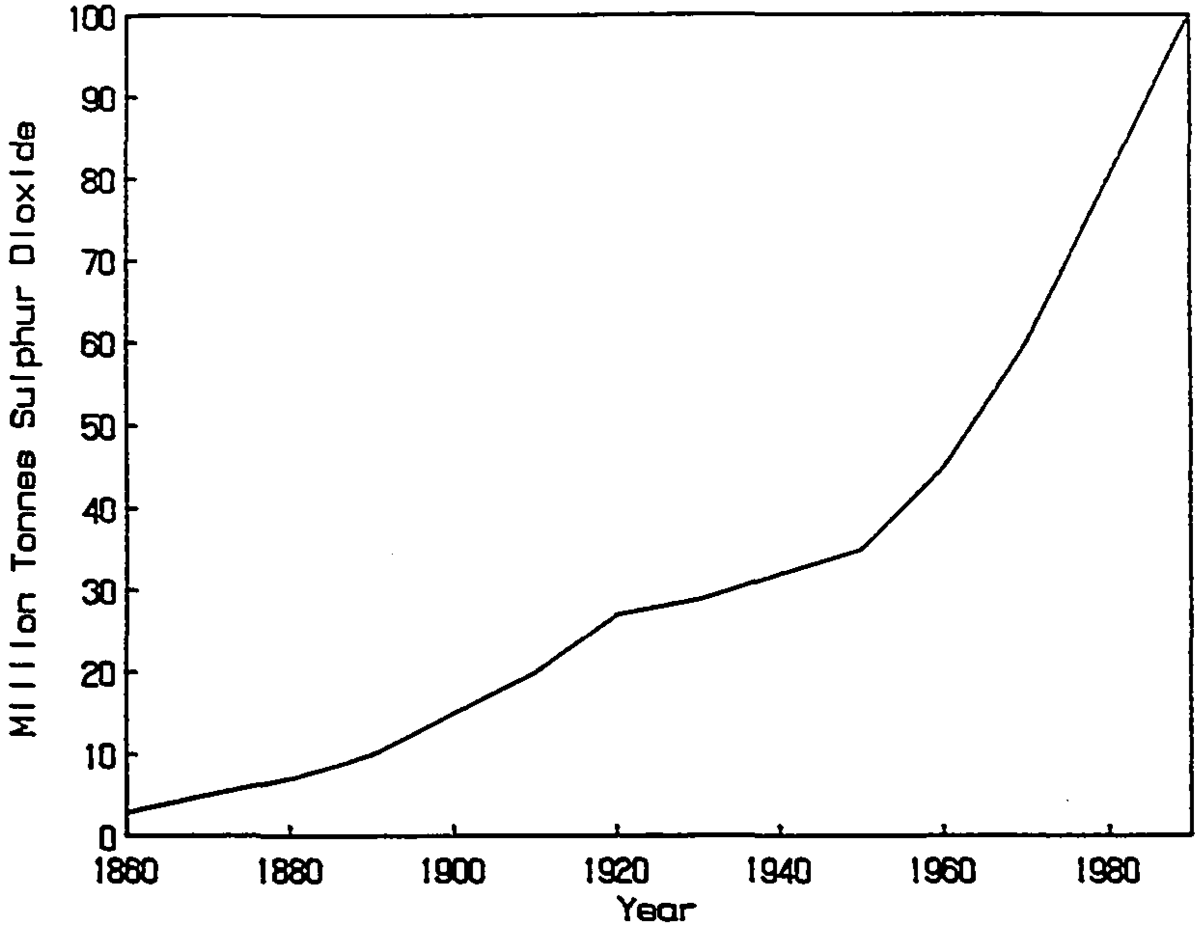


Figure 1.1 Annual global SO_2 emissions

(Goudie, 1986)

Table 1.1

Global Industrial SO_2 Sources

Source	million tonnes/year
Coal Combustion	50
Oil Combustion	25
Lignite Combustion	10
Copper Smelter	7
Other	2

(Goudie, 1986)

1990 US Clean Air Act imposes a limit on SO_2 emissions from fossil fuel burning power plants of 5.2×10^{-4} mg/J by the year 2000 (Smock, 1991). A limit on total emissions from all facilities of 8.9 million tonnes will also apply. This level is 10 million tonnes of SO_2 less than was produced in 1980 in the United States. For comparison, at the present time, Canada produces twice as much SO_2 per capita as the United States (Record et al., 1982).

1.3 SO_2 Control Technology

Facilities producing SO_2 containing effluent gases have the following alternatives for complying with the government standards.

a) Old plants can be permanently closed.
b) Coal burning power plants can switch to low sulphur coal or natural gas.
c) Smelters can switch to hydrometallurgical processes.
d) Equipment can be retrofitted to remove SO_2 before it is exhausted to the environment.

For many very old smelters or power plants, it may be possible to simply close the facility. However, for those that are still capable of operating efficiently, this option cannot be considered. Coal burning power plants can switch to low sulphur (< 1%) coal if it is available. However, not only are low sulphur coal supplies becoming more scarce, and more expensive, but there is a social factor to consider as well. For example, the American Electric Power Company owns several power plants in the state of Ohio. These facilities burn locally mined high sulphur coal. If the company converted only its 2600 MW Gavin Plant, which consumes six million tonnes of coal per year, to out-of-state low sulphur coal, 1258 local miners will be put out of work (Smock, 1991). In this case, retrofitting a SO_2 removal system may not be the least expensive option, but it is the most politically viable.

A coal burning power plant can also convert to natural gas. It is not yet known how many plants will do so, however, it is suspected that because natural gas is more expensive than coal, it will probably not be a major part of the compliance strategy (Smock, 1991).

Smelters have fewer options than fossil fuel burning power plants. If closing the facility is not an option, the smelter could convert to a hydrometallurgical process which does not produce SO_2. This conversion would cost billions of dollars. The only economically viable option for smelters is to remove SO_2 from their flue gases.

Because the removal of SO_2 from flue gas is the principle approach to SO_2 emission control used by both fossil fuel burning power plants and ore smelting facilities there have been many studies on the subject, many of which have led to bench-scale and pilot plant operations. However, only a few of these have found applications in industrial practice. The following sections provide an overview of the early development of SO_2 control technology, as well as a brief description of SO_2 removal processes which have found large-scale industrial application in recent years.

1.3.1 Early History of SO_2 Control Technology

At the beginning of the twentieth century, the environmental problems associated with SO_2 emissions were more localized. For example, SO_2 produced from the primitive smelting operations at Sudbury, Ontario virtually sterilized the soil in the surrounding area. In addition, sulphuric acid fog episodes occurred in Donora, Pennsylvania, and London, England in 1948 and 1952, respectively killing over 4000 people. In the case of industrial sources, the response to such episodes was simply to build taller chimneys, thereby dispersing the SO_2 over a larger area. While this method solved the localized problems, the result was the widespread acid rain problem described above (Sander, et al., 1984).

The earliest studies related to the removal of sulphur dioxide from flue gases began in the middle of the nineteenth century. The objective of flue gas desulphurization during this period was the recovery of sulphur in a commercially usable form (Marten, 1977). Water was used as the primary SO_2 absorbent. A portion of the absorbed gas reacts with the water to eventually form sulphuric acid. Early large-scale SO_2 control systems in power plants simply used river water.

Subsequent research focused on the design of more efficient absorption towers as vast quantities of water were required for such operations. In 1930, research conducted for the Battersea Station flue gas desulphurization (FGD) unit in England showed that 45 to 58 tonnes of water were required for each tonne of coal consumed in order to achieve complete SO_2 removal (Thau, 1930). A better understanding of absorption processes was required.

The late 1920's was a period of extensive research into the use of vanadium, zeolites, copper compounds, platinum, and iron compounds as catalysts. Metals were found to improve SO_2 solubility in water by promoting the oxidation of SO_2 to SO_3 which reacts with water to form sulphuric acid. These studies were perhaps the first stages in developing catalytic processes for FGD operations.

The reduction of sulphur dioxide to elemental sulphur using carbon or hydrocarbons has been studied since the beginning of this century. In most cases, the processes have been applied to the more concentrated smelter gases rather than power plant flue gases.

The earliest known method was developed in the 1910's and was known as the thiogen process. Initially, it was found that the reduction reactions were slow and did not go to completion. The presence of calcium sulphide was found to improve the reaction rates. A variation of this process resulted in the development of the wet thiogen process. In this case, barium sulphide in an aqueous solution was used as the reducing agent (Young, 1917).

In 1916, Lamoreaux patented a system for reducing SO_2 from smelter gas to elemental sulphur using carbon monoxide, hydrogen sulphide, hydrogen, or hydrocarbon vapour. The gases were passed over activated carbon to promote the reduction. There were, however, no extensive kinetic or thermodynamic studies of these systems until 1933 when experimental studies of the reduction reactions were first performed by Yuskevitch and Karzhavin. In these studies, it was found that methane, in the presence of a bauxite catalyst could reduce SO_2 to elemental sulphur with a conversion of 89-95% at 900°C.

In 1938, Lepsoe of the Consolidated Mining and Smelter Company of Canada investigated the thermodynamics of the reduction reactions using carbon, carbon monoxide, carbonyl sulphide, hydrogen, hydrogen sulphide, and methane. Reduction reactions with hydrogen and H_2S were further studied in 1944 by the Union Oil Company of California; however, it was not until the increase in the environmental concern over SO_2 emissions during the 1960's that SO_2 reduction was studied with more interest.

1.4 Flue Gas Desulphurization Processes

Processes for the removal of SO_2 from flue gases can be separated into both wet and dry scrubbing processes, catalytic oxidation processes resulting in the manufacture of sulphuric acid, and SO_2 reduction processes resulting in the production of elemental sulphur. Some scrubbing processes which have been used industrially in the last two decades include the following (Rosenberg, et al., 1975).

- Wet limestone scrubbing
- Alkali scrubbing without regeneration
- Alkali scrubbing with thermal regeneration
- Magnesium oxide scrubbers

These processes are all described in detail elsewhere in the literature, and since they are not the subject of this thesis they will not, with the exception of wet limestone scrubbing, be discussed further.

1.4.1 Wet Limestone Scrubbing of SO_2

The limestone slurry scrubbing process is the most widely used process for removal of SO_2 from fossil fuel burning power plants. In fact, this method is used to treat between 80 and 85% of all SO_2 produced by power plants. The popularity of this process is based on its efficiency and relatively low cost (Rochelle, 1983). In this process, SO_2 is scrubbed from the flue gas using a $CaCO_3$ slurry producing a slurry containing both $CaSO_3$ and $CaSO_4$.

There are two major disadvantages associated with this type of scrubbing operation. Firstly, no sulphur product is recovered and is therefore wasted. Secondly, the end product, which is a slurry of calcium sulphate, must be landfilled. Since space available for landfill both in Canada and the United States is rapidly diminishing, either viable alternatives will have to be found for the disposal of the slurry or alternative economical SO_2 treatment methods will have to be developed.

1.4.2 Catalytic Oxidation of SO_2

As stated above, the flue gas produced by a smelter is rich in sulphur dioxide in comparison to that produced by power plants. In Canada, much of this SO_2, through the process of catalytic oxidation, is made into sulphuric acid which is a saleable product. Similarly, catalytic oxidation has also been used for the removal of SO_2 from the flue gases of fossil fuel burning power plants.

In the catalytic oxidation process shown in Figure 1.2, the flue gas is first passed through a dust collector and then through an electrostatic precipitator to remove virtually all the remaining dust particles or fly ash. The clean gas then flows through a fixed catalytic bed of vanadium pentoxide operating at a temperature of 450°C where the SO_2 is oxidized to SO_3. The gas is cooled to 95°C, resulting in the formation of sulphuric acid mist and condensed droplets which are then removed in a packed absorption tower followed by an electrostatic precipitator. The precipitated product is 78% sulphuric acid. Using this process, approximately 85% of the SO_2 is converted to sulphuric acid (Miller, 1974).

While the catalytic oxidation of SO_2 is technically well suited for controlling SO_2 emissions from smelters, large volumes of sulphuric acid are produced. If the market for this product is saturated, or if the market is not close to the smelter, the acid has to be transported long distances or stored indefinitely. Because sulphuric acid is an extremely corrosive chemical, there are dangers

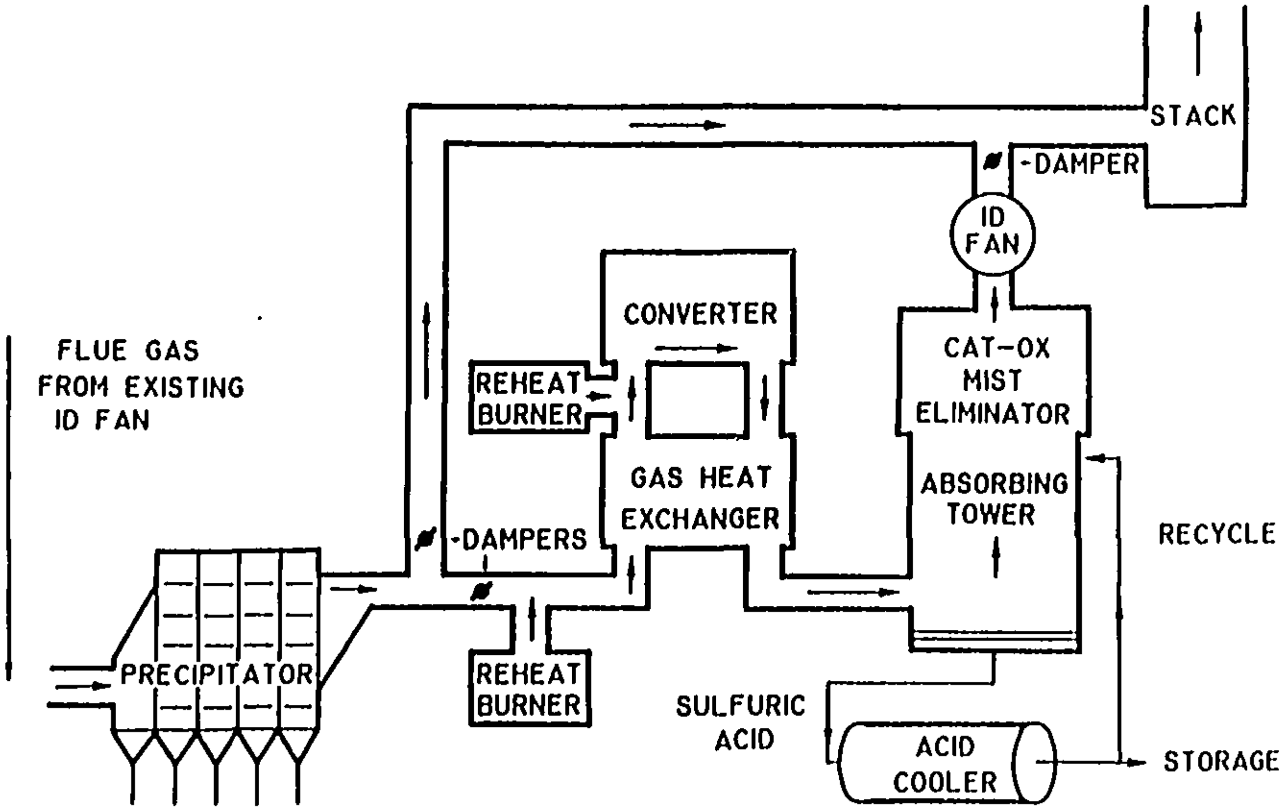


Figure 1.2 Schematic diagram of a SO_2 catalytic oxidation process (Miller, 1974)

associated with its transport and storage which result in high handling costs and potential damage to the environment.

1.5 Sulphur Dioxide Reduction

An alternative process to those described above, which has been implemented in industry in the past is the reduction of SO_2. Sulphur dioxide reduction has the advantage of producing elemental sulphur as its end product. Since elemental sulphur is saleable, the landfill problems such as those associated with the wet limestone scrubbing process, are eliminated. In addition, since elemental sulphur is not a hazardous material, the costs of handling, transport, and storage are significantly lower than for sulphuric acid, as are the risks for potential environmental problems.

Elemental sulphur is used in industry primarily for the production of SO_2 and sulphuric acid. However, it is also used directly in the production of volcanization compounds, pesticides, plasticizers for bulk plastics, and in the manufacture of construction materials such as bricks, mortar, and asphalt (Sander, et al., 1984).

At the present time, the Claus process, where H_2S is reacted with SO_2, is the most common method used by industry to produce elemental sulphur. However, for large scale pollution abatement systems, natural gas has been the most widely used reducing agent.

In 1970, the Allied Chemical Corporation commenced operation of a plant to reduce SO_2 produced from a sulphide ore roasting facility owned by Falconbridge Nickel Mines Ltd. located near Sudbury, Ontario (Hunter and Wright, 1972). The unit was designed to recover 450 tonnes/day of sulphur from a 12% SO_2 roaster gas. The process is shown schematically in Figure 1.3. The process consisted of three main sections: gas purification, SO_2 reduction, and elemental sulphur recovery. In the first section, excess water vapour, as well as gaseous and particulate matter were removed.

The reduction section consisted of two heat generators, A and B, and the catalyst-packed bed reactor, C. In this section, half the SO_2 was catalytically reduced to elemental sulphur with methane. The remaining SO_2 was converted to H_2S. The reactions involved in this process are summarized as follows:

$$CH_4 + 2\ SO_2 \dashrightarrow CO_2 + 2\ H_2O + S_2 \qquad (1.2)$$

$$3\ CH_4 + 4\ SO_2 \dashrightarrow 3\ CO_2 + 4\ H_2S + 2\ H_2O \qquad (1.3)$$

Sensible heat from the reactor exit gases was recovered in the regenerators and then used to preheat the reactor feed gases in order to increase the overall efficiency of the process.

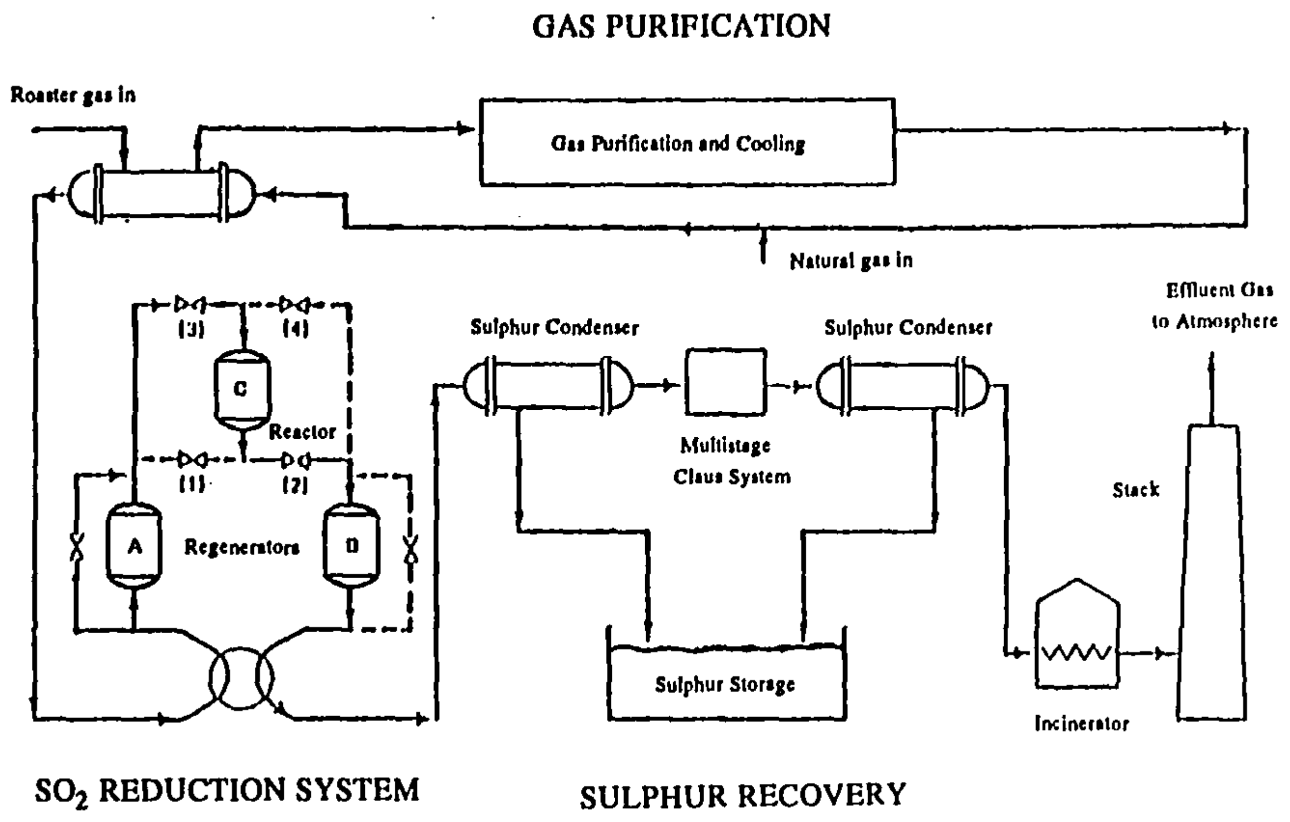


Figure 1.3 The Allied Chemical process

(Hunter and Wright, 1972)

The catalyst used to promote the reactions was developed and patented by Allied specifically for SO_2 reduction. The catalyst was developed to be stable at temperatures to 1100°C and to achieve efficient methane utilization.

The sulphur recovery section consisted of a sulphur condenser, and a multi-stage Claus conversion unit followed by a second sulphur condenser. The unreacted SO_2 from the reduction stage and H_2S were reacted in the Claus unit according to the following reaction:

$$2\ H_2S + SO_2 \longrightarrow 2\ H_2O + 3\ S \qquad (1.4)$$

The remaining gas was burned to remove traces of H_2S before venting to the atmosphere.

This system was designed to be adaptable to a wide variety of SO_2 reduction applications including fossil fuel burning power plants and smelters. For the lower SO_2 concentration applications, a unit designed to remove and concentrate SO_2 from the flue gas was required as a preliminary stage. The process as shown in Figure 1.3 could then be used to reduce the SO_2 in the concentrated stream.

1.6 Significance and Scope of This Study

Towards the middle of the 1970's, the price of sulphur dropped to approximately $30/tonne (Figure 1.4) and the price of natural gas, as supplies became uncertain, increased dramatically to near $1.00/gigajoule (Figure 1.5) making the Allied Chemical process uneconomical. However, over the last five years, the price of sulphur has averaged approximately $100/tonne and the price of natural gas has decreased and stabilized at $3.30/gigajoule. These price trends, coupled with the shortage of landfill space for calcium sulphate from wet limestone scrubbing, and the potential dangers associated with the handling of sulphuric acid, once again make SO_2 reduction processes a good subject for investigation.

While it is clear that the current sulphur-natural gas price ratio will not make the Allied Chemical process economically viable, it is also clear that modifications to the process can make a SO_2 reduction process more efficient. One such modification is to develop a catalyst which will promote the production of elemental sulphur according to reaction 1.2 and therefore decrease the proportion of SO_2 which is reduced to H_2S (reaction 1.3).

The benefit of increased selectivity for the production of elemental sulphur to the economics of the process is two-

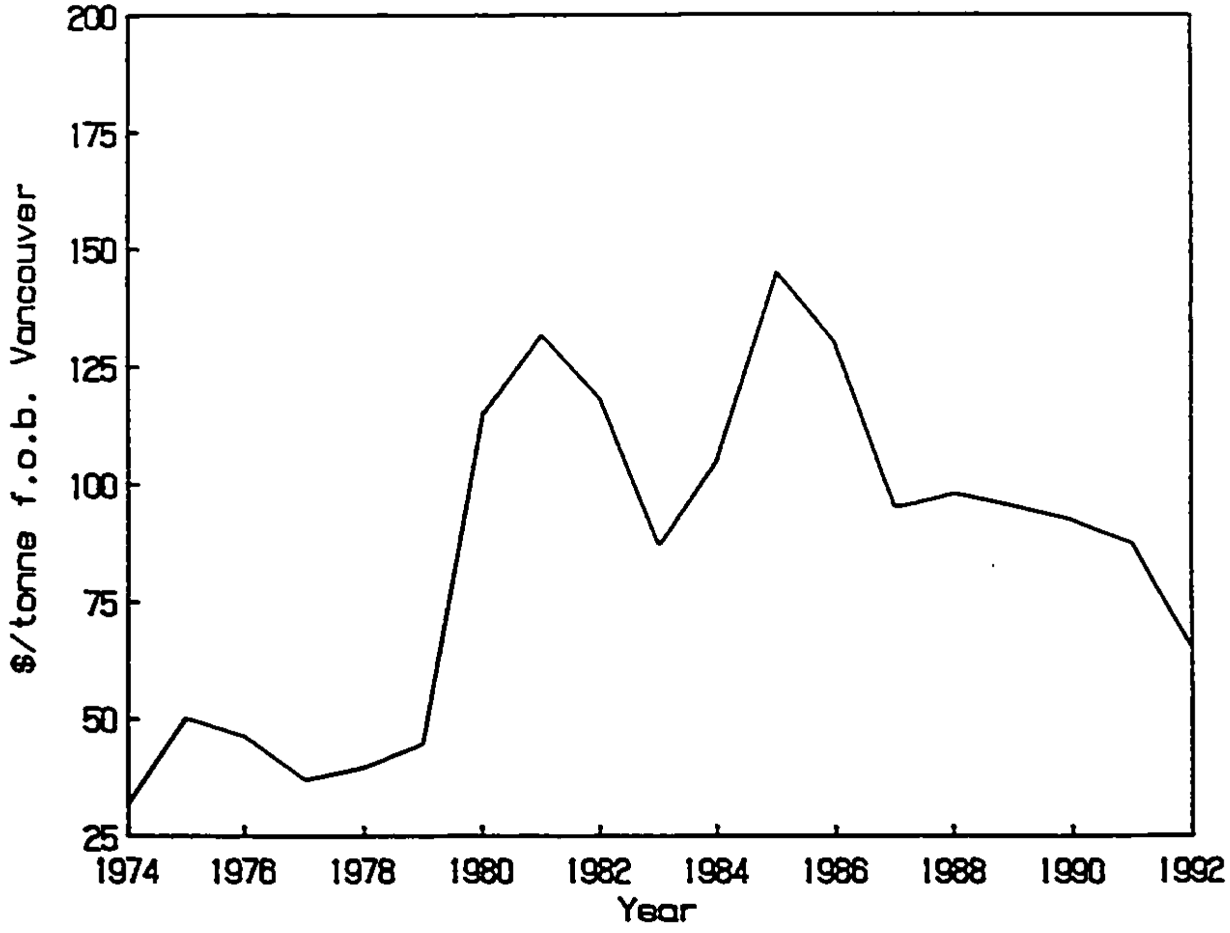


Figure 1.4 Sulphur price trends

(Sulphur, 1992)

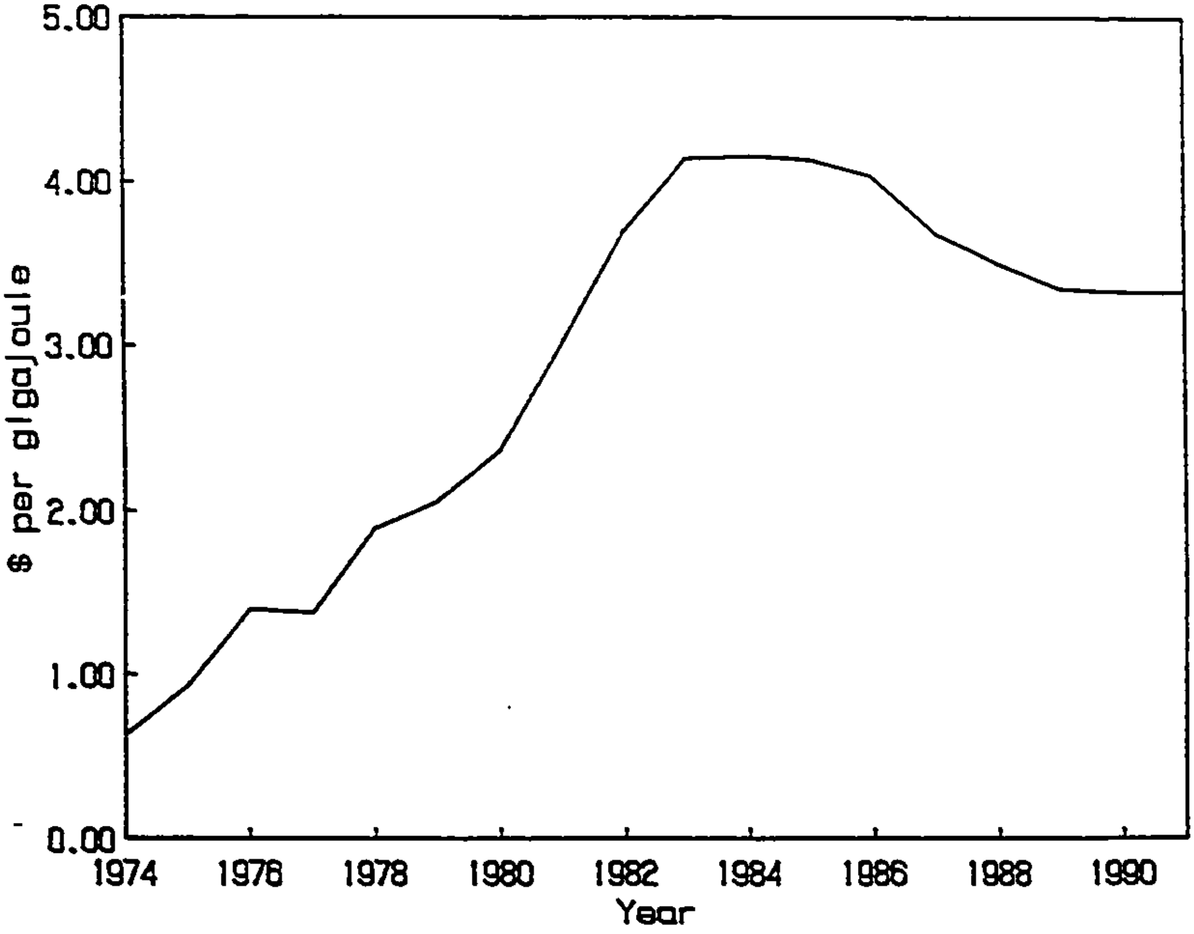


Figure 1.5 Natural gas price trends

(Energy, Mines and Resources Canada, 1991) fold. Firstly, as little as 0.5 moles of methane are required to reduce one mole of SO_2. This represents a decrease of 15% in the methane requirement from the Allied process. Secondly, if the quantity of H_2S produced in the reduction stage is decreased, the Claus conversion unit can be reduced in size or eliminated completely, thereby reducing the capital and operating costs of the process. The general objective of the present thesis, therefore, was to develop a catalyst with improved selectivity and activity for the reduction of sulphur dioxide with methane.

This thesis consists of eight chapters. This introductory chapter is followed by a literature survey of the recent methods of sulphur dioxide reduction including kinetic and thermodynamic studies. In this chapter, a survey of the relevant catalyst investigations is also included. Chapter 3 contains the definition and scope of the study. The materials and methods of the experimental part of the project are discussed in Chapter 4. The results and discussion of the catalyst development work are included in Chapters 5 and 6. The kinetic model and mechanism of the reaction of sulphur dioxide with methane over the developed catalyst are given in Chapter 7. Finally, Chapter 8 contains the conclusions, original contributions, and recommendations for future work.

CHAPTER 2

LITERATURE SURVEY

Sulphur dioxide reduction has been studied using a wide variety of reducing agents including carbon, hydrogen sulphide, carbon monoxide, hydrogen and natural gas of which the primary component is methane. While most of these studies have focused on the effect of parameters such as reactant concentrations, and reactor temperature and pressure, many studies in recent years have also been performed where the focus is the effect of the catalyst on the reduction process.

In this chapter, a literature review is made concerning sulphur dioxide reduction processes using various reducing agents, the effectiveness of certain transition metal sulphides as catalysts for the reduction of sulphur dioxide with methane, the use of supported metal sulphides for hydrodesulphurization and SO_2 reduction reactions, and finally, the structure of these catalysts and the effect of preparation variables on their effectiveness as catalyst for hydrodesulphurization.

2.1 Reduction of SO_2 with Coal

The interest in using coal as a reducing agent is based primarily on the great abundance and relatively low cost of coal. The reduction of SO_2 with coal can be described as a "quasi-catalytic" process since the coal provides active sites for reaction and acts as the reducing agent in that it is consumed during the reaction. In order to obtain a better understanding of the mechanisms involved in this reaction, studies have been performed by various researchers including Panagiotidis et al. (1988), Moulton (1985), and Ratcliffe and Pap (1980).

2.1.1 Mechanism Studies for SO_2 Reduction with Coal

Ratcliffe and Pap (1980) investigated the reactivity of lignite and various types of coal in a thermogravimetric reactor system at temperatures between 600 and 800°C. They determined that the reaction between SO_2 and coal takes place in two distinct stages. The initial stage involves the volatilization of the coal. The second stage which is characterized by the reduction of SO_2 with the coal char surface, was found to be the overall rate limiting step and is controlled by the surface properties of the remaining coal char. It was concluded that the higher reactivity which was observed with lignite is attributable to a greater number of available active sites on the surface of the coal.

It was also found in this study that the coal deactivated over time. This was attributed to the formation of stable carbon-sulphur complexes on the surface, effectively poisoning the active sites. Alkali and alkaline earth metals in the lignite ash act as catalysts for the reaction between SO_2 and the complexes according to reaction 2.1.

$$\text{C-S (complex)} + SO_2 \xrightarrow[\text{site}]{\text{catalyst}} CO_2\ (g) + S_2 \qquad (2.1)$$

The presence of these metals in lignite further enhance the rate of SO_2 reduction in comparison to that of the other coals.

The primary objectives of the Moulton (1985) study included the production of a high purity sulphur, free from coal tar, and to determine the catalytic effect of fly ash produced during the reactions on overall reaction rates. Again, the temperature range considered was between 600 and 800°C. From the experimental results, it was concluded that if the coal devolatilization reaction is separated from the second reaction step of SO_2 reduction with the char, sulphur with a hydrocarbon content of less than 1% can be produced from SO_2 and coal. In addition, the coal ash, particularly that containing iron, was found to catalyze the reaction between SO_2 and the coal volatiles.

Moulton (1985) also proposed a process in which the reaction steps could be separated but suggested that further research was necessary to determine its viability. The process is based on the Tri-Gas low-BTU coal gasification process which uses a series of three fluidized beds. In this modified process, dried, ground coal is devolatilized in the first bed at 480°C. The devolatilized coal, or char, is then transferred to the second bed where it is gasified at temperatures between 870 and 980°C. The remaining carbon and ash are transferred to the third bed which also operates in the same temperature range as the second reactor bed. Sulphur dioxide rich gas is fed to the third reactor where it is heated and partially reduced. This stream is subsequently passed through the first bed where it is mixed with the coal volatiles and finally the volatiles are reacted with the SO_2 reducing it to elemental sulphur in the second bed. The product gas stream is later cooled for removal of the relatively pure elemental sulphur.

The kinetics of the reduction of SO_2 with anthracite was studied by Panagiotidis et al. (1988). Their experiments were performed using a fixed bed reactor operating in the temperature range of 750 to 850°C. In experiments with feed gas mixtures containing only SO_2 and N_2, the products consisted primarily of CO_2 and elemental sulphur. This study also confirmed the earlier findings of Ratcliffe and Pap (1980) where SO_2 conversion decreased with time due to carbon-sulphur complex formation. In the presence of water vapour, which would be the industrial case, the reaction mechanism was altered and the SO_2 conversion increased because of decreased complex formation; however, the quantity of H_2S produced increased significantly.

2.1.2 Patented Processes

Several patents exist in the literature describing processes for the reduction of SO_2 with coal, two of which are held by the Sumatomo Heavy Industries Ltd. (1980). The first of these processes involves reacting the SO_2 in a moving bed tower of granular carbon material at 700 to 900°C and then through a similar tower of granular catalyst at a temperature of 250 to 700°C. The catalyst contains various metal oxides supported on bauxite, Al_2O_3, SiO_2, or TiO_2. The second process involves reacting the SO_2 at a temperature of 700 to 900°C in a reaction zone packed with a mixture of coal or coke and a solid catalyst similar to those listed above. In both processes, the sulphur is subsequently condensed. Carbonyl sulphide, H_2S and CS_2 are also formed as by-products and require additional treatment.

2.1.3 Summary

Coal reduction of SO_2 has been only used on a limited basis for several reasons. Firstly, although low cost coal is available, swelling and caking properties of these coals cause reactor plugging. Secondly, the production of high quality sulphur is difficult since the coal's volatile matter contains tars which condense and mix with the sulphur product. Thirdly, high temperatures are required for the reactions to proceed at reasonable rates which when coupled with the presence of water vapour result in the production of by-products such as H_2S, COS, and CS_2. Finally, the reactor configurations using coal are complicated and, hence, more expensive to design and operate, and the reactions are more difficult to control than other SO_2 reduction processes using gaseous reducing agents.

2.2 SO_2 Reduction with Hydrogen Sulphide

The reduction of SO_2 with H_2S is the most widely used process for the production of elemental sulphur. This process, which is known as the Claus process, has the following reaction stoichiometry:

$$SO_2 + 2\ H_2S \dashrightarrow 2\ H_2O + 3\ [S] \qquad (2.2)$$

Elemental sulphur is denoted as [S] in order to account for all the sulphur species S_2 to S_8.

Hydrogen sulphide is generally obtained for this process from the sweetening of natural gas. In some cases, natural gas reserves in Alberta contain as much as 30% H_2S (Berk, 1984) and, therefore, there is a plentiful supply of this reducing agent in that area of Canada. Hydrogen sulphide can also be produced from the reduction of SO_2 with hydrogen or hydrocarbons. The Claus process would then be a second stage in such a sulphur recovery process and will, as such, be discussed in more detail in sections 2.4 and 2.5.

2.2.1 Catalyst Development

The research which has been conducted on the Claus process in the last decade has concentrated on the development of catalysts and the investigation of the resulting reaction mechanism. The objective is to develop a Claus unit which releases less SO_2 to the environment. At the present time, a typical plant handling 300 tonnes/day of H_2S with a recovery rate of 97% releases approximately 18 tonnes of SO_2 per day into the atmosphere (Oil Gas-European Magazine, 1988).

Typically, most Claus conversion units employ some form of alumina as a catalyst. Zotin and Faro (1989) investigated the influence of the basicity of alumina catalysts on their activity for the Claus reaction. Experiments were carried out in a tubular flow micro-reactor at 250°C. Two series of catalysts were examined including impurity free η, γ, and χ-aluminas as well as sodium doped η, γ, and χ-aluminas. It was observed that the order of activity for Claus reaction was:

$$\chi > \gamma > \eta$$

which corresponded to the order of SO_2 chemisorption capacity or basic site density. However, when sodium was added to the aluminas, activity dropped possibly due to the creation of strongly basic sites which led to the formation of unreactive chemisorbed SO_2 molecules.

2.2.2 Patent Review

In a Hungarian Patent by Feher et al. (1988) a process is described whereby a cobalt-molybdenum supported on gamma-alumina catalyst is used to reduce the CS_2 and COS present in the off-gases from a Claus unit with H_2 to H_2S at temperatures of 250 to 300°C. The resulting H_2S is then recycled to the Claus unit where it reacts with SO_2. The losses of sulphur are reported to be reduced by as much as 30% if the ratio of CS_2 and COS to H_2 is maintained between 1.0 and 1.2.

2.2.3 Summary

While the Claus process is an efficient method of recovering sulphur from SO_2 containing waste streams, and research is continuing to further increase sulphur recovery, this process is only feasible where large volumes of H_2S are available, as in Alberta. In the case of a smelter or coal burning power plant located in the eastern part of North America, large quantities are not easily available. Therefore, the Claus unit is not likely to find widespread implementation as a primary method of SO_2 removal in the future.

2.3 SO_2 Reduction with Carbon Monoxide

Carbon monoxide is a product of the steam reforming of methane and coal gasification processes according to the following reactions:

Steam reforming of methane:

$$CH_4 + H_2O \dashrightarrow CO + 3\ H_2 \qquad (2.4)$$

Coal gasification:

$$C + O_2 \dashrightarrow CO_2 \qquad (2.5)$$

$$C + CO_2 \dashrightarrow 2\ CO \qquad (2.6)$$

Since both natural gas and coal are plentiful and the technology exists for both processes, the potential supply of carbon monoxide is unlimited and its use as a reducing agent for SO_2 has thus been studied extensively.

2.3.1 Kinetic Studies

The use of a copper catalyst to promote the reduction of sulphur dioxide with carbon monoxide has been investigated by Querido and Short (1973), Okay and Short (1973) and Quinlan et al. (1973). In the study by Querido and Short (1973), it was found that the major reaction that removes sulphur dioxide is:

$$2\ CO + SO_2 \rightarrow [S] + 2\ CO_2 \qquad (2.6)$$

However, an important side reaction also occurs.

$$2\ CO + [S] \rightarrow 2\ COS \qquad (2.7)$$

This reaction was both homogenous and promoted by the catalyst at temperatures above 313°C.

Thermodynamically, numerous other reactions were also found to be possible, particularly in the presence of water and hydrogen which are often present in stack gases as well as the synthesis gas from which the CO is obtained.

It also was found that complete reduction of SO_2 with CO could be achieved over the Cu supported on alumina catalyst at temperatures greater than 450°C, CO to SO_2 ratios greater than unity, and at a contact time of 0.2 seconds. At these conditions, production of COS limited the sulphur removal efficiency to about 70%.

In order to reduce the quantity of COS produced, a dual reactor configuration was required. In the second reactor, the following reaction occurs.

$$2\ COS + SO_2 \dashrightarrow 3\ [S] + 2\ CO_2 \qquad (2.8)$$

Using the same Cu on alumina catalyst, and a temperature of 250°C in the second reactor, a sulphur removal efficiency of 97% was achieved. However, the requirement of dual reactors significantly increases costs and is, therefore, a major drawback to the use of carbon monoxide as a reducing agent.

2.3.2 Catalyst Development

Subsequent studies have focused on the development of a catalyst as a means of minimizing the production of COS in the first reactor. Zanevskaya <u>et al</u>. (1986) investigated the activities of iron, chromium, copper and nickel oxide supported on gamma-alumina catalysts containing 85% Al_2O_3 and 15% metal oxide each. The tests showed that with the chromium oxide catalyst at temperatures greater than 390°C and concentration ratios of CO to SO_2 less than 2.2, sulphur dioxide is reduced only to elemental sulphur, while at CO/SO_2 ratios greater than 2.2, COS is formed in addition to elemental sulphur.

It was also noted in the above study that the catalysts were reduced by the carbon monoxide at temperatures 20°C lower than required for the reduction of SO_2. This reduction further increased the catalyst activity. It was further observed that the addition of oxygen to the system decreased SO_2 conversion, probably by a combination of catalyst oxidation and reaction between oxygen and carbon monoxide to form CO_2 before CO could reduce SO_2. The addition of CO_2 was found to have no effect on the sulphur product distribution. A comparison of the catalysts was not included.

Hibbert and Campbell (1988) studied the catalytic behaviour of $La_{1-x}Sr_xCoO_3$ on the reaction of SO_2 and CO in a flow system at temperatures ranging from 500 to 650°C. Various catalyst compositions were used with $x = 0.3$, 0.5, 0.6, and 0.7. Reaction 2.6 was found to go to completion for stoichiometric mixtures of CO and SO_2 in the absence of oxygen. The $La_{0.7}Sr_{0.3}CoO_3$ catalyst ($x = 0.3$), at 550°C, gave the highest removal of sulphur dioxide at 99% with no COS formation. Once again, an excess of CO resulted in the production of COS. However, temperature was not found to have any effect on the product distribution within the temperature range tested.

Although these catalysts were introduced into the reactor as oxides, the presence of CO was found to reduce the catalyst and the adsorbed sulphur formed from the reduction of SO_2 resulted in the sulphidation of the catalyst. Excess concentrations of CO result in the formation of COS by reacting with the sulphided catalyst to yield a CO reduced catalyst according to reaction 2.9 as there is no SO_2 remaining with which the CO can react.

$$CO + \text{"sulphided catalyst"} \longrightarrow COS + \text{"CO reduced catalyst"} \qquad (2.9)$$

The chief recommendation arising from this study is that the activity of sulphides as catalysts for the reduction of SO_2 with CO needs further investigation since, as in the case of hydrodesulphurization catalysts, it is the metal sulphides, and not the oxides which are the main catalyzing components of the respective catalysts.

2.3.3 Patent Review

In addition to the above studies, there are numerous patents describing SO_2 reduction processes with CO. These include Denisov et al. (1987), Shakhatakhtinkii et al. (1985), Shakhatakhtinkii et al. (1981), and Babcock-Hitachi (1981). All of these patents describe processes using different catalysts for promoting the reduction to elemental sulphur. In the case of the Babcock-Hitachi (1981) process, the catalyst used contains MoO_3, NiO and/or CoO supported on TiO_2. It is claimed that the catalyst is active at temperatures as low as 150°C. In fact, when gas containing 12% SO_2, 5% CO and 20% H_2 was contacted with the patented catalyst, 99% conversion was achieved at 350°C compared to only 71% with a $NiO-MoO_3/Al_2O_3$ catalyst. However, no information concerning product distribution is given.

2.3.4 Summary

Despite the many studies and patents in the literature outlining processes and describing catalysts for the reduction of SO_2 with CO, no large scale industrial operation using CO as a reducing agent has ever been constructed. The primary reason is that of supply. Although in the future there may be substantial supplies of CO, at the present time there is not a large supply available and thus CO is relatively expensive. While other reducing agents may be less effective at the low operating temperatures at which SO_2 can be reduced with CO, natural gas, for example is presently much less expensive and is easily available in the large quantities necessary for industrial processes.

2.4 SO_2 Reduction with Hydrogen

Although hydrogen is not available naturally in large quantities, it can be produced by at least the following four methods (Berry, 1980).

i) Steam reforming of hydrocarbons
ii) Coal gasification

iii) Electrolysis of water

iv) Thermochemical decomposition of H_2S

The first two methods are the same as those described for the production of carbon monoxide in the previous section. The electrolysis of water, while technically feasible, is still economically unviable because of the large expenditure of electricity required. Finally, the thermochemical decomposition of compounds such as H_2S is, as yet, technically unproven, but has the potential to supply some of the future hydrogen demand. Therefore, like carbon monoxide, the potential supply of hydrogen is significant and its use as a reducing agent for sulphur dioxide has also been investigated extensively.

2.4.1 Mechanism of the Reduction of SO_2 with H_2

Murdock and Atwood (1974) studied the reduction of SO_2 with hydrogen in a packed-bed tubular reactor, in the temperature range of 300 to 400°C. In their investigation, they used activated bauxite as the catalyst. It was found that the rate of H_2S production increased rapidly with increasing hydrogen concentration and decreased slowly with increasing SO_2 concentration. Therefore, it appears that the reduction of SO_2 with H_2 progresses in two steps according to the following reactions.

$$SO_2 + 2\ H_2 \dashrightarrow 2\ H_2O + [S] \qquad (2.9)$$

$$H_2 + [S] \dashrightarrow H_2S \qquad (2.10)$$

It is proposed that the sulphur produced in the first reaction reacts with excess hydrogen in the second reaction. This study gives no indication as to how sulphur could be produced selectively. A two stage process involving a Claus conversion unit would probably be necessary.

A study of the surface reactions occurring during the reduction of SO_2 with H_2 over γ-alumina was performed by Nam and Gavalas (1991). Using temperature-programmed desorption (TPR) techniques, they showed that, in the presence of H_2, there are two types of adsorbed SO_2: a weakly adsorbed species which easily desorbs without reduction, and a strongly adsorbed species which is reduced to elemental sulphur or H_2S. Hydrogen sulphide is formed through reduction of adsorbed elemental sulphur or by reaction of H_2 with desorbed sulphur on the reactor wall. The amount of weakly adsorbed SO_2 decreased as the temperature was increased from 400°C to 500°C.

The conclusion from this study is that if alumina is to be used to catalyze the reduction of SO_2 with H_2, then the production of H_2S cannot be avoided if the temperature is to be high enough to achieve reasonable reaction rates. Consequently, further research will be required to find a catalyst with improved adsorption characteristics.

2.4.2 Catalyst Development

In a recent study by Alkhazov et al. (1991) alumina supported nickel oxide, molybdenum oxide, and nickel molybdate catalysts were tested for the reduction of SO_2 with H_2. The alumina supported nickel molybdate catalyst was the same as that used in the hydrodesulphurization of hydrocarbons.

The experiments were carried out in a tubular flow reactor operating at atmospheric pressure and a temperatures ranging from 200 to 500°C. The initial concentration of SO_2 used in this study was 5% and that of H_2 was varied between 10 and 15% corresponding to feed ratios of H_2/SO_2 of 2.0 and 3.0. Alumina alone did not exhibit any catalytic activity nor did the pure MoO_3. All other catalysts showed significant activity above 350°C and with contact times of 1.0 to 2.5 seconds.

It was observed that the activity of each of the catalysts increased with time. This was attributed to the sulphidation of the metal oxides. In the case of the $NiO-MoO_3/Al_2O_3$ catalyst, the composition after 30 hours of operation was found to include NiS, Mo_2O_3 and MoS_2. The pure MoO_3 catalyst, which did not show any activity, did not undergo any chemical change. Therefore, it was concluded that the sulphidation of the catalysts was due to the reaction products consisting of H_2S and elemental sulphur, except at the feed ratio of 3.0 where the only sulphur bearing product was H_2S.

It was also noted that the sulphided Ni-Mo/Al_2O_3 catalyst had a higher activity than when Ni was supported on alumina alone. When molybdenum was supported on alumina, activity was found to increase as the Mo content was increased. Therefore, the higher activity of the sulphided Ni-Mo/Al_2O_3 catalyst was attributed to the presence of the MoS_2 phase.

2.4.3 Patent Review

Many of the patents describing processes which can use hydrogen as a reducing agent for SO_2 involve the use of other reducing agents as well such as carbon monoxide or hydrocarbons and are described in other sections. One process which used hydrogen as the primary reducing agent and found industrial application in the past is the SCOT process.

The SCOT process (Shell Claus Off-gas Treating) process was developed by Shell Internationale Petroleum in The Netherlands (Naber et al., 1973). This process which consisted of two stages was developed to achieve virtually complete removal of sulphur compounds present in the off-gas from sulphur recovery units. The first stage is a reduction stage where all sulphur components including COS, CS_2, SO_2 and elemental sulphur are catalytically reduced over a CO-Mo/Al_2O_3 catalyst to H_2S using H_2 or a CO/H_2 mixture at a temperature of 300°C. The second stage is an absorption stage where the H_2S is selectively removed by amine absorption/regeneration and is recycled to the Claus unit for complete sulphur recovery. The amine is regenerable and, hence, there are no secondary waste streams.

Another patented process which uses only hydrogen for the reduction of SO_2 is held by UOP Inc. (1987). In this process, flue gas containing SO_2 is heated to 730°C and contacted with a 15-50% CaO catalyst supported on Mg-Al_2O_3 having a surface area of 159 m^2/g. The heated flue gas is then mixed with hydrogen and reacted at 730°C. It is claimed that up to 100% of the SO_2 can be removed.

2.4.4 Summary

Although hydrogen will be available in greater supply in the future, its cost of production by any method will likely make it uneconomical as a reducing agent. In addition, it has proven to be difficult, even with the development of various catalysts, to selectively reduce SO_2 to elemental sulphur without the production of H_2S. As a result, processes employing hydrogen as a reducing agent will have to use a Claus conversion unit for additional gas treatment further adding to process costs. Hydrogen is, therefore, unlikely to play a major role in future SO_2 treatment processes.

2.5 Reduction of SO_2 with Methane

Because of its availability and relatively low price, natural gas or methane, has been the reducing agent most used in large scale industrial processes for SO_2 removal from stack gases. World-wide proved reserves of natural gas total 127.4 trillion m^3 of which 2.21% or 2.8 trillion m^3 are located in Canada (True, 1992). Since the supply of natural gas is large and stable, and there is a pipeline distribution network which makes it available in all areas of Canada, at a relatively low price, natural gas is likely to be the most economically viable option as a reducing agent in SO_2 reduction processes.

2.5.1 Studies of the Reduction of SO_2 with CH_4 over Alumina

The primary reaction between SO_2 and CH_4 is:

$$2\ SO_2 + CH_4 \dashrightarrow 2\ H_2O + 2\ [S] + CO_2 \qquad (2.11)$$

In addition to the primary products, a number of side reactions may result in the production of undesired sulphur by-products, H_2S, COS, and CS_2. Other possible by-products of the above reaction system include CO, H_2 and elemental carbon.

The kinetics of the reduction of sulphur dioxide with methane in the presence of an alumina catalyst has been studied by various researchers including Sarlis and Berk (1988), Helmstrom and Atwood (1978), and Averbukh et al. (1968).

In their study, Averbuhk et al. (1968) found that at a SO_2/CH_4 molar feed ratio of 2.0, it is possible to obtain equilibrium yields of elemental sulphur as high as 100%, with the highest yields being obtained at the highest temperature tested of 1327°C. When the pressure was decreased, yields of elemental sulphur increased. At the lower feed ratios, the sulphur yield decreased. In fact, for a molar feed ratio of 1.0, as much as 99.8% of the sulphur in the product stream was found to be H_2S.

A quartz flow-type reactor was used for the kinetic and mechanism experiments. The concentration of SO_2 was varied between 10 and 40 % and the molar feed ratio of SO_2/CH_4 was varied between 1.0 and 2.0. The temperatures ranged from 800 to 1300°C.

It was concluded that the rate of reduction of SO_2 with CH_4, at temperatures between 850 and 1000°C is independent of the concentration of SO_2 and is controlled by the rate of pyrolysis of methane which is described by the first order kinetic equation:

$$r(CH_4) = A \exp(-E/RT)\ [CH_4] \qquad (2.12)$$

$$A = 7.08 \times 10^{13}$$

$$E = 364\ 705\ \text{j/mol}$$

where $r(CH_4)$ is the rate of consumption of methane.

In the investigation by Helmstrom and Atwood (1978), the reduction of SO_2 with CH_4 was studied using bauxite as the catalyst. Temperatures ranged from 550°C to 650°C and the pressure was maintained at one atmosphere. The SO_2 to CH_4 ratio was kept above 2.0. The SO_2 and CH_4 concentrations were varied from 0.04 to 0.79 atm and from 0.02 to 0.28, respectively. These conditions were chosen in order to minimize the production of by-products such as H_2S, COS, and CS_2. Under these conditions, the reaction stoichiometry was found to be as written in equation 2.11.

Helmstrom and Atwood determined that there were virtually no homogeneous reactions at temperature below 800°C. This suggests that the reaction rates being measured at the high temperatures used in the study by Averbukh _et al_. (1968) were probably a mixture of homogenous and heterogeneous reactions.

Helmstrom and Atwood developed two rate expressions, a single-site and a double-site model, which equally well predicted SO_2 and CH_4 reaction rates. The single site model is written as follows:

$$r(CH_4) = \frac{[3.34 \times \exp(-12300/RT)]\ P_{CH_4}}{[1 + 6.85\times10^{-4} \exp(22850/RT)\ P_{SO_2}]} \qquad (2.13)$$

The double-site model is written as follows:

$$r(CH_4) = \frac{[16.4 \times \exp(-6200/RT)]\ P_{CH_4}}{[1 + 3.13\times10^{-3} \exp(17600/RT)\ P_{SO_2}]^2} \qquad (2.14)$$

where $r(CH_4)$ = rate of consumption of CH_4 (gmol/kg-s).

P_i = partial pressure of species i (atm).

T = temperature (K).

R = 1.987 cal/mol-K

Under the reaction conditions used in the above study, the reaction rates are low. For an industrial process for the reduction of SO_2 using an alumina catalyst, reaction temperatures would have to be higher to increase the reaction rates. Sarlis and Berk (1988) reported rates of production of elemental sulphur and other reaction products at temperatures between 650 and 750°C and at molar feed ratios between 0.5 and 2.5. The quartz tubular flow reactor used in this study was run as a differential reactor in order that the initial feed compositions would reflect the effect of the average reactant concentrations on the reaction rates.

In addition to elemental sulphur, CO_2 and water, the products of the reaction at these conditions were found to be H_2S, COS, and CO. It was found that the formation of the by-products could be minimized by maintaining the molar feed ratio of SO_2/CH_4 above 2.0 and the temperature below 725°C. At these conditions, the yield of elemental sulphur was approximately 90%. However, the rate of production of elemental sulphur also decreased with decreasing methane partial pressure.

Sarlis and Berk (1988) also included a thermodynamic analysis of the SO_2-CH_4 system. Using feed mixtures containing 45% inert argon and appropriate amounts of SO_2 and CH_4 to make molar feed ratios of 0.5, 1.0, 1.5, 2.0, and 2.5, the equilibrium composition was determined at the temperatures of 627 and 727°C.

The primary sulphur containing by-product was found to be H_2S and its equilibrium concentration was maximized at a feed ratio of 1.0, confirming the findings of Averbukh <u>et al</u>. (1968). The concentrations of both COS and CS_2 were insignificant in comparison to that of H_2S. The mole fraction of elemental sulphur was found to become significant only at molar feed ratios greater than 1.5.

Overall conversion of SO_2 was 100% only at ratios less than 1.0. Above this ratio, conversions remained high, but decreased to approximately 70% at a ratio of 2.5. A comparison with experimental results showed that thermodynamic yields of elemental sulphur were consistently lower than experimental values. The conclusion from this comparison is that the kinetic experiments were not performed at equilibrium and that short contact times are desirable for promoting the yield of elemental sulphur.

The thermodynamic results also showed that significant amounts of hydrogen and carbon monoxide were present at equilibrium, particularly at the higher temperature. Elemental carbon was also found to exist at equilibrium at feed ratios less than 1.0 and 0.5 at 627°C and 727°C, respectively. The presence of elemental carbon at equilibrium was a factor not considered in a previous thermodynamic investigation of the SO_2/CH_4 system by Helmstrom and Atwood (1977). It can be concluded from these results that in order to obtain a pure sulphur product, free from carbon contamination, the reactor should be operated at lower temperatures even though somewhat lower rates of SO_2 reduction are obtained.

Akhemedov <u>et al</u>. (1986) investigated the reduction of SO_2 with methane using a aluminum-chromium catalyst. The feed gas mixtures contained 9-12% SO_2, and mole fractions of methane corresponding to feed ratios of SO_2/CH_4 of between 1.0 and 2.2. Experiments were performed at various volumetric flow rates in a quartz reactor tube loaded with the alumina-chromium catalyst. The temperature was varied between 600 and 900°C.

A maximum yield of elemental sulphur of 77.4% was obtained at the temperature of 750°C and a contact time of 0.14 s^{-1}. The addition of water vapour to the system increased the amount of H_2S produced and decreased the maximum sulphur yield to 65.6%. The experiments showed that H_2S was produced even at a SO_2/CH_4 ratio of 2.2. However, it was concluded that the aluminum-chromium catalyst has improved catalytic characteristics over alumina alone for use in the reduction of SO_2 with CH_4 when considering that the reduction could be run at a temperature as low as 750°C and a SO_2 conversion of 93 to 96% could be achieved when taking a subsequent Claus treatment into account.

2.5.2 Patent Review

In addition to the Allied Chemical process described in Chapter 1, there are many patents in the literature describing processes for the reduction of SO_2 with CH_4 with elemental sulphur as the by-product. One such process is the Citrex process developed by Peabody Engineered Systems (Vasan, 1975).

The first stage of this process involves scrubbing the flue gas free of fly ash and other particulate matter. A buffered, recyclable, citrate solution is then used in a countercurrent scrubber, at a temperature of 50 to 60°C, to remove SO_2 from the gas stream. The SO_2 containing liquor from the scrubber is then contacted in a reactor operating at atmospheric pressure and 600°C with H_2S to convert all the SO_2 to sulphur and water in a complex process resembling a liquid phase Claus conversion. Some of the elemental sulphur is then reduced to H_2S with natural gas to be recycled to the Claus unit. This unit has an overall SO_2 removal efficiency of 95 to 97% and can be used to treat low SO_2 concentration gases from power plants or high concentration gases from smelters.

Another patent, by McMillan (1971), also describes a process using a gaseous hydrocarbon as the reducing species. This process, which is shown in Figure 2.1, first involves mixing sulphur dioxide with a gaseous hydrocarbon. The mixture is preheated to 500 to 560°C. This mixture is then mixed with the combustion products of a hydrocarbon in order to increase the temperature to the range of 650 to 1050°C. The gas is then sent to a series of catalytic reactors where a portion of the sulphur dioxide is converted to H_2S and

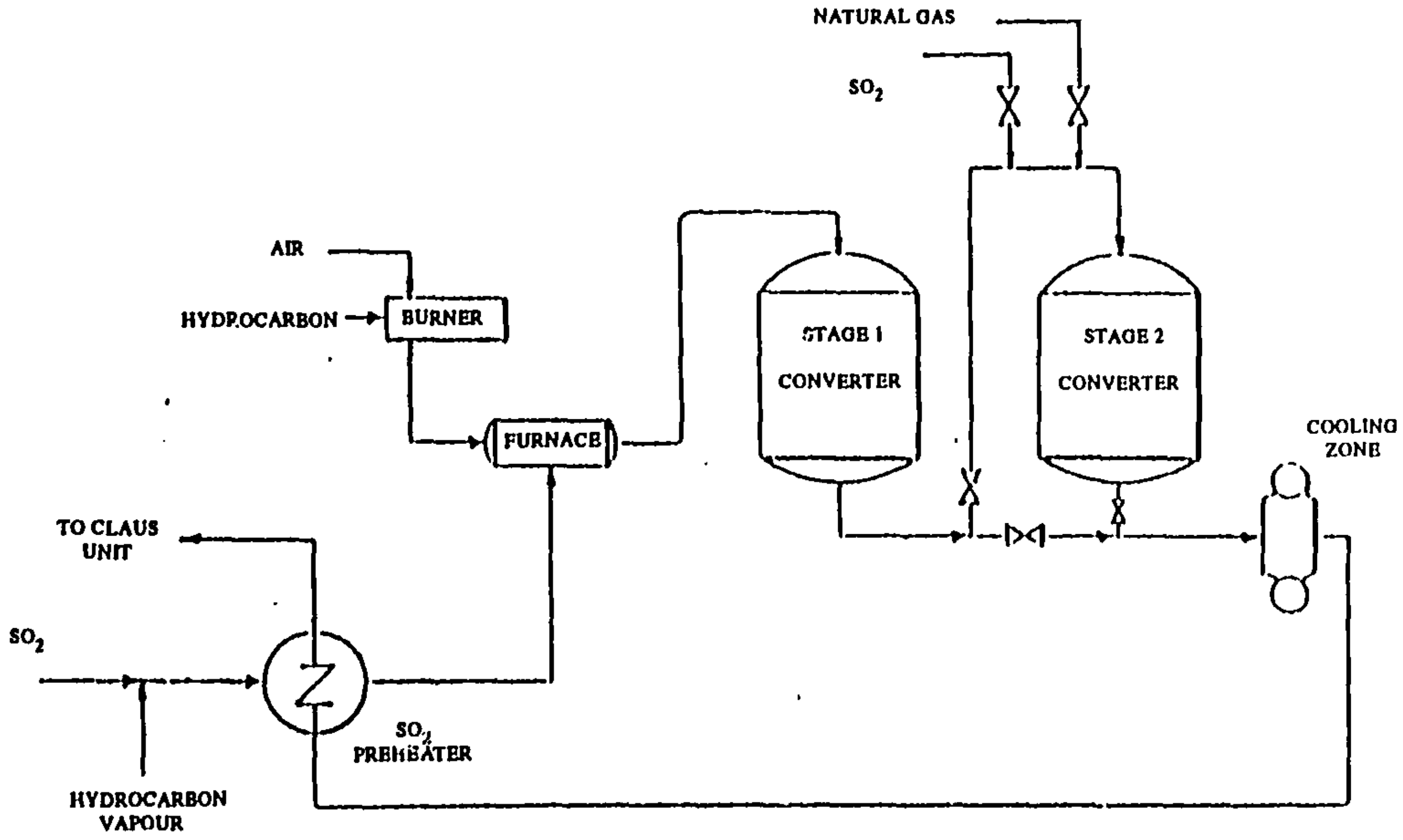


Figure 2.1 SO_2 reduction process

(McMillan, 1971)

elemental sulphur. The converted gas is then cooled and delivered to a Claus unit. The catalytic reactors are operated at temperatures less than 1100°C and the catalyst used is generally some form of alumina.

Other patents describe processes using various catalysts and operating temperatures. Most of these processes involve reacting SO_2 with either methane or other hydrocarbons to produce mixtures of elemental sulphur and H_2S or only H_2S. In these types of processes, a type of Claus conversion unit is always necessary. A list of these patents is given in Table 2.1.

One of the disadvantages often associated with SO_2 reduction processes is that they are technically not well suited for treating low concentration SO_2 streams such as those from fossil fuel burning power plants. For this reason, their application has been almost exclusively limited to the treatment of high SO_2 concentration smelter stack gases. Recently, Union Carbide developed a process trade-marked CANSOLV (Barnett and Sarlis, 1992) which is based on a regenerable aqueous amine scrubbing solution that has the capacity to remove over 99% of SO_2 from any stream. The product of this process is a concentrated stream of sulphur dioxide suitable for natural gas reduction to elemental sulphur. Therefore, the catalytic reduction of

Table 2.1

Patents Involving Natural Gas Reduction of SO_2

Title	Catalyst
U.S Patents	
Catalytic Reduction of Sulfur Dioxide, (Bridwell and Carlson, 1973).	Calcium Aluminate
Process for Reduction of SO_2, (Stiles, 1973).	Cobalt Chromite on Al_2C_3
German Patents	
Sulfur recovery from Sulfur Dioxide-Rich Flue Gases, (Marold and Heisel, 1988).	Hydrogenation Catalyst
Catalytic Reduction of Sulfur Dioxide, (Michener et al., 1971).	Calcium Aluminate
Soviet Patent	
Method for Recovering Sulfur from Sulfur-Containing Gases, (Zal'tsman et al., 1980).	Al_2O_3
Japan Patents	
Reduction of Sulphur Dioxide in Waste Gas, (Suehiro et al., 1991).	Group VIa and VII elements on Al_2O_3
Sulfur Dioxide Reduction Catalyst, (Chiyod Chemical Engineering and Construction Co., 1980).	Cu and Vanadium oxides on Al_2O_3
Reduction of Sulfur Dioxide, (Muronaka et al., 1980).	Cu, Ag, or Zn oxides on Al_2O_3

SO_2 could now be used in conjunction with the CANSOLV process to treat any SO_2 concentration waste stream.

2.5.3 Summary

Natural gas, of which the primary component is methane, is in plentiful supply and is available at a relatively low price in comparison to the other possible reducing agents for SO_2. For this reason, many studies and patents are found in the literature. The studies have revealed that the production of by-products such as H_2S, is difficult to inhibit by varying reaction conditions including reactant feed concentrations and ratios, and reactor temperatures. The production of H_2S as opposed to elemental sulphur increases consumption of methane and necessitates a Claus conversion step for sulphur recovery increasing costs.

As a result of the limited success in promoting reaction 2.11 without the production of by-products using alumina or bauxite, various other catalysts have been studied for the reduction of SO_2. As stated in section 2.5.1, an alumina-chromium catalyst also met with limited success. In the following section, studies with various transition metal sulphides are discussed. The outcome of these investigations formed the basis of the study in this thesis.

2.6 Transition Metal Sulphides as Catalysts

Metal sulphides are generally considered to be high temperature catalysts. In fact, when used as hydrogenation catalysts, they become more active at high temperatures than metallic catalysts. Sulphide catalysts, such as MoS_2, also have a high capacity for hydrogen adsorption and they resist poisoning, especially by sulphur compounds, and coking (Mitchell, 1977). In addition, transition metal sulphides are also known to catalyze the decomposition of H_2S (Chivers et al., 1980). For these reasons, three pure transition metal sulphides, MoS_2, WS_2, and FeS were selected for study by Mulligan and Berk (1989) as catalysts for the reduction of SO_2 with CH_4.

2.6.1 SO_2 Reduction with CH_4 over Pure MoS_2, WS_2, and FeS

In the study by Mulligan and Berk (1989), the catalysts were tested for the reduction of SO_2 with CH_4 in the temperature range of 650 to 750°C and with inlet molar feed ratios of SO_2/CH_4 ranging from 0.5 to 2.0. Using x-ray diffraction analysis, both the MoS_2 and WS_2 were found to be stable under all reaction conditions. Iron sulphide, on the other hand, was found to incorporate sulphur in its crystal structure, forming non-stoichiometric iron sulphide (pyrrhotite).

The surface areas, as measured by the BET method, of both MoS_2 and WS_2 were low. After an initial period of experimentation when the surface areas decreased, the surface areas of MoS_2 and WS_2 stabilized at approximately 3.7 and 2.3 m^2/g. Because of problems in measuring the surface area of FeS, a stable measurement was not obtained, and reaction rate results, which were based on the surface area, were reported for MoS_2 and WS_2 only.

For the purpose of comparing catalysts, catalytic activity was defined as the rate of consumption of sulphur dioxide. In addition, selectivity for the production of elemental sulphur was defined as follows.

$$s = \frac{r(S)}{r(H_2S) + r(COS)} \qquad (2.15)$$

where r(i) is the rate of production of species i in mol/m^2-s. Values for selectivity can range from zero, where no elemental sulphur is formed, to infinity where the only sulphur bearing product is elemental sulphur. Finally, carbon dioxide yield was defined as:

$$\%\ Y(CO_2) = \frac{r(CO_2)}{r(CH_4)} \times 100\% \qquad (2.16)$$

This expression gives the percentage of carbon from reacted methane which appears in the product stream as the desired carbon product, carbon dioxide.

Direct comparison of the catalysts based on the above criteria was made at a temperature of 700°C and a molar feed ratio of 1.0. It was found that in comparison to alumina, MoS_2 provided significantly higher sulphur selectivities than alumina and activities equal to those of alumina. Again comparing to alumina, WS_2 also provided significantly higher selectivities, however, the activity was found to be twice that of alumina. Although reaction rates were higher for WS_2 than for MoS_2, MoS_2 was concluded to be a better overall catalyst because of the lower production of by-products, less elemental carbon production, and lower cost.

Several recommendations resulted from the above study including the following. Although pure crystalline MoS_2 was a promising catalyst for the reduction of SO_2 with CH_4, there are two problems which had to be solved if the catalyst were to be used in a large-scale industrial process. First, the pure MoS_2 pellets used in the study had a low specific surface area which was 1/25th that of alumina. This implies that a relatively large mass of MoS_2 would be required to obtain conversions found with much smaller quantities of alumina. The second consideration is cost, as pure MoS_2 is prohibitively expensive. It was recommended that a catalyst support for MoS_2 such as alumina or silica-alumina be used, thus providing the required high surface area and a cost more in line with the traditionally used alumina pellets.

2.6.2. Supported Molybdenum Catalyst Research

A sulphided cobalt-molybdenum catalyst using alumina as a support has been used for the reduction of sulphur oxides in the liquid phase (Universal Oil products Company, 1974). An aqueous solution of sodium thiosulphate was reduced using hydrogen with reaction temperatures ranging from 125 to 175°C. No kinetics were reported; however, conversions to sulphur were found to be as high as 98%, depending on the catalyst preparation procedure and reaction temperature.

In a more recent study, the reduction of SO_2 with CH_4 using two hydrodesulphurization (HDS) catalysts was studied by Sarlis and Berk (1992). One of the catalysts used was 3.5% CoO-14% MoO_3/Al_2O_3 and the other was 10-12% MoO_3/Al_2O_3. Kinetic results were reported for the reduction of SO_2 with molar feed ratios of SO_2 to CH_4 from 0.5 to 2.5 and temperatures from 650 to 750°C. The cobalt-containing catalyst was the more active of the two. However, the molybdenum catalyst was more selective for the production of elemental sulphur. In addition, a proposed mechanism based on the kinetic results attributed the production of the undesired by-products to the cracking of CH_4. The catalysts were also found to become sulphided as the reaction between SO_2 and CH_4 progressed. The sulphidation was attributed primarily to the elemental sulphur produced during the reaction. The effect of the molybdenum or cobalt loading on the catalyst performance was not investigated nor was the stability of the supported catalysts.

Although the above cases are examples of the use of supported molybdenum catalysts, such catalysts are primarily being used for hydrodesulphurization reactions. Therefore, most of the research on this catalyst reported in the literature is based on this reaction system. An HDS catalyst is used to catalyze the reactions to remove sulphur from hydrocarbons and gasified coal. Because of this industrial importance, the literature abounds in information concerning the effect of process variables on the activity and selectivity of this catalyst.

The exact structure of molybdenum supported on alumina is still a subject for debate. For example, most HDS catalysts include a promoter such as cobalt which increases significantly the activity of a molybdenum supported catalyst. The reasons presented in the literature for explaining the promoting role of cobalt are numerous and have been summarized by Massoth (1978). The promoting role of cobalt has been ascribed to:

1) an increase in Mo dispersion over the support surface by preventing the crystallization of MoS_2,
2) An intercalation effect with MoS_2 leading to the formation of Mo^{3+},

3) a specific kinetic effect where cobalt may affect adsorption-desorption properties, and

4) a decrease in deactivation due to decreased coking.

One of the more recent contributions to the list is from Topsoe et al., (1987) who conclude that the promotional effect of cobalt is due to an increased electron density on the neighbouring sulphur and molybdenum atoms.

2.6.3 Effect of Catalyst Preparation on HDS Activity

The catalytic behaviour of supported HDS catalysts containing molybdenum is dependent on the manner in which the catalysts are prepared. Makovsky et al. (1984) used various analytical techniques to identify the oxide species present in a $CoO-MoO_3/Al_2O_3$ catalyst. Some of the species identified include $CoMoO_4$, Co_3O_4, MoO_3, $CoAl_2O_4$, and $Al_2(MoO_4)_3$. It was found that the species present depends on the catalyst preparation conditions such as the degree of calcination of the Al_2O_3 support before impregnation. Alumina can exist in many different phases which is dependent not only on the starting material, but also on the heating rates and presence of impurities (Gitzen, 1970). Figure 2.2 is an alumina phase diagram showing the possible pathways for phase transition. The different alumina phases can have varying concentrations of acid sites leading to catalysts with different characteristics (John and Scurrell, 1977).

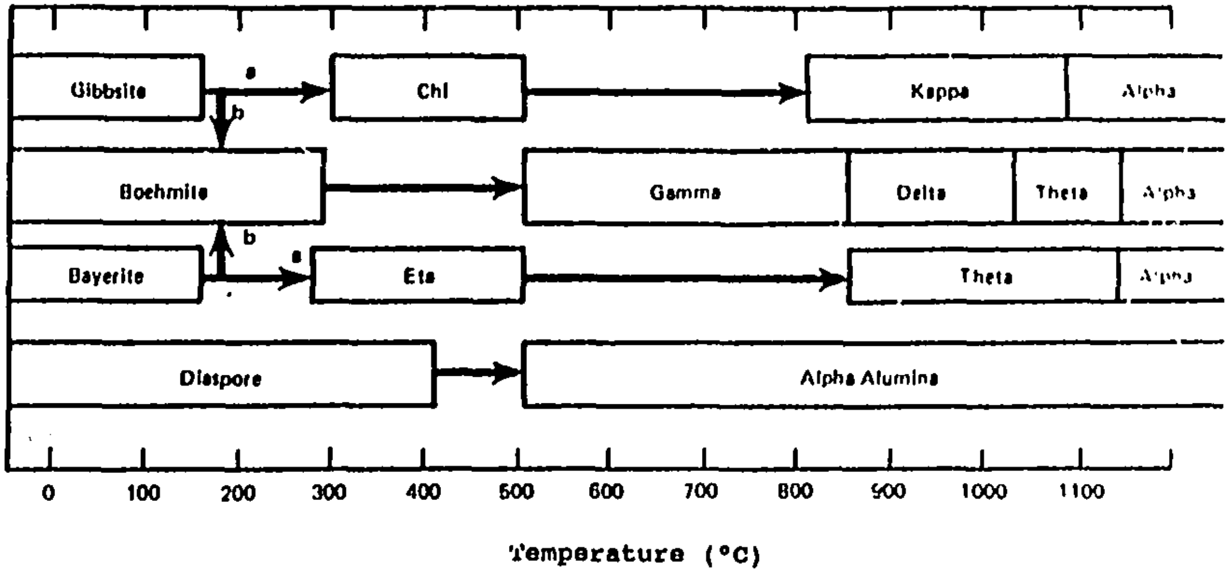
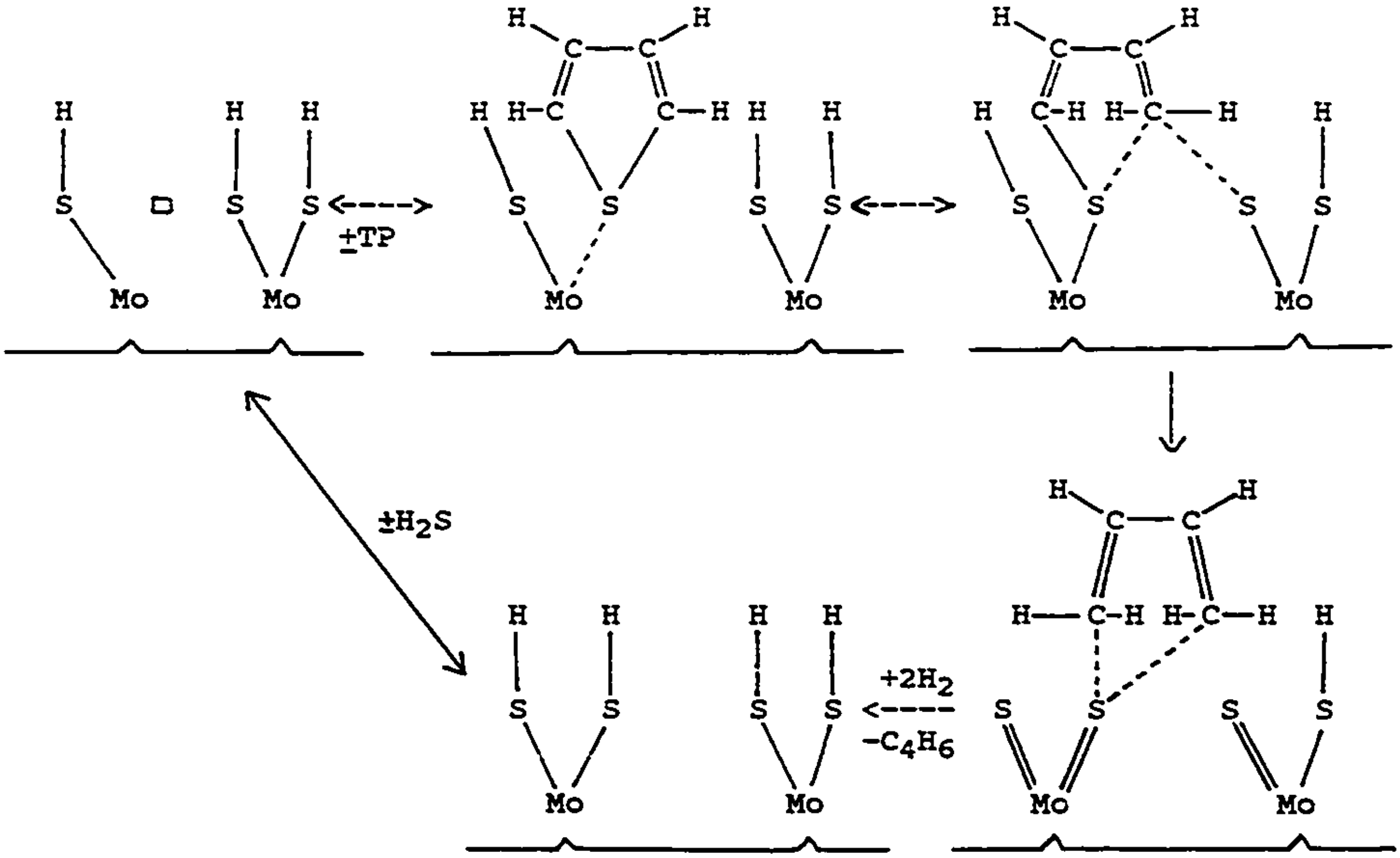


Figure 2.2 Alumina phase diagram

(Gitzen, 1970)

The sulphide form of the Co-Mo/Al_2O_3 catalyst is the active form for HDS. Consequently, there is a relationship between the oxide species initially present as described above, and the subsequent characteristics of the sulphide phase, affecting the catalytic activity. The relationship between catalyst sulphidation and activity for thiophene hydrodesulphurization has been studied by Massoth and Kibby (1977). Firstly, it was found that the activity of a MoO_3/Al_2O_3 catalyst was similar when either H_2S or thiophene was used as the sulphiding agent with the predominant reaction being the exchange of oxygen with sulphur atoms, with some anion vacancies also being formed. Catalysts which were prereduced with hydrogen, sulphided to a lesser extent than the oxide form. As far as activity is concerned, the oxidized catalyst initially was inactive, followed by a period of high activity, and then a gradual decline in activity. However, prereduced catalyst showed high initial activity, followed by declining activity. In the case of the oxidized catalyst, initially no vacancies were present, and some were formed during the reaction with thiophene. On the other hand, the catalyst prereduction procedure resulted in vacancy formation and high initial activity. Therefore, it appears that vacancies are necessary for thiophene (TP) reaction according to the mechanism shown in Figure 2.3 and activity decreases over



Vacancy - □

Figure 2.3 Thiophene reaction mechanism

(Massoth and Kibby, 1977)

time as the vacancies become poisoned with coke, H_2S, and sulphur.

Other catalyst preparation procedures can affect the subsequent structure and, therefore, activity of the catalyst. These include the pH of the impregnating solution, the order of use of impregnating solutions for bimetallic catalysts, and lastly, the addition of cations to the support. In the first case, it was found that when an acidic $(NH_4)_6Mo_7O_{24}$ impregnating solution was used, the resulting Mo/Al_2O_3 catalyst had a higher activity than when a similar basic solution was used (Houalla, et al., 1983). This was explained by the fact that better molybdenum dispersion was achieved in acidic media.

In addition to cobalt, nickel has also been used as a promoter in a bimetallic molybdenum based catalyst. Ledoux, et al. (1987) studied the effect of preparation of $Ni-Mo/Al_2O_3$ on its activity for HDS reactions. The results showed that there was no difference in activity for catalysts prepared by successive impregnations or coimpregnation of molybdenum and nickel salts.

The presence of metal cations in alumina can have a significant effect on the activity of a supported molybdenum catalyst. The effect of sodium on the hydrodesulphurization of thiophene was studied by Lycourghiotis and Vattis (1982).

A summary of the results yields the following two points. Firstly, in the preparation of Co-Mo/Al_2O_3, the results of the above study by Ledoux, et al., (1987) were similar. The order of the impregnation had no effect on the activity. Secondly, the sodium doping of the support led to a progressive decrease in the activity. This was attributed to the partial scavenging of Mo^{VI} by Na^+ to form $NaMoO_4$.

2.6.4 High Temperature Stability

HDS catalysts have been extensively characterized with respect to their surface area, structure, and chemical composition at temperatures below 500°C, the upper limit for these reactions. However, the lowest temperature at which the reduction of SO_2 with CH_4 has been found to occur at reasonable rates is 650°C and, hence, the stability is not known. An important aspect of the stability of the catalyst is the crystallinity of the MoS_2 phase on the surface. Crystallization of MoS_2 has been observed at HDS reaction conditions when the initial MoO_3 content exceeds 10 wt% at which point it is no longer well dispersed over the alumina surface in a monomolecular layer (Okamoto et al., 1977). However, it was also found that if a large degree of molybdenum sulphidation is desired, higher loadings of MoO_3 are required. While crystallization of MoS_2 leads to catalyst deactivation for HDS reactions, pure crystalline MoS_2 has itself been found to be catalytic for the reduction of SO_2 with CH_4 (Mulligan and Berk, 1989). Since the reaction temperatures are above 650°C, and the sublimation temperature of MoS_2 is only 450°C, it is possible that the MoS_2 phase could be removed from the support surface.

2.7 Literature Review Summary

1) Sulphur dioxide can be reduced using a variety of different reducing agents such as coal, hydrogen sulphide, carbon monoxide, hydrogen, and methane. The reduction of sulphur dioxide with methane has received the most attention because methane is available in plentiful supply and has a relatively low cost, and is potentially less hazardous than the other gases. In addition, a high quality sulphur is obtained as an end product.

2) In most studies of the SO_2 reduction with CH_4 system, some form of alumina has been used as a catalyst. When alumina catalyst is used, both elemental sulphur and large quantities of H_2S are produced. This implies that a relatively large amount of methane results in the production of H_2S which has to be treated further in a Claus conversion stage.

3) Molybdenum sulphide has been shown to be selective for the production of sulphur and have an activity equal to

that of alumina. Because of its high cost and low surface area, MoS_2 must be supported on a suitable support material such as alumina or silica-alumina.

4) Alumina supported MoS_2 is currently being used as an hydrodesulphurization (HDS) catalyst. For HDS reactions, the addition of a promoter such as cobalt to the catalyst increases the activity. The loading of both the molybdenum and the cobalt promoter have an effect on the performance of the catalyst as does the molybdenum sulphidation procedure, and the state and composition of the alumina support.

5) The temperature of the HDS reaction system is always less than 500°C. Therefore, no studies have been performed to determine the effect of high temperatures (650 to 750°C), necessary for the reduction of SO_2 with CH_4, on the behaviour of the MoS_2 phase on the support surface.

CHAPTER 3

RESEARCH OBJECTIVES

As evidence concerning the detrimental effects of SO_2 on the environment accumulates, and as government regulations regarding SO_2 emissions become more strict, the development of effective and economical SO_2 treatment methods becomes more necessary. The reduction of SO_2 with methane is an interesting alternative to the methods currently being used because elemental sulphur which is produced as an end product is saleable and easily handled safely.

Although processes implemented in past based on the reduction of SO_2 with CH_4 have met with limited economic success, the process can be made more cost effective by developing a catalyst which will reduce the production of H_2S. The minimization of H_2S production will reduce the overall cost of the process by reducing the size or eliminating the subsequent Claus conversion stage, and by reducing the CH_4 requirement.

The primary objective of this research is to support MoS_2 on a support material such as alumina or silica-alumina and examine its effectiveness as a catalyst for the reduction of SO_2 with CH_4. The catalyst must show high selectivity for the production of elemental sulphur, activity equal to, or greater than, that of alumina, and stability under the severe reaction conditions.

3.1 Statement of Objectives

1) To investigate the effect of the catalyst preparation variables including molybdenum loading and support material on the effectiveness of supported MoS_2 as a catalyst for the reduction of SO_2 with CH_4.

2) To determine the high temperature stability of the supported MoS_2 catalyst.

3) To compare the activity, selectivity, CO_2 yield, and elemental carbon production of the supported catalyst with alumina and pure MoS_2.

4) To compare the methods of catalyst sulphidation using H_2S with the method using SO_2 and CH_4 and examine the thermodynamics of these heterogeneous systems.

5) To determine the reaction kinetics and the rate law of the SO_2 reduction with CH_4 over the developed catalyst.

CHAPTER 4

MATERIALS AND METHODS

In this chapter, the procedures used to prepare and analyze the catalysts, and the equipment used in the preparation of the catalysts and the determination of reaction rate data, are described. In addition, the calculation procedures used in the computer program for the determination of reaction rates from the raw data are discussed.

4.1 Catalyst Preparation

Spherical activated alumina pellets with an average diameter of 2 mm were obtained from ALCAN Chemicals, Brockville, ON. As specified by the manufacturer, these pellets contained approximately 65% η-alumina, 30% χ-alumina, and 5% boehmite. Cylindrical SiO_2-Al_2O_3 pellets were purchased from STREM Chemicals, MA. These pellets were 2 mm in both diameter and length, and had a composition of 87% SiO_2 and 13% Al_2O_3. Reagent grade ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and cobalt nitrate $Co(NO_3)_2\cdot 6H_2O$ were both obtained from Johnson Matthey Inc., Melvern, PA. All the compressed gases that were used in the preparation of the catalysts and in the kinetic experiments were purchased from either Cryo-Gas or Matheson of Canada. Table 4.1 shows the grade, purity, and supplier of each gas.

Table 4.1

Supplier and Purity of Compressed Gases

Gas	Supplier	Grade	Purity
Ar	Matheson	Ultra High Purity	99.999%
Air	Cryo-Gas	Zero Zero	HC < 0.1 ppm
CH_4	Matheson	Commercial	> 93%
H_2S	Matheson	Technical	99.0%
SO_2	Cryo-Gas Matheson	Anhydrous Pure	99.98%
He	Cryo-Gas	High Purity	99.995%
N_2	Matheson	Prepurified	99.998%

Before impregnation, both types of pellets were conditioned to remove volatile contaminants at 600°C for 6 hours in a flow of argon in a tubular reactor (See section 4.3.1) and then kept dry in an oven at 125°C. The supported molybdenum catalysts were prepared by impregnating the pellets with solutions of ammonium heptamolybdate. Preliminary experiments showed that 100 g of either alumina or silica-alumina support material can absorb 100 cm^3 of solution; thus the desired loading of the catalyst, whether 5, 10 or 15% Mo, was obtained by fixing the concentration of ammonium heptamolybdate in the impregnating solution (Table 4.2). The loading of the catalyst, which is expressed as a percentage, is calculated by dividing the mass of elemental molybdenum contained in a catalyst sample by the sum of the masses of alumina and elemental molybdenum in that sample. For example, a 15% Mo loading is defined as 15 g of the element molybdenum added to 85 g of dried support pellets. The molybdenum loading was based on the element, and not on the sulphide or oxide, because the oxidation and sulphidation states of the molybdenum change throughout the preparation procedure and reaction process while the quantities of both Mo and support material in most cases remained constant throughout.

Having determined the appropriate concentrations, the solutions for impregnation of the pellets were prepared by dissolving the ammonium heptamolybdate in deionized water.

Table 4.2

Concentration of Impregnating Solution

Catalyst Mo Loading	Ammonium Heptamolybdate Concentration (g/cm^3)
5% Mo	0.097
10% Mo	0.204
15% Mo	0.324

The solution was then mixed with the pellets and allowed to soak at room temperature for a period of 6 hours. Throughout this period, the pellets were occasionally stirred to allow air bubbles to escape thus maximizing contact between pellets and solution. The pellets were then placed in a oven at 110°C for 16 hours to remove ammonia and water.

Once dried, the pellets were calcined in a flow of zero zero grade air in the reactor tube at 500°C for a period of 24 hours. The product of this procedure was MoO_3 supported on either Al_2O_3 or SiO_2-Al_2O_3 as determined by X-ray diffraction analysis (See section 4.2.3). The alumina supported catalysts were then sulphided by one of the sulphidation procedures described below. All silica-alumina supported catalysts were sulphided using H_2S.

In the case of sulphidation with H_2S, the quartz reactor tube was first purged with argon. The flow of argon was then replaced with a flow of 12% H_2S in argon, and the temperature was increased to 600°C. This procedure was continued until the uptake of H_2S was completed as determined by gas chromatographic analysis of the reactor exit gases. For a 15 g sample of a 15% Mo/Al_2O_3 catalyst, approximately 5 hours were required. Following sulphidation, the flow of H_2S was replaced by pure argon and the temperature was increased to 750°C to remove any excess sulphur from the catalyst pores to ensure that all sulphur present was combined with molybdenum. Samples were then stored in a desiccator at ambient temperature until use.

In the case where MoO_3/Al_2O_3 catalysts were sulphided with SO_2 and CH_4, the following procedure was used. After purging the reactor with argon, a gas flow containing a mixture of 25% SO_2, 25% CH_4, and 50% Ar was fed to the reactor. The sulphidation temperatures used were 650°C, 700°C, or 750°C. For all temperatures, the sulphidation procedure was considered to be completed when steady state was achieved as determined by gas chromatographic analysis of the reactor exit gases. At intervals of 15 minutes, samples were analyzed until three consecutive analyses yielded results within 5% of each other.

The steps in preparing the 5% Co-15% Mo/Al_2O_3 catalysts pellets were essentially the same as described above. The main difference, however, was in the composition of the impregnating solution. An appropriate quantity of cobalt nitrate (0.248 g/cm^3 solution) was added to the ammonium heptamolybdate solution. This solution was then mixed with the dried alumina pellets in the same proportions as described above.

4.2 Catalyst Characterization

4.2.1 Surface Area Analysis

The surface areas of each of the catalysts were measured before and after experimentation using a Micromeritics Flowsorb Model 5200 surface area analyzer which measures surface areas using the BET method. The total flow of gas through the instrument was 0.5 cm^3/s of which 70% was helium and 30% was nitrogen. This apparatus was calibrated on a daily basis.

Normally, 0.5 g catalysts samples were degassed at a temperature of 200°C until constant weight was achieved. The dried samples were then transferred immediately to the test port where the sample holder was immersed in liquid nitrogen for nitrogen adsorption from the gas stream until the reading of the thermal conductivity detector (TCD) of the analyzer stabilized. The nitrogen was then desorbed by replacing the cold nitrogen bath with a warm water bath. The quantity of nitrogen desorbed was used by the instrument to calculate the surface area of the catalyst sample. Replicates were performed for each sample and showed that measurements varied by less than 2%.

4.2.2 Scanning Electron Microscopy

A scanning electron microscope (JOEL model 840 A) was used to determine the degree of change in the catalyst surface texture due to reaction conditions. The instrument was also equipped with a Tracor Northern model TN5402 energy dispersive x-ray analyzer which provided qualitative elemental analyses of the catalyst surface.

Catalyst pellets were first snapped in half and glued to sample holders using carbon paint. The half-pellets were placed on the sample holders with the inside surface exposed. The samples were then carbon coated in order to minimize charging during analysis. The surfaces were examined using a power of 10 kV and magnifications ranging from 300 to 10000 times. X-ray mapping, using a Tracor Northern model TN5700 image analysis system, was also performed in order to verify the uniformity of the molybdenum and cobalt distributions throughout the pellets.

4.2.3 X-Ray Diffraction Analysis

X-ray diffraction (XRD) analysis was used to determine the bulk composition of the crystalline phases present in the pellets. For XRD analysis, the samples were required to be in powder form. This was accomplished by using a mortar and pestle. Catalyst samples were pulverized under liquid nitrogen to prevent oxidation.

Powdered samples were placed in a 12.5 mm sample holder for analysis. The diffractometer consisted of a copper x-ray generator (American Instrument model Max 3100), a Philips goniometer (model PW 1050/65), and a Philips diffractometer controller (model PW 1710). For the analyses, the generator was set at 40 kV and 20 mA and the scanning rate was set at 0.02 deg/s over an angle range of 10 to 100°.

The x-ray diffraction pattern generated from the above analysis is unique for each crystalline material. The experimentally determined powder diffraction pattern consists of a list of d-spacings, calculated from the diffraction angles, and the corresponding intensity of the reflected beam. Each pure crystal has a characteristic diffraction pattern which has been filed by the Joint Committee on Powder Diffraction Standards (JCPDS, 1979). The powder patterns of the catalysts samples were then compared to the standards for a qualitative analysis of catalysts' components.

4.2.4 Wet Chemical Analysis

Catalyst samples weighing 0.1 g each were dissolved in 100 cm^3 of aqua regia at 60°C for a period of 72 hours. A 10 cm^3 sample of the resulting solution was then diluted to 100 cm^3 with deionized water and analyzed for molybdenum and aluminum content using an atomic absorption spectrophotometer (Thermo Jarell Ash Corp. Model Smith-Hieftje II). Aluminum and molybdenum cathode tubes supplied by Corning, ON., were used.

The atomic absorption spectrophotometer was calibrated each day of analysis using molybdenum and aluminum atomic absorption standard solutions purchased from Aldrich, WI. The calibrations were also verified after each five samples. Replicates were also performed. Error associated with the measurements was typically within 5%. In all cases, molybdenum was the only element detected as alumina was not dissolved by the aqua regia solution.

4.2.5 CHNOS Analyzer

An elemental analyzer (Control Equipment Corp. Model 240XA) was used to determine the quantity of sulphur present in the pellets. Before use, the analyzer was calibrated with a sulphur standard and tested with pure crystalline MoS_2. The error was within 3%. The catalyst samples to be analyzed by this instrument were in powder form, prepared in the same manner as described in section 4.2.3.

The analytical procedure for sulphur is as follows. Approximately 1 to 3 mg of sample are mixed with 50 mg of WO_3 which acts as an oxidizing catalyst, and then placed in a flow of helium in the sample holding tube at a temperature of 1000°C. Pulses of oxygen are then introduced into the helium stream to oxidize the sample. The helium and combustion products which include SO_2 are then passed through a bed of magnesium chlorate to remove water and then through a column of copper at a temperature of 840°C to remove any nitrogen oxide compounds. Finally, the stream flows through a column of Ag_2O which removes the SO_2. A TCD is used to detect the concentration difference between the inlet and outlet of the Ag_2O column. From these readings, the quantity of sulphur in the original sample can be determined.

4.3 Experimental System and Procedures

4.3.1 Experimental Set-up

The experimental system used for the preparation of the catalysts and the determination of reaction rates is shown in Figure 4.1. The feed gases including sulphur dioxide,

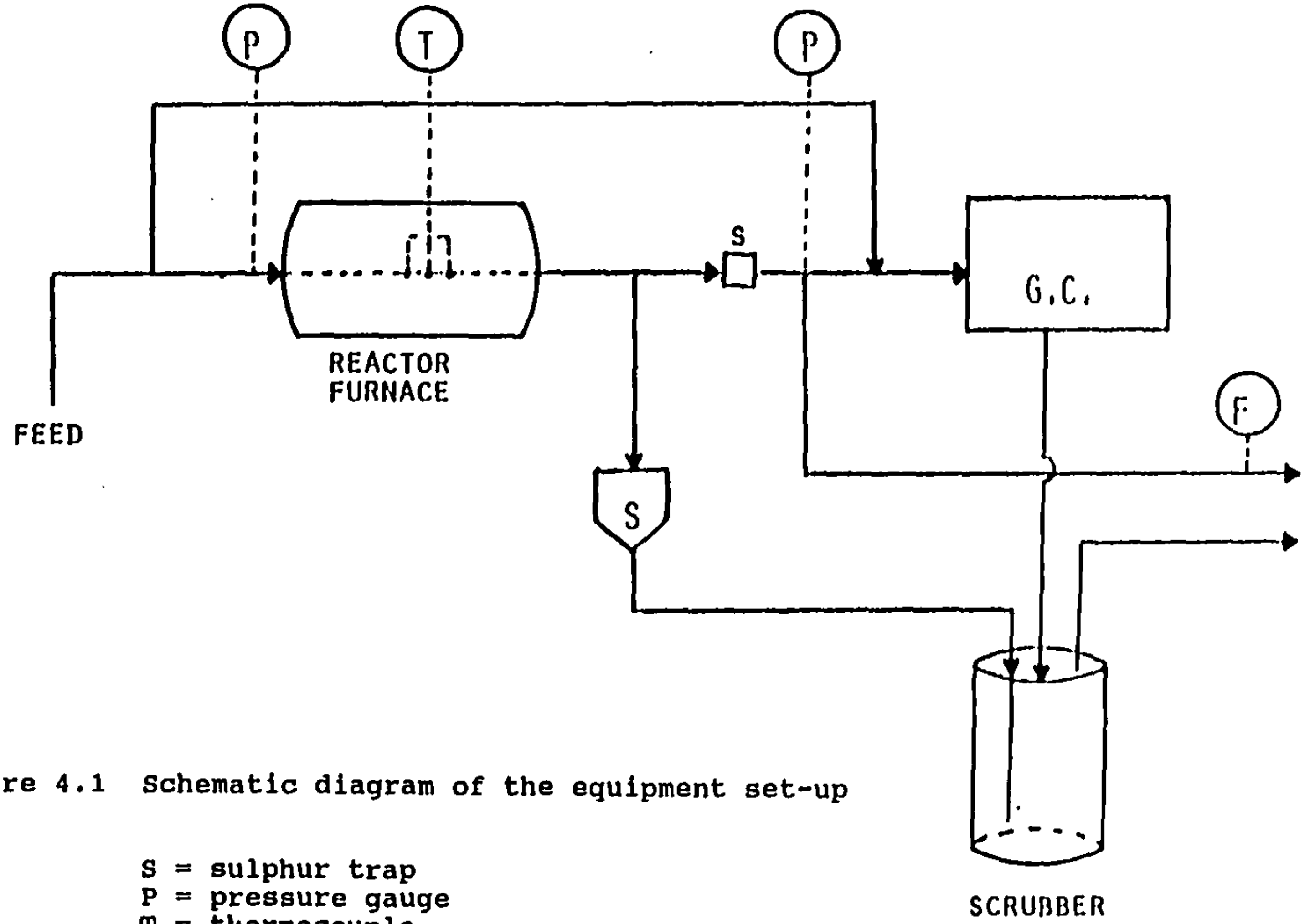


Figure 4.1 Schematic diagram of the equipment set-up

S = sulphur trap
P = pressure gauge
T = thermocouple
F = bubble flowmeter

methane, and argon, the carrier gas, or H_2S or air were delivered at a pressure of 20 psig. The flowrates of each of the gases were measured by rotameters, and controlled by needle valves. The rotameters were calibrated using a bubble flowmeter. The calibration curves for the rotameters are given in Appendix A. The gases were then mixed and delivered to the reactor in stainless steel 316 tubing.

The reactor was a 65 cm long, 2.5 cm I.D. quartz tube (Figure 4.2). It was heated in a single zone heavy duty Lindberg model 1500 tubular furnace. The catalyst was located in the middle of the tube where the temperature was kept uniform. The remainder of the tube was filled with quartz chips to improve mixing and to reduce void volume. The total volume of the reactor, flanges, and tubing between the point of gas delivery and the reactor exit sampling port, excluding the volume occupied by the catalyst pellets and the quartz chips, was approximately 360 cm^3.

The temperature of the reactor bed was measured by three thermocouples (chromel-alumel type K) purchased from Thermoelectric, Montreal, PQ. An OMEGA Model 650 digital temperature read-out was used to allow for continuous temperature monitoring. To verify the uniformity of temperature along the catalyst bed, the thermocouples, which were inserted through the entrance of the reactor along the

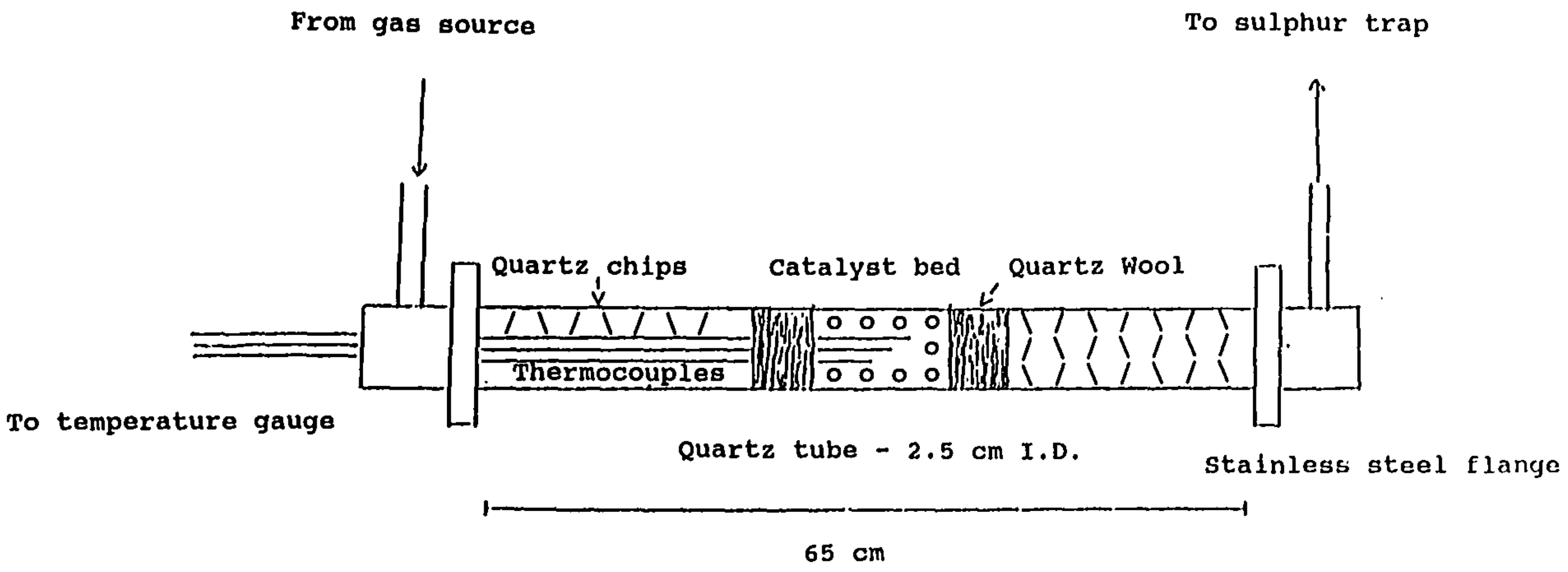


Figure 4.2 Reactor Design

centreline, were positioned at the beginning, in the middle, and at the end of the catalyst bed.

If an analysis of the reactor exit gases was not being done, the gases as they left the reactor were diverted through a large sulphur trap and then through a scrubber containing a 20% solution of NaOH. The gases were then exhausted to the fume hood.

If a sample of the reactor exit gases was being taken, the gases flowed from the reactor exit through a U-tube, cooled by an ice bath. In this trap, sulphur, water, and any CS_2 that may have been formed were condensed. The flow rate of the remaining gases was then measured by a bubble flowmeter at ambient conditions. The gas samples were taken directly from the reactor exit line by gas-tight syringes and injected immediately into the gas chromatograph.

4.3.2 Gas Analysis

The gas chromatograph (HP Model 5780) was fitted with two columns. The first one was a Poropak QS column, 120 cm long and the second was a Molecular Sieve 5A column, 90 cm in length. The two columns were connected in series. The Molecular Sieve column was normally connected to the detector. However, the two columns were connected to each other through a 4-port valve, which when switched into the on position enabled the Poropak QS column to be connected directly to the detector, by-passing the Molecular Sieve column.

After injection, the gas sample flowed into the Poropak column where H_2S, SO_2, COS, and CO_2 were separated from Ar, O_2, N_2, CH_4, and CO which flowed into the second column. Oxygen and nitrogen entered the syringe during the sampling procedure and were present in the sample in quantities less than 0.2% each. The valve was then switched on in order to analyze the gases from the Poropak column, and then switched off to analyze for the gases held back in the Molecular Sieve column.

A thermal conductivity detector (TCD) was used to detect the gases. The helium carrier gas had a flowrate through the columns of 0.33 cm^3/s and a separate flow of 0.5 cm^3/s through the detector used as a reference, representing a total flow of 0.83 cm^3/s. The detector temperature was set at 160°C. These conditions were selected in order to maximize the relative sensitivity of the TCD. The detector signal was then processed by a HP 3390 integrator.

The chromatograph and integrator were calibrated by injecting known amounts of pure species. Based on the retention times, a temperature program where oven temperatures varied between 40 and 130°C was used to ensure good peak resolution (Appendix B). For each of the gases, linear equations were obtained by plotting the number of moles of each species injected against the peak area as determined by the integrator. The following is a list of these equations.

$$\text{Moles } SO_2 = 1.475 \times 10^{-12} * \text{Area} \qquad (4.1)$$

$$\text{Moles } CH_4 = 2.641 \times 10^{-12} * \text{Area} \qquad (4.2)$$

$$\text{Moles } CO_2 = 2.050 \times 10^{-12} * \text{Area} \qquad (4.3)$$

$$\text{Moles } H_2S = 1.841 \times 10^{-12} * \text{Area} \qquad (4.4)$$

$$\text{Moles } COS = 1.450 \times 10^{-12} * \text{Area} \qquad (4.5)$$

$$\text{Moles } CO = 2.144 \times 10^{-12} * \text{Area} \qquad (4.6)$$

Elemental sulphur, water, and elemental carbon were determined by elemental balance. In addition, it was possible to detect the presence of H_2 and CS_2; however, preliminary experiments showed that H_2 and CS_2 were absent in all experiments thus the detector was not calibrated for these gases.

4.3.3 Description of a Typical Experimental Run

Before and after experimentation the bulk composition of each of the catalysts was determined by x-ray diffraction. In addition, the surface areas were measured using the surface area analyzer.

At the beginning of each experiment, the gas flowrates were set by the rotameters. The reaction mixture was sent through the reactor as the temperature stabilized to the reaction temperature. This was done in order to flush oxygen from the system, thereby preventing oxidation of the catalyst. At intervals of fifteen minutes samples were taken from the reactor exit stream and analyzed by gas chromatograph until three consecutive analyses yielded integrated peak areas with 5% of each other indicating that steady state was achieved. At the end of an experimental run, the reacting gases were shut off leaving only a flow of argon. The reactor was then allowed to cool to room temperature before the catalyst was removed for analysis.

4.4 Data Evaluation

The rate of production of species i can be calculated from the expression:

$$r(i) = \frac{F(i) - F(i)_o}{A} \qquad (4.7)$$

Where $F(i)$ = exit molar flowrate of i (mol/s)

$F(i)_o$ = inlet molar flowrate of i

A = total surface area of catalyst (m^2)

$r(i)$ = rate of production of species i ($mol/s\text{-}m^2$)

From the calculation of the individual rates of production of each of the species present in the system, the yields of elemental sulphur and carbon dioxide can be calculated. For the purpose of data analysis, sulphur was considered as one species [S]. Therefore, the sulphur yield is defined as follows:

$$Y(S) = \frac{r(S)}{r(SO_2)} \times 100\% \qquad (4.8)$$

where r(i) is the rate of production of species i as calculated above. Similarly, carbon dioxide yield is defined in the following manner:

$$Y(CO_2) = \frac{r(CO_2)}{r(CH_4)} \times 100\% \qquad (4.9)$$

A Fortran computer program was used for the purpose of calculating the reaction rates from the raw data. This program required the input of the catalyst weight and specific surface area, the G.C. analyses of the inlet and the outlet gases, the inlet and the outlet volumetric flowrates, and ambient temperature and pressure.

Using the ambient conditions, the inlet and the outlet volumetric flowrates were converted to molar flowrates. The inlet G.C. areas were converted to moles using the calibration factors. Knowing the inlet mole fractions of gases, and the total molar flowrate, the individual inlet molar flowrates could be calculated. Since argon is inert, its molar flowrate was conserved. The molar flowrates of the individual elements (carbon, sulphur, oxygen, and hydrogen) were also conserved.

From the analysis of the inlet gases, the ratios of each of the elements to argon were determined. These ratios were the same at the exit of the reactor. Therefore, since CO_2, H_2S, COS, SO_2, Ar, CH_4, and CO were measured quantitatively at the exit, water, hydrogen, elemental sulphur and carbon, could be calculated by elemental balance. The reaction rates were then calculated directly from the exit molar flowrates for all species other than SO_2 and CH_4. The reaction rates of these two species were determined by calculating the difference between their respective inlet and outlet molar flowrates. The sulphur and carbon dioxide yields were then calculated directly from the rates as defined in equations 4.8 and 4.9. Finally, the mass balances were checked by converting the calculated exit molar flowrate to a volumetric flowrate which was then compared with the measured value. The two values were found to be consistently within 2%.

4.5 Reactor Flow Characteristics

In order to determine the deviation of the tubular quartz reactor from plug flow ideality, the residence time distribution was determined experimentally by a step input of methane into the argon flow. The initial flow of argon through the reactor packed with catalyst and quartz chips was 4.0 cm^3/s at 1 atm and 25°C. At time zero, the flow of argon was replaced with methane at the same volumetric flowrate. Samples of the exit gas were taken every 20 seconds from the sampling port in the reactor exit line where experimental samples were normally taken. The samples were then analyzed by the gas chromatograph for methane concentration until argon could no longer be detected.

CHAPTER 5

REDUCTION OF SO_2 WITH CH_4 OVER SUPPORTED MOLYBDENUM CATALYSTS

The objective of this chapter is to investigate the effect of the catalyst preparation variables including molybdenum loading on the effectiveness of supported MoS_2 as a catalyst for the reduction of SO_2 with CH_4. This chapter is divided into five sections. The first two sections include the results and discussion of the preliminary and catalyst stability experiments, respectively. The third section describes the experimental conditions used for the kinetic experiments. The fourth section is a discussion of the results of the kinetic experiments performed using supported molybdenum catalysts with different molybdenum loadings and the effect of a promoter and support material composition. The final section is a comparison between a supported molybdenum catalyst and alumina using integral conversion conditions.

5.1 Preliminary Experiments

5.1.1 Characterization of the Reactor

The experiments to determine the reactor flow characteristics were carried out in duplicate using the procedure described in section 4.5. The temperature of the reactor was maintained at 700°C. The space time calculated at 25°C and 1 atm using the reactor volume of 360 cm^3 and the gas flow rate of 4.0 cm^3/s in this experiment, was 90 seconds.

A plot of the ratio of the CH_4 exit concentration (C) at the sampling port and the inlet CH_4 concentration (Co) versus time is shown in Figure 5.1. Also shown in the figure are the results of C/Co calculated from a series-of-stirred-tank mathematical model of the residence time distribution of the gas (Smith, 1981). In this model, the actual reactor is simulated by a number of ideal stirred tank reactors in series with the total volume of the stirred tank reactors being the same as the actual reactor. A small number of stirred tanks represents a large degree of back mixing whereas an infinite number of stirred tanks represents ideal plug flow behaviour. In addition, an estimate of the reactors' average residence time can be determined from this model.

The experimental data show that the first detectable concentrations of methane appear between 40 and 60 s. The concentration of methane reaches 97% at 120 s. The model fits the data if a series of 20 stirred tank reactors and an average residence time of 80 seconds is used. Firstly, this result shows that since the space time calculated at 25°C is similar to the average residence time

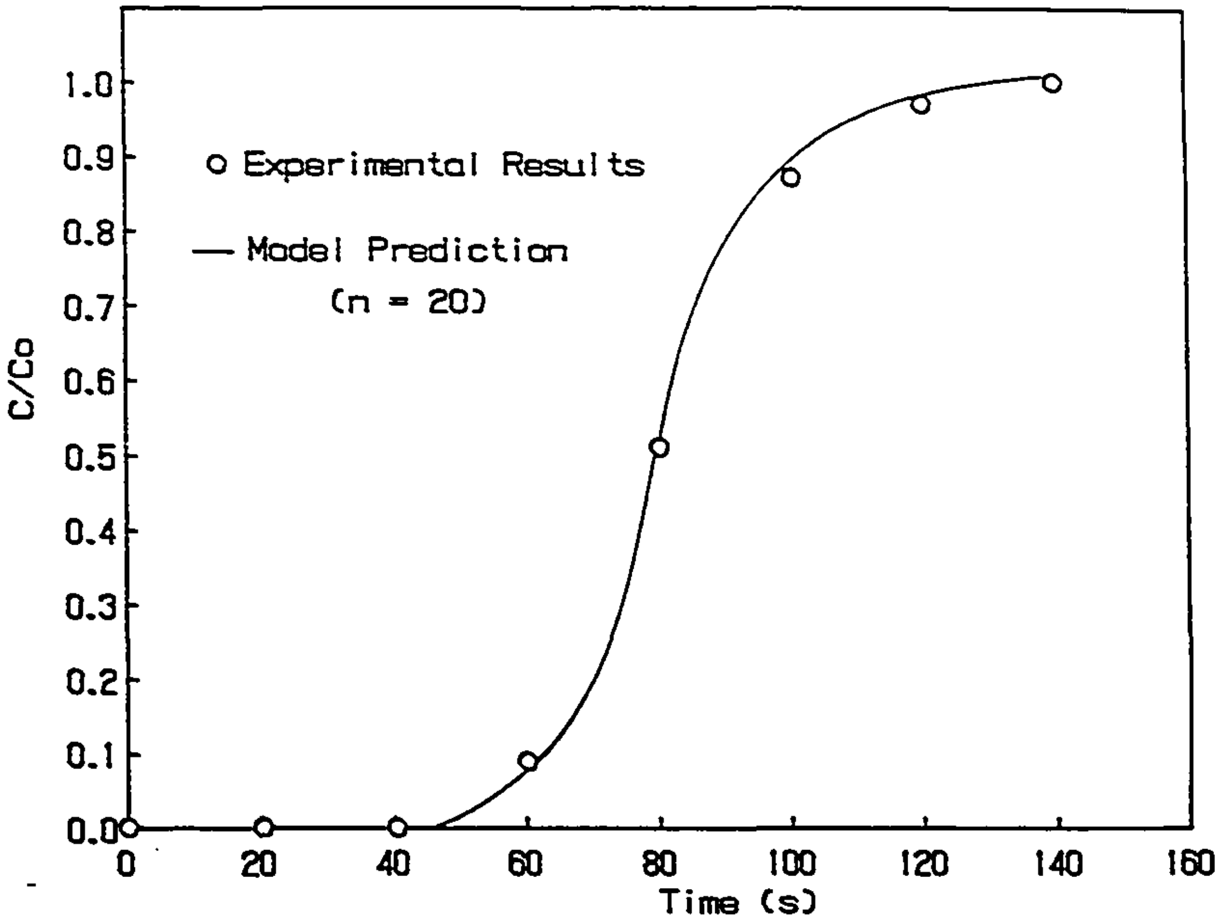


Figure 5.1 Comparison of the experimental results with a methane tracer with the results predicted by the model described in 5.1.1

estimated from the model, there is not a strong effect of temperature on the gas flow rate. This is due to the fact that a single zone furnace was used which only heated the catalyst bed area, leaving the remaining portion of the reactor tube cool. Secondly, the number of stirred tank reactors implies that the system as a whole, behaves in a manner closer to an ideal plug flow reactor, rather than a stirred tank.

5.1.2 Determination of Reaction Products

The second set of preliminary experiments was designed to determine if there were any homogeneous reactions occurring between either the reactants SO_2 and CH_4 or among the product stream components.

When no catalyst packing was present in the reactor, there was no reaction between SO_2 and CH_4 at any of the concentrations considered in this study at temperatures below 800°C. In order to determine if homogeneous reactions were occurring among reaction products in the case when catalyst packing was present in the reactor, gas samples were taken at the exit of the catalyst bed using a 1.5 mm O.D. stainless steel sampling line inserted into the reactor. A comparison of the analyses of samples taken from this point with those taken from the sampling port showed no difference in composition indicating the absence of homogeneous reactions among the reaction products.

Experiments were also performed at temperatures ranging from 650 to 750°C using various catalysts prepared for this study. Depending on the experimental conditions, it was found that the reaction products were CO_2, H_2S, H_2O, COS, elemental sulphur, and carbon. No H_2 or CS_2 were detected under any conditions. These results indicate that the information obtained from the data evaluation procedure outlined in section 4.4 was sufficient for calculating the rates of reaction of all possible components.

5.1.3 Characterization of the Catalysts

The third set of preliminary experiments had the objective of determining the repeatability and the effectiveness of the procedures used for preparing catalysts. In order to accomplish this, two sets of catalysts were prepared according to the procedures outlined in section 4.1. The first set consisted of three samples of 15% Mo catalyst supported on alumina sulphided using a 12% H_2S in argon mixture. The second set consisted of two 15% Mo/Al_2O_3 catalysts sulphided at a temperature of 650°C using a mixture of 25% SO_2, 25% CH_4, and 50% argon.

Plates 5.1 and 5.2 show the x-ray diffraction patterns of the H_2S sulphided set and the SO_2/CH_4 sulphided catalysts, respectively. A comparison of the three patterns in Plate 5.1 show that there is no difference in the major peaks indicating that the three catalyst samples have a similar qualitative composition. The same patterns were obtained for both the 5% and 10% molybdenum catalysts. Similarly, in Plate 5.2, it can be seen that the two patterns are virtually identical and, therefore, these catalysts are also similar in composition to each other. The sharp "spikes" which are present in both figures, represent power surges during the XRD analysis procedure.

Kinetic experiments were also performed to determine catalyst preparation repeatability using a temperature of 700°C and a molar feed ratio of SO_2 to CH_4 of 1.0 corresponding to a feed composition of 25% SO_2, 25% CH_4 and 50% Ar. The catalysts were compared on the basis of activity, and the yields of sulphur and carbon dioxide. The results are presented in Table 5.1 and show that there is no difference in the activity or the yields of the catalysts prepared using the same sulphidation method. From these results it was concluded that the catalyst preparation methods were repeatable. However, there is a significant difference found when the activities of the catalysts sulphided using H_2S or SO_2 and CH_4 are compared to each other. This will be discussed extensively in Chapter 6.

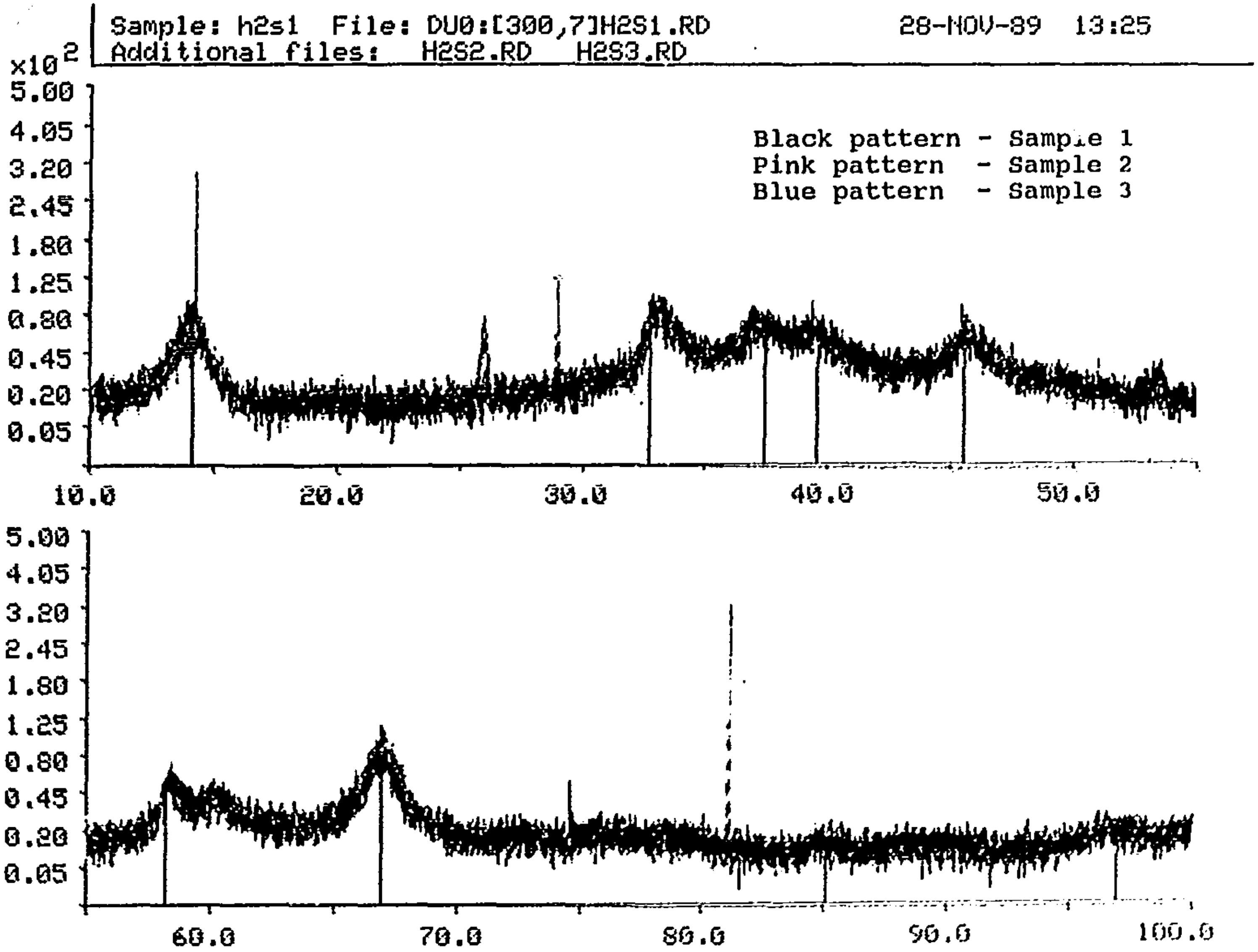


Plate 5.1 X-ray diffraction patterns of 15% Mo/Al_2O_3

catalysts sulphided with H_2S

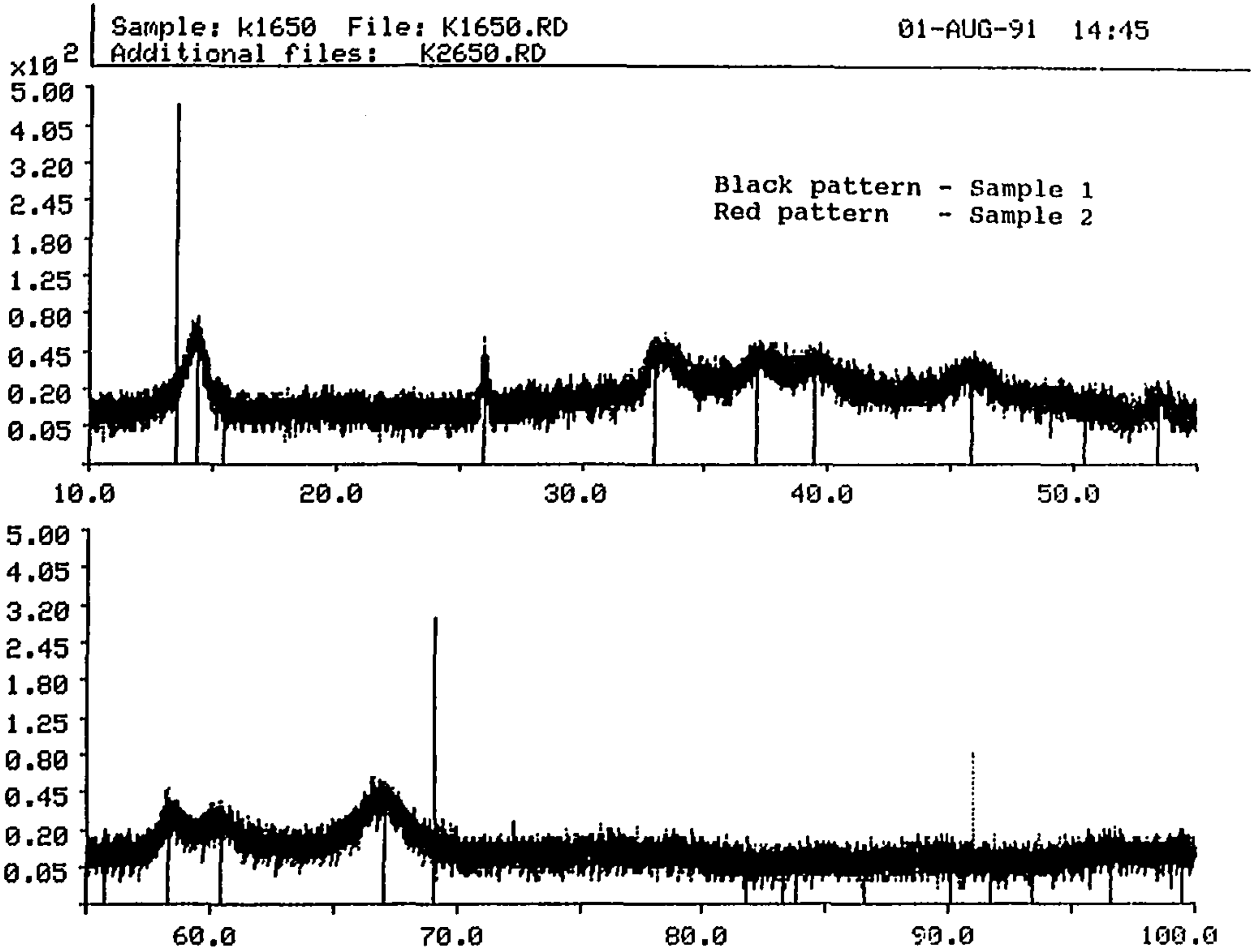


Plate 5.2 X-ray diffraction patterns of 15% Mo/Al_2O_3 catalysts sulphided with SO_2 and CH_4

Table 5.1

Repeatability of Catalyst Preparation Methods

(T =700°C, SO_2/CH_4 = 1.0)

Catalyst	Activity (gmol/m^2-s)	Sulphur Yield (%)	CO_2 Yield (%)
H_2S Sulphided (15% Mo/Al_2O_3)			
Sample 1	6.2×10^{-8}	92.0	91.0
Sample 2	5.8×10^{-8}	92.5	90.3
Sample 3	6.1×10^{-8}	91.8	91.5
SO_2-CH_4 Sulphided (15% Mo/Al_2O_3)			
Sample 1	4.2×10^{-8}	93.3	90.9
Sample 2	4.0×10^{-8}	92.4	91.5

Plate 5.3 shows the x-ray diffraction analysis of oxidized and sulphided 5% Co-15% Mo/Al_2O_3 pellets before use in reaction. The diffraction angles of the most intense peaks for each of the observed species are given in Table 5.2. The analysis of the oxidized catalyst confirmed the presence of $CoMoO_4$, MoO_3, and alumina. The analysis of the sulphided catalyst showed that the major crystalline phases consisted of MoS_2, MoO_2, Co_9S_8, $CoMoO_4$, and alumina. XRD analysis of the 5, 10, and 15% Mo/Al_2O_3, also before use in reaction, showed that MoS_2, MoO_2, and alumina were the only species detected (see Plate 5.1). Thermodynamic analysis showed that the sulphidation procedure with H_2S should result in the complete conversion of MoO_3 to MoS_2; however, some MoO_3 was reduced to MoO_2 without being sulphided. This will also be extensively discussed in Chapter 6.

The last step in determining the effectiveness of the catalyst preparation procedures involved using x-ray mapping and wet chemical analysis. X-ray mapping of split pellets showed that the impregnation procedure resulted in uniform distribution of molybdenum and cobalt. Plate 5.4a is a scanning electron micrograph of an oxidized 15% Mo/Al_2O_3 split pellet magnified 35 times. The reason for using an oxidized pellet and not a sulphided pellet was that sulphur interferes with the image analysis of molybdenum. The image analysis shown in Plate 5.4b of the same pellet indicates

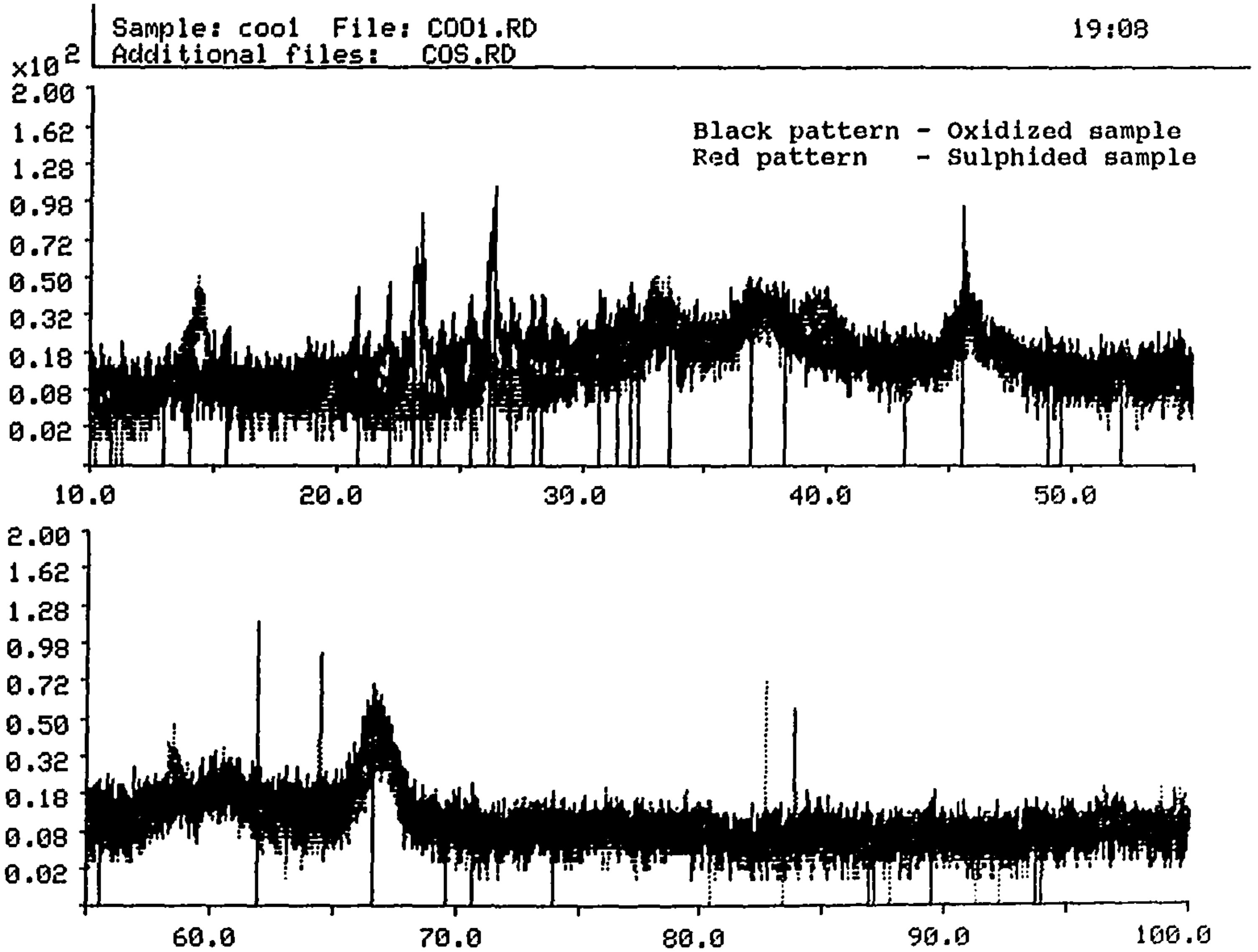


Plate 5.3 X-ray diffraction patterns of oxidized and sulphided 5% Co-15% Mo/Al_2O_3 catalyst samples

Table 5.2

Diffraction Angles of Most Intense Peaks for Species Present in the Catalysts

Species	Angles
MoO_2	25.9°, 37.0°
MoO_3	27.5°, 22.9°
MoS_2	14.3°, 32.9°
$CoMoO_4$	26.5°, 23.8°
Co_9S_8	52.1°, 29.9°
Al_2O_3	66.9°, 45.8°

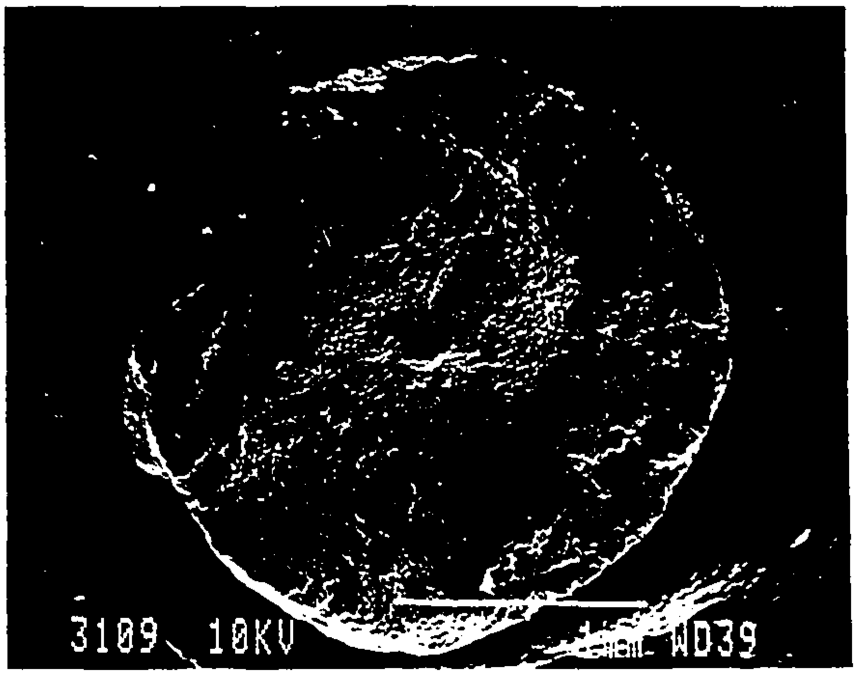


Plate 5.4a Scanning electron micrograph of an oxidized 15% Mo/Al_2O_3 catalyst pellet

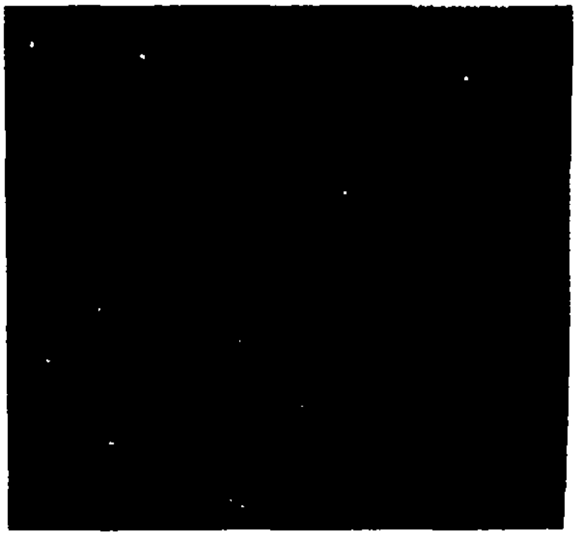


Plate 5.4b Molybdenum distribution in an oxidized 15% Mo/Al_2O_3 catalyst pellet

that molybdenum is uniformly distributed. Any dark areas can be attributed to the texture of the surface. Wet chemical analysis verified that all samples contained the desired quantity of molybdenum.

5.2 Catalyst Stability

As stated in Chapter 2, it was not known how stable the supported molybdenum catalyst would be in terms of composition, molybdenum retention, and surface area, once exposed to the severe reaction conditions required for the reduction of SO_2. In order to determine the effect of long term exposure of the catalyst to high temperature the following experiment was performed. A sample of the 15% Mo/Al_2O_3 catalyst sulphided with H_2S was charged to the reactor. The SO_2 reduction was carried out at a temperature of 700°C using a molar feed ratio (SO_2/CH_4) of 1.0. Steady state was achieved in 6 hours. The reacting gases, SO_2 and CH_4, were then shut off, leaving only a flow of argon. The temperature was maintained at 700°C for a period of 48 hours. Following this period, the flow of both reacting gases was resumed and steady state was again obtained. It was found that all reaction rates, and hence, yields of sulphur and carbon dioxide were unchanged from the first steady state to the second. A complete analysis of the composition of the 15% Mo/Al_2O_3 catalyst after use in the reaction (Table 5.3) shows that the components remained

Table 5.3

Composition of the Sulphided 15% Mo/Al_2O_3 Catalyst

Component	%
MoS_2	17.0
MoO_2	4.2
Al_2O_3	78.8

unchanged by the reaction. A sample calculation for the catalyst composition is shown in Appendix C.

In addition, the surface areas of each of the catalysts considered in this study were measured and are presented in Table 5.4. These values were changed by less than 5% during experimentation indicating that the catalysts were not significantly sintered. In addition, Plates 5.4a and 5.4b which are scanning electron micrographs of the inner surface of an unused and a used (100 hours at 700°C) 15% Mo/Al_2O_3 catalyst, respectively, show that there was no change in the surface texture confirming that the catalysts were not sintered. From this, from the kinetic results, and from the chemical analysis, it was concluded that the catalyst is stable, even after exposure to the severe reaction conditions.

5.3 Experimental Conditions for Catalyst Comparison

The SO_2 reduction experiments performed for the comparison of the supported catalysts listed in Table 5.4 were carried out in the temperature range from 650 to 725°C at 25°C intervals. Two ratios of inlet SO_2 to CH_4 concentrations were used, 1.0 and 2.0. The concentrations of each of the gases for these ratios are given in Table 5.5. The molar feed ratio of 1.0 was selected because it was determined in a previous work that high SO_2 consumption

Table 5.4

Surface Area Analysis of the Catalysts

Catalyst	Specific Surface Area (m^2/g)
Al_2O_3	135.0
SiO_2-Al_2O_3	247.2
15% Mo/SiO_2-Al_2O_3	175.0
5% Co-15% Mo/Al_2O_3	75.1
5% Mo/Al_2O_3 *	91.4
10% Mo/Al_2O_3 *	80.2
15% Mo/Al_2O_3 *	112.9
15% Mo/Al_2O_3 **	118.6
15% Mo/Al_2O_3 ***	103.2
15% Mo/Al_2O_3 ****	98.6

* Sulphided with H_2S at 600°C

** Sulphided with SO_2/CH_4 at 650°C

*** Sulphided with SO_2/CH_4 at 700°C

**** Sulphided with SO_2/CH_4 at 750°C

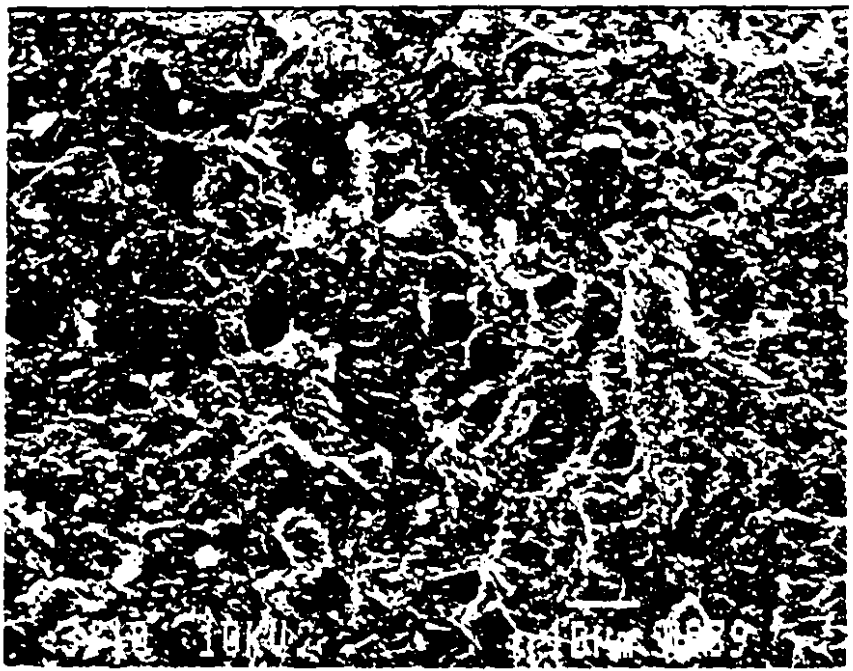


Plate 5.5a Surface texture of an unused 15% Mo/Al_2O_3 catalyst sulphided with H_2S

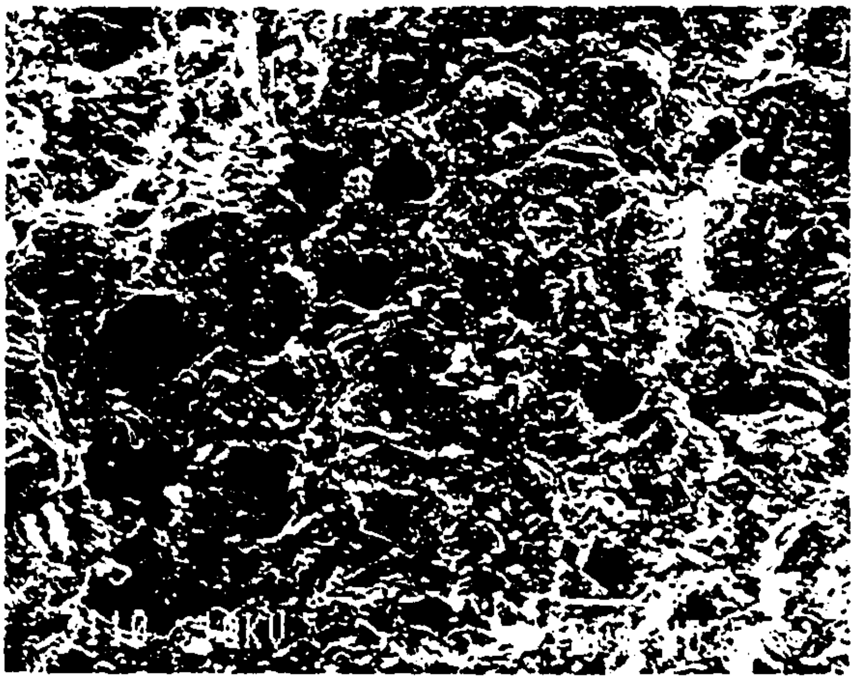


Plate 5.5b Surface texture of a used 15% Mo/Al_2O_3 catalyst sulphided with H_2S

Table 5.5

Composition of Inlet Gas Mixtures at Different Feed Ratios

SO_2/CH_4 feed ratio	SO_2 (%)	CH_4 (%)	Ar (%)
1.0	25	25	50
2.0	30	15	55

rates as well as high yields of elemental sulphur and CO_2 were obtained at this ratio (Mulligan, 1988). A ratio of 2.0 was also used because it represents the stoichiometric ratio between SO_2 and CH_4 in reaction 2.11. With the exception of the integral rate data presented in section 5.5, all results were obtained using differential conversions below 20% so that the reactions can be considered to take place at the average of the inlet and exit concentrations (Massaldi and Maymo, 1968).

5.4 Reduction of SO_2 with CH_4 over Mo/Al_2O_3 Catalysts

5.4.1 Sulphur Species Results

Figure 5.2 is a plot of the activity, or rate of SO_2 consumption versus temperature, at a feed ratio of 1.0, for various loadings of molybdenum. For comparison, the results for alumina, and pure MoS_2, are also included. The highest activity is found when the 15% Mo loading is used. The results are comparable to those obtained with pure MoS_2 (Mulligan and Berk, 1989). Experiments using a 21% Mo/Al_2O_3 have also been performed, but the results are not shown since they are also the same as those of the 15% loading. The 5 and 10% Mo/Al_2O_3 activities are virtually equal at all temperatures, but are somewhat lower than those found for 15% Mo/Al_2O_3. Alumina is the least active. In fact, the

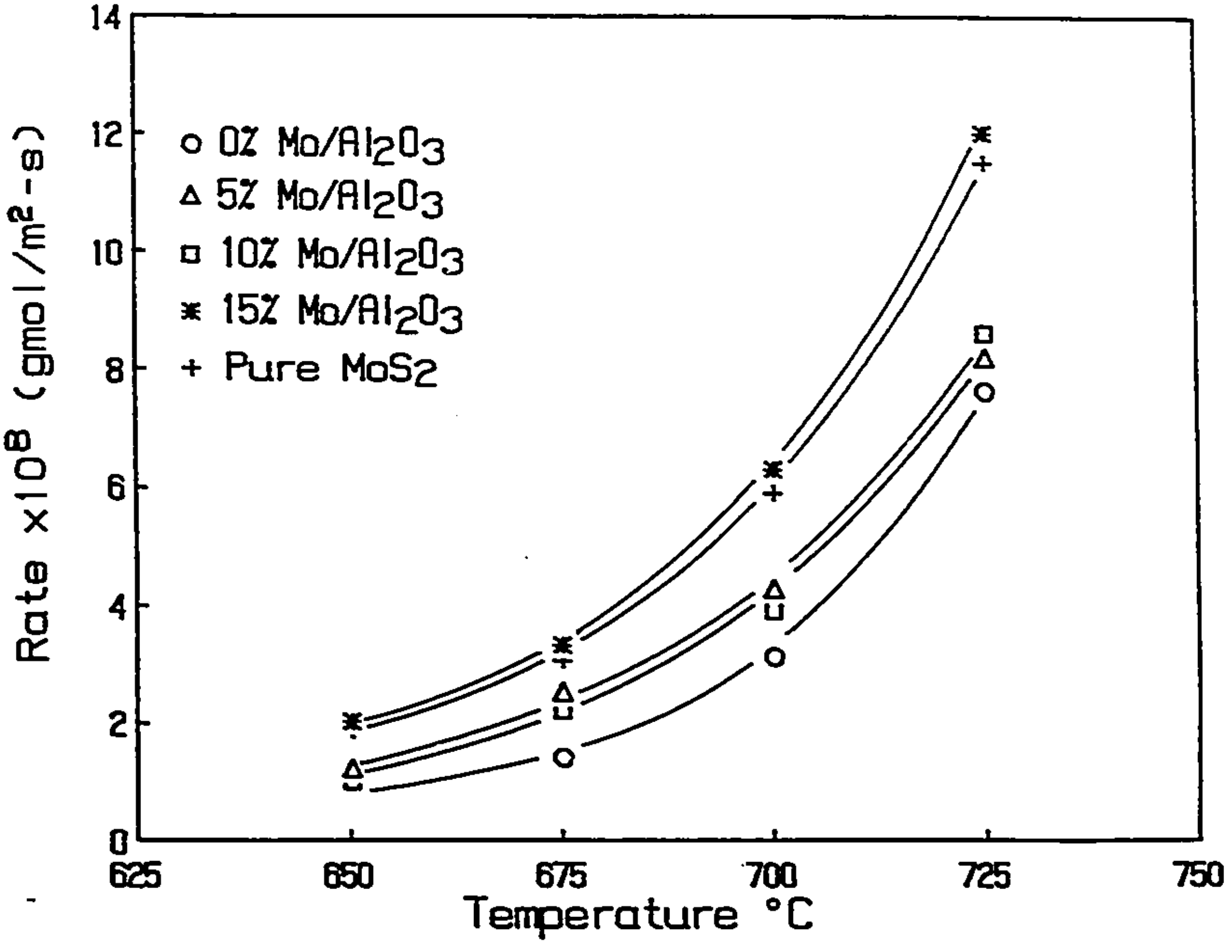


Figure 5.2 Effect of temperature on activity using catalysts with various molybdenum loadings

rates with the 15% Mo/Al_2O_3 catalyst are approximately double those of alumina.

The sulphur yield for a feed ratio of 1.0 is plotted versus temperature in Figure 5.3. In general, the sulphur yield decreases with increasing temperature. The highest yields are found when 15% Mo/Al_2O_3 is used. The lowest yields are obtained with alumina. As with the activities, the 5 and 10% Mo/Al_2O_3 catalyst yields are almost identical to each other and are between the yields of alumina and 15% Mo/Al_2O_3.

The rates of production of elemental sulphur are plotted in Figures 5.4. For all catalysts, at all temperatures, the major sulphur containing product was found to be elemental sulphur. Sulphur production rates plotted in Figure 5.4 clearly show one of the advantages of using 15% Mo/Al_2O_3 for the reduction of SO_2 with CH_4. Since one of the primary objectives of this work was to find a catalyst for this reaction system to selectively produce elemental sulphur, a high sulphur production rate is desirable. Clearly, the 15% Mo/Al_2O_3 catalyst does not only provide a higher sulphur yield, but it also provides the highest sulphur production rates. The 5 and 10% Mo/Al_2O_3 catalysts have sulphur production rates similar to each other, but lower than those found with the higher loading.

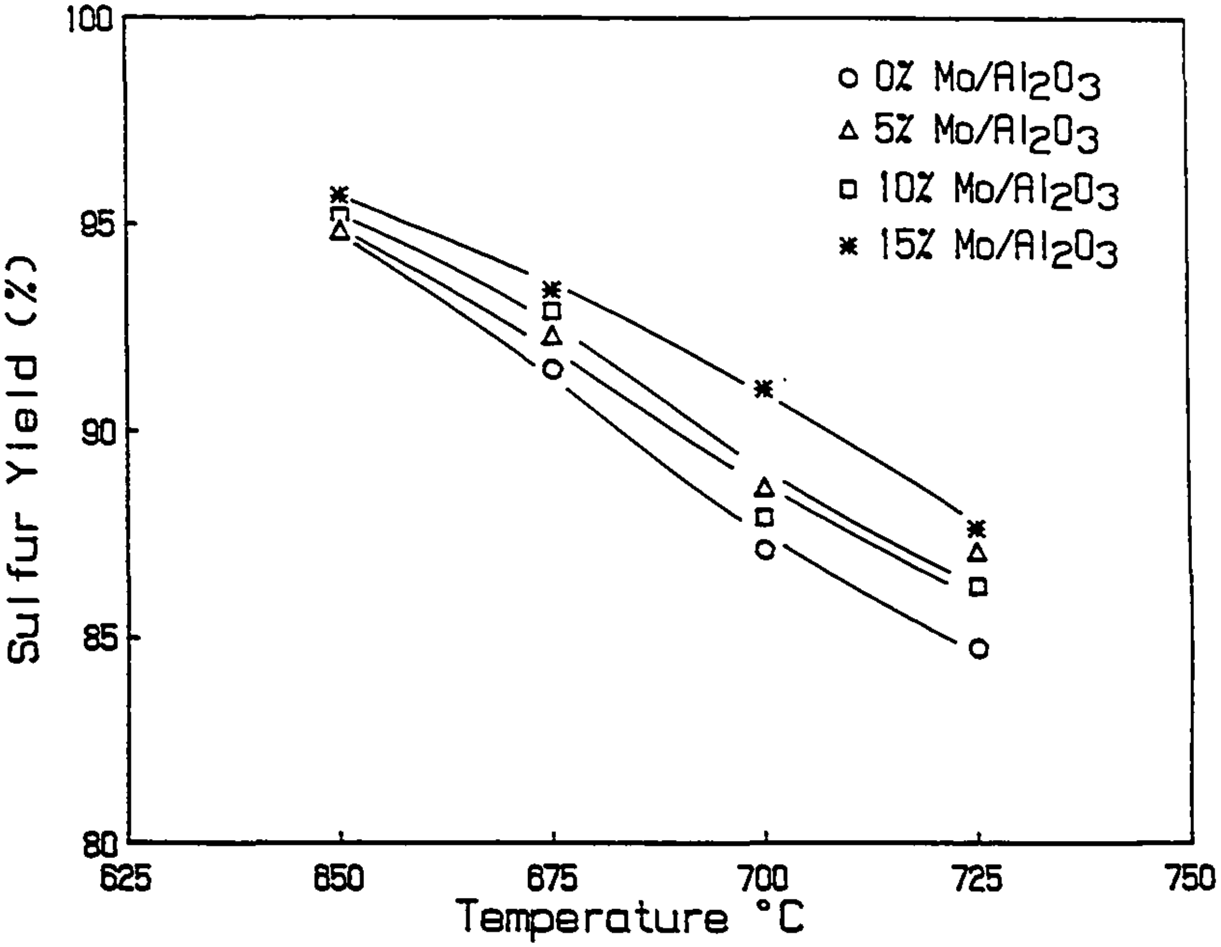


Figure 5.3 Effect of temperature on sulphur yield using catalysts with various molybdenum loadings

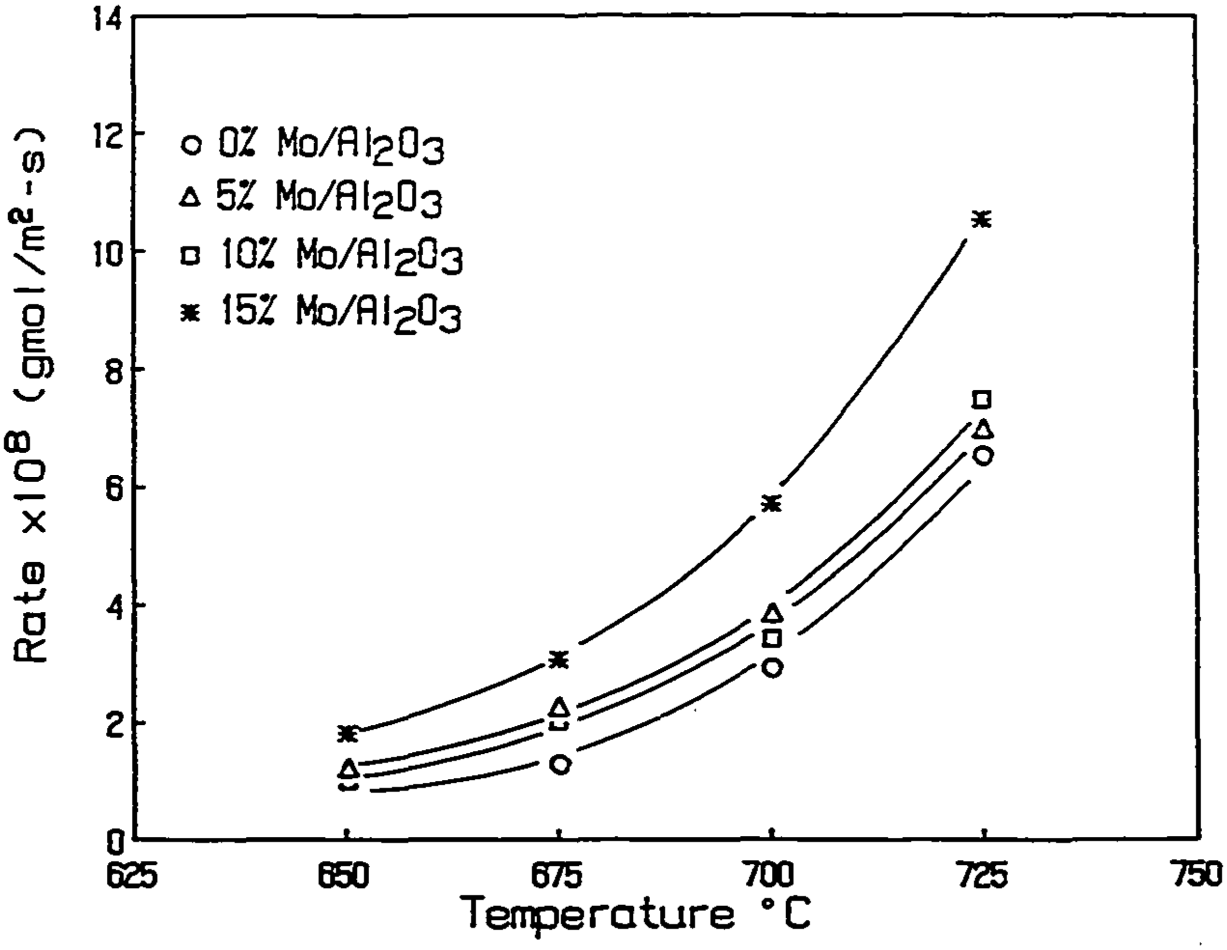


Figure 5.4 **Effect of temperature on rate of sulphur production using catalysts with various molybdenum loadings**

The sulphur rates with alumina are the lowest and are approximately half those of 15% Mo/Al_2O_3.

While the major sulphur containing product was elemental sulphur, both H_2S and COS were also formed under all conditions. The rates of production of H_2S and COS are plotted in Figures 5.5 and 5.6, respectively. As can be seen in Figure 5.5, at temperatures below 725°C, the rates of production of H_2S are approximately the same for all molybdenum loadings, while those of alumina are the lowest. However, Figure 5.6 shows that the rates of production of COS with alumina are approximately twice those with the supported molybdenum catalysts. Therefore, while the rates of production of H_2S increase with the activities of the molybdenum catalysts, the rates of production of COS decrease.

The conclusion from the analysis of the rates of reaction of the sulphur bearing species is that the 15% Mo/Al_2O_3 catalyst has the highest activity for the consumption of SO_2 which is accompanied by a proportional increase in the production of H_2S. However, when compared to alumina, there is an overall increase in the sulphur yield with the 15% Mo/Al_2O_3 catalyst because there is a decrease in the production of COS greater than the increase in H_2S production resulting in an increase in the number of moles of sulphur produced per mole of SO_2 consumed.

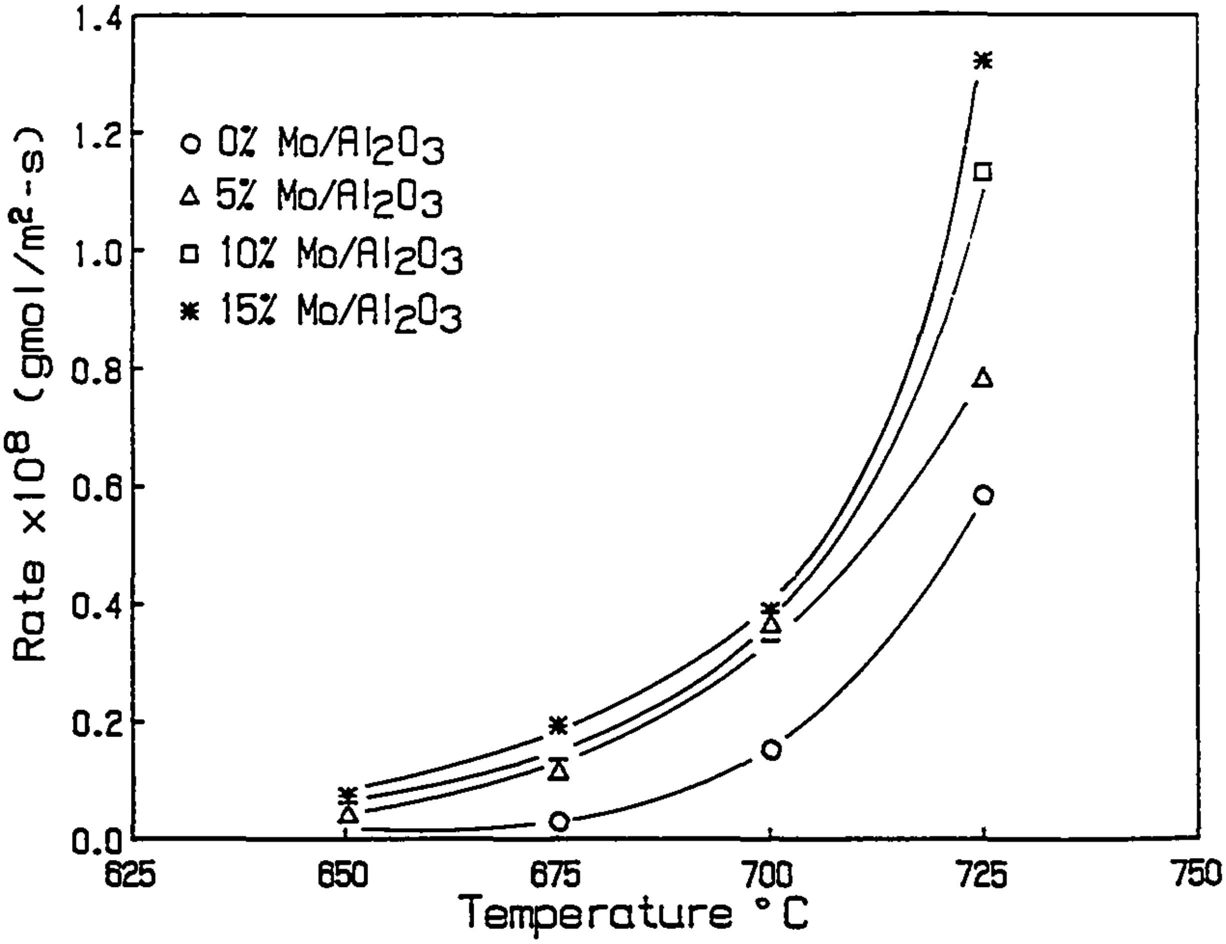


Figure 5.5 Effect of temperature on rate of H_2S production using catalysts with various molybdenum loadings

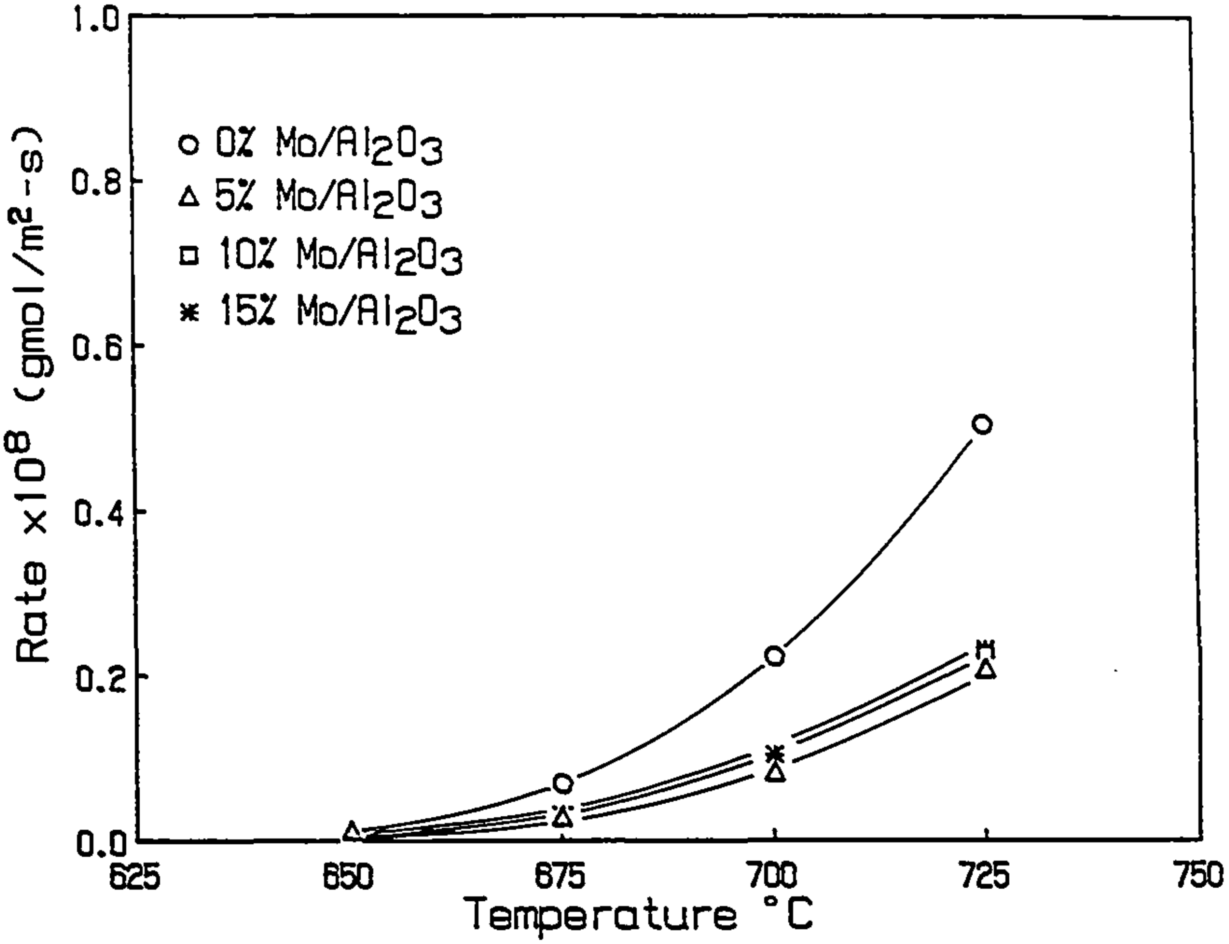


Figure 5.6 Effect of temperature on rate of COS production using catalysts with various molybdenum loadings

5.4.2 Carbon Species Results

Because the cost of methane is a major expense in processes employing the reduction of SO_2 with CH_4, the effect of molybdenum loading on the rates of CH_4 consumption and production of carbon containing species has also been considered. Figure 5.7 is a plot of CH_4 consumption as a function of temperature for various molybdenum loadings. Because of the stoichiometric relationships which exist in reaction 2.11, the rate of CH_4 consumption is highest for the 15% Mo/Al_2O_3. However, the rates of CH_4 consumption for the other catalysts are not decreased proportionally with the lower SO_2 consumption rates shown in Figure 5.2 in comparison to the 15% Mo/Al_2O_3 catalyst. In fact, the ratio of the rates of consumption of SO_2 to CH_4 for alumina range from a value of 1.68 at 725°C to 1.56 at 675°C. However, the values of this ratio using the 15% Mo/Al_2O_3 catalyst range from 1.80 to 1.93 which are closer to the stoichiometric value of 2.0 indicated by equation 2.11. This is significant in that 10% less CH_4 is required to reduce one mole of SO_2 if the 15% Mo/Al_2O_3 catalyst is used as opposed to alumina.

Figure 5.8 is a plot of CO_2 yield versus temperature. Carbon dioxide yields greater than 72% were obtained with all loadings at all temperatures while the yields with alumina ranged from only 40% to 70%. In general, the yields

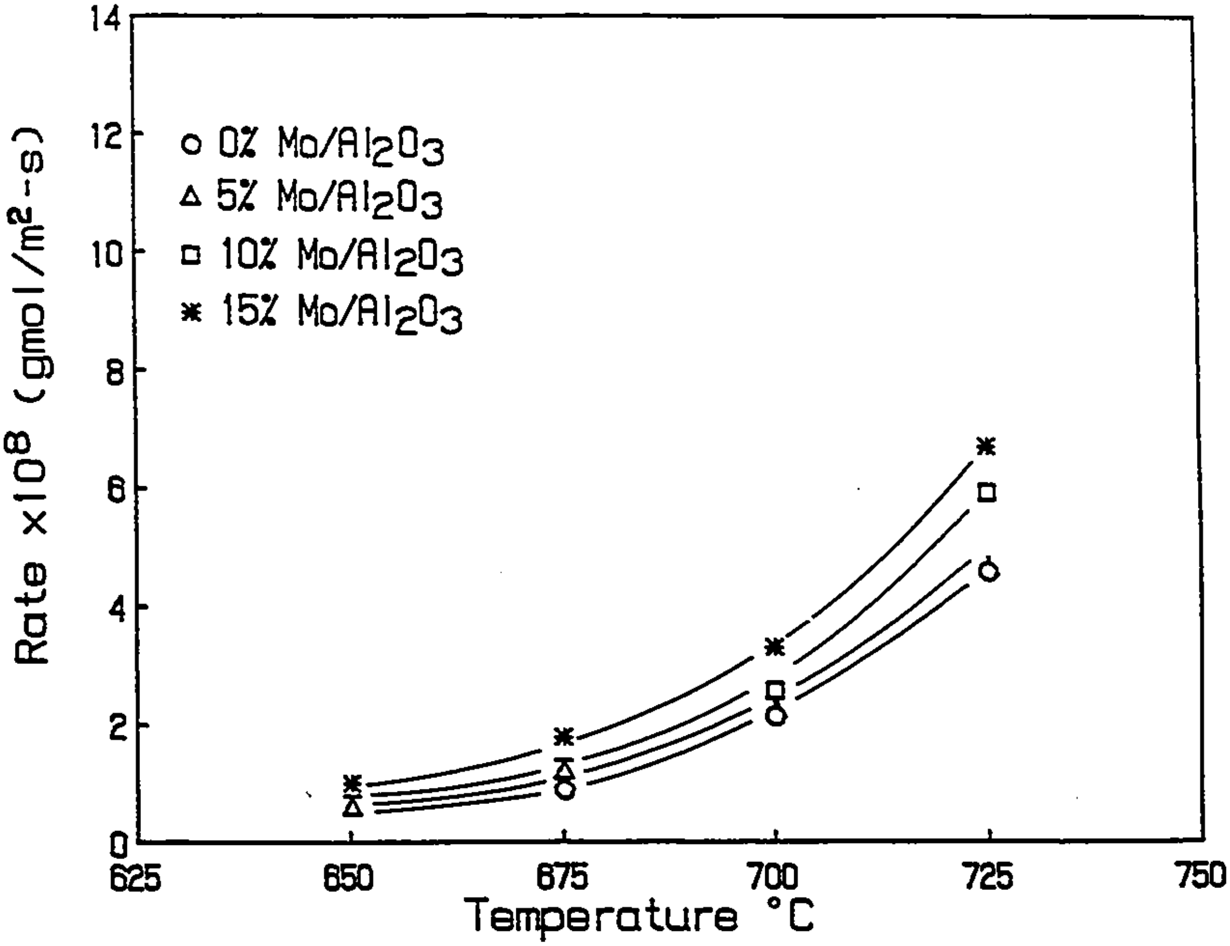


Figure 5.7 Effect of temperature on rate of methane consumption using catalysts with various molybdenum loadings

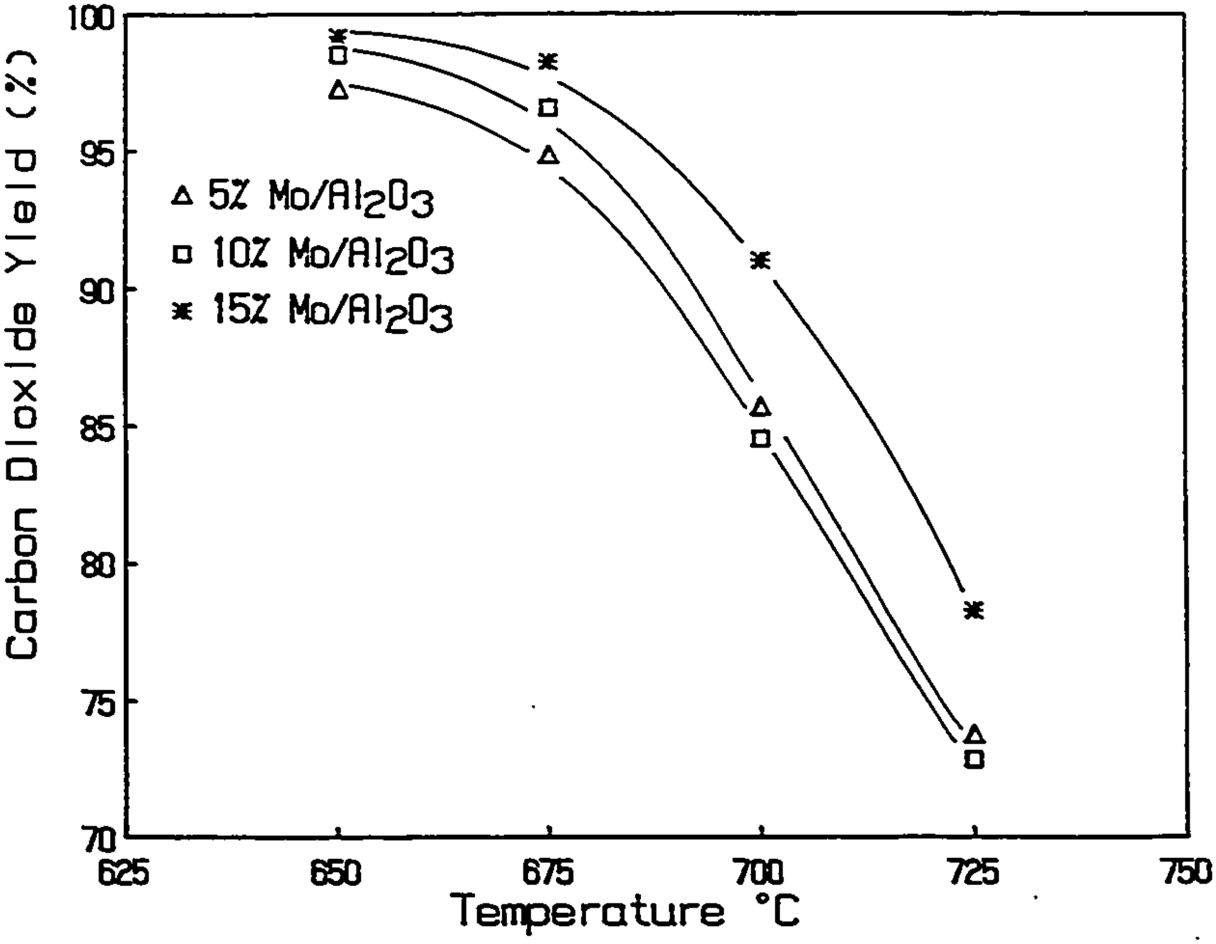


Figure 5.8 Effect of temperature on carbon dioxide yield using catalysts with various molybdenum loadings

shown in Figure 5.8 decrease with increasing temperature, particularly as the temperature is increased to 725°C. The 15% Mo/Al_2O_3 catalyst was again found to provide the highest yield, especially at the highest temperatures tested.

The rates of CO_2 and elemental carbon production are plotted in Figures 5.9 and 5.10, respectively. Carbon dioxide is the most abundant carbon containing product. The rates of production of CO_2 with the 15% Mo/Al_2O_3 catalyst are the highest of all the catalysts. Once again, the results for the 5 and 10% Mo/Al_2O_3 are similar to each other while the rates obtained with alumina are much lower than those obtained with the other catalysts, particularly at 675°C. This is due to the high production of CO with alumina which accounts for over 30% of the carbon from reacted methane. No carbon monoxide was observed at temperatures below 725°C with any of the supported molybdenum catalysts.

Since carbon deposition on the catalyst surface can lead to the eventual deactivation of the catalyst, it is necessary to include the effect of temperature on carbon production rates in the discussion. As shown in Figure 5.10, there is a significant increase in the production of elemental carbon at 725°C. This explains the decrease in CO_2 yields at this temperature shown in Figure 5.8. There is only a slight difference between the three supported

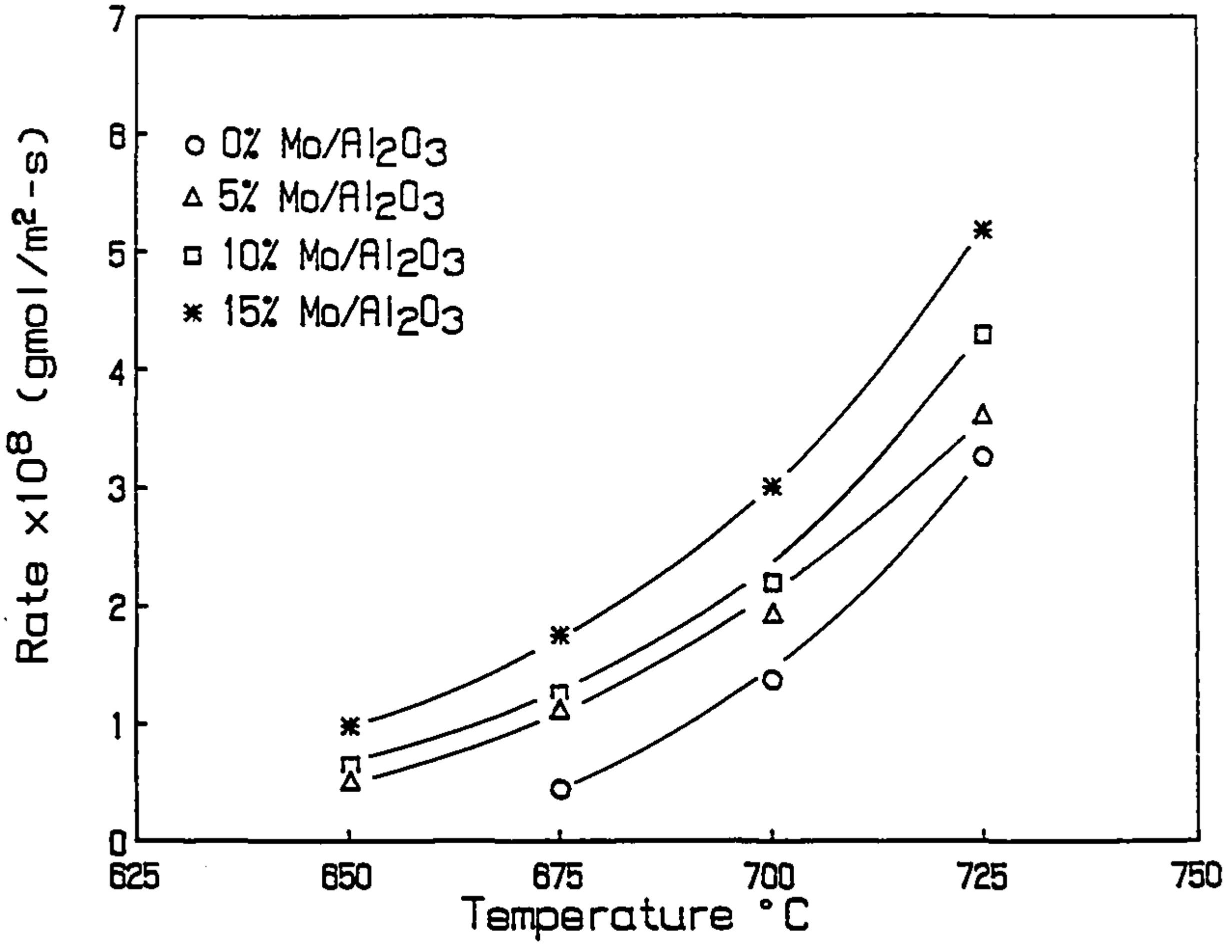


Figure 5.9 Effect of temperature on rate of CO_2 production using catalysts with various molybdenum loadings

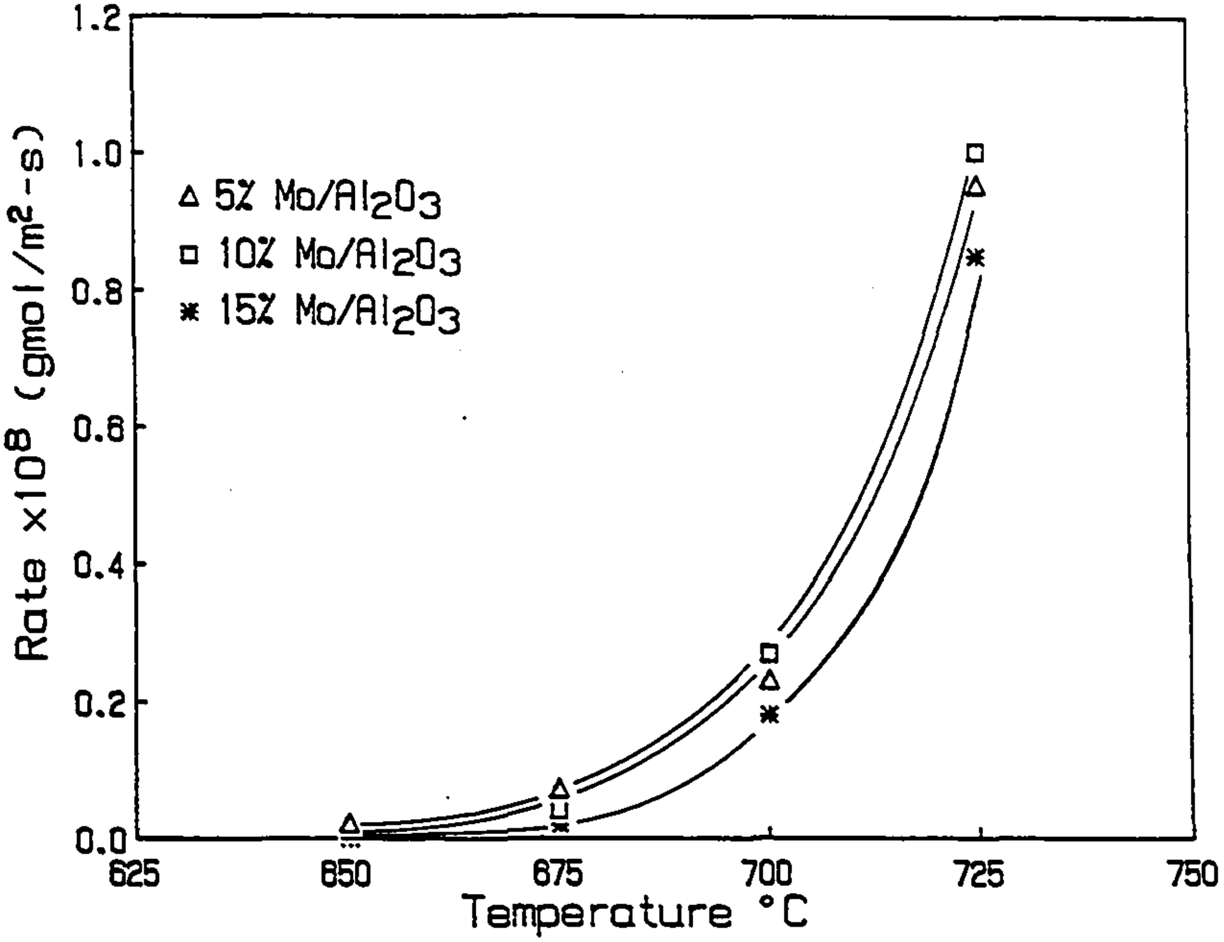


Figure 5.10 Effect of temperature on rate of elemental carbon production using catalysts with various molybdenum loadings

catalysts. On the other hand, compared to pure MoS_2, the rates with the supported molybdenum catalysts are found to be approximately one half (Mulligan and Berk, 1989), while no elemental carbon was produced with alumina even at 725°C. There was no deactivation of any catalysts used in this study, therefore, any carbon which was formed was deposited on the quartz chips after the catalyst bed and not on the catalyst surface.

Although the activity results indicated that the 15% Mo/Al_2O_3 catalyst behaved in the same manner as pure MoS_2, the results for elemental carbon show that there is a difference between the two catalysts. The effect of the support was to improve the performance of the catalyst by decreasing the production of elemental carbon while maintaining the other qualities associated with the pure compound such as high activity and sulphur yield.

No carbon monoxide was found with any supported molybdenum catalyst at temperatures below 725°C. On the other hand, when alumina was used as the catalyst, CO was produced at all temperatures. In fact, as stated above, 30% of the carbon from the reacted methane appeared as CO. Another important difference between the supported molybdenum catalysts and alumina was discussed earlier when the rates of production of H_2S and COS shown in Figures 5.5 and 5.6 were compared. For the supported molybdenum catalysts, the H_2S production rate was 2 to 4 times that of COS while for alumina, the reverse was found to be true. Clearly, a different reaction mechanism is involved when molybdenum is supported on alumina.

There is a definite trend in the results with respect to the loadings of molybdenum. The results obtained with the 5 and 10% Mo catalysts were consistently similar to each other. The 15% Mo loading showed the best overall results, (i.e. high activity and yields), which were also similar to those of pure crystalline MoS_2. Although no positive identification of the surface was made, the degree of MoS_2 crystallization may be a factor. The 5 and 10% Mo loadings provide only limited MoS_2 crystallization on the alumina support surface. On the other hand, the 15% Mo loading is sufficient to allow for significant crystallization. This may explain the results consistent with pure MoS_2 and will be discussed more extensively in Chapter 6.

5.4.3 Effect of Molar Feed Ratio

To this point in the discussion, only the effect of temperature on the performance of the different catalysts using a feed ratio of SO_2 to CH_4 of 1.0 has been considered. From these results the 15% Mo/Al_2O_3 catalyst was determined to be the best of those tested. In order to investigate the effect of reactant concentration, experimentation continued using the same catalyst and a molar feed ratio of 2.0.

The activity and sulphur and CO_2 yields are given in Figures 5.11, 5.12, 5.13, respectively. The effect of the feed ratio on activity is significant, especially at the higher temperatures at which the rate of SO_2 consumption falls by over 50% when the feed ratio is changed from 1.0 to 2.0. Since the CH_4 concentration was decreased from 25 to 15% (see Table 5.5), while that of SO_2 was increased from 25 to 30%, it can be concluded that SO_2 actually has little affect on the reaction rate in comparison to CH_4 (see Chapter 7). In addition, the effect of the molar feed ratio on sulphur yield is also significant. Increasing the feed ratio from 1.0 to 2.0, increased the sulphur yield by up to 4% at 725°C. On the other hand, the CO_2 yield was relatively unaffected by this change. Because of the possible decreased carbon production from the cracking of methane at the lower concentrations of CH_4, higher CO_2 yields were expected. However, CO_2 yields obtained for a feed ratio of 1.0 were already high, and a decrease in CH_4 concentration could only provide insignificant improvements in the CO_2 yield.

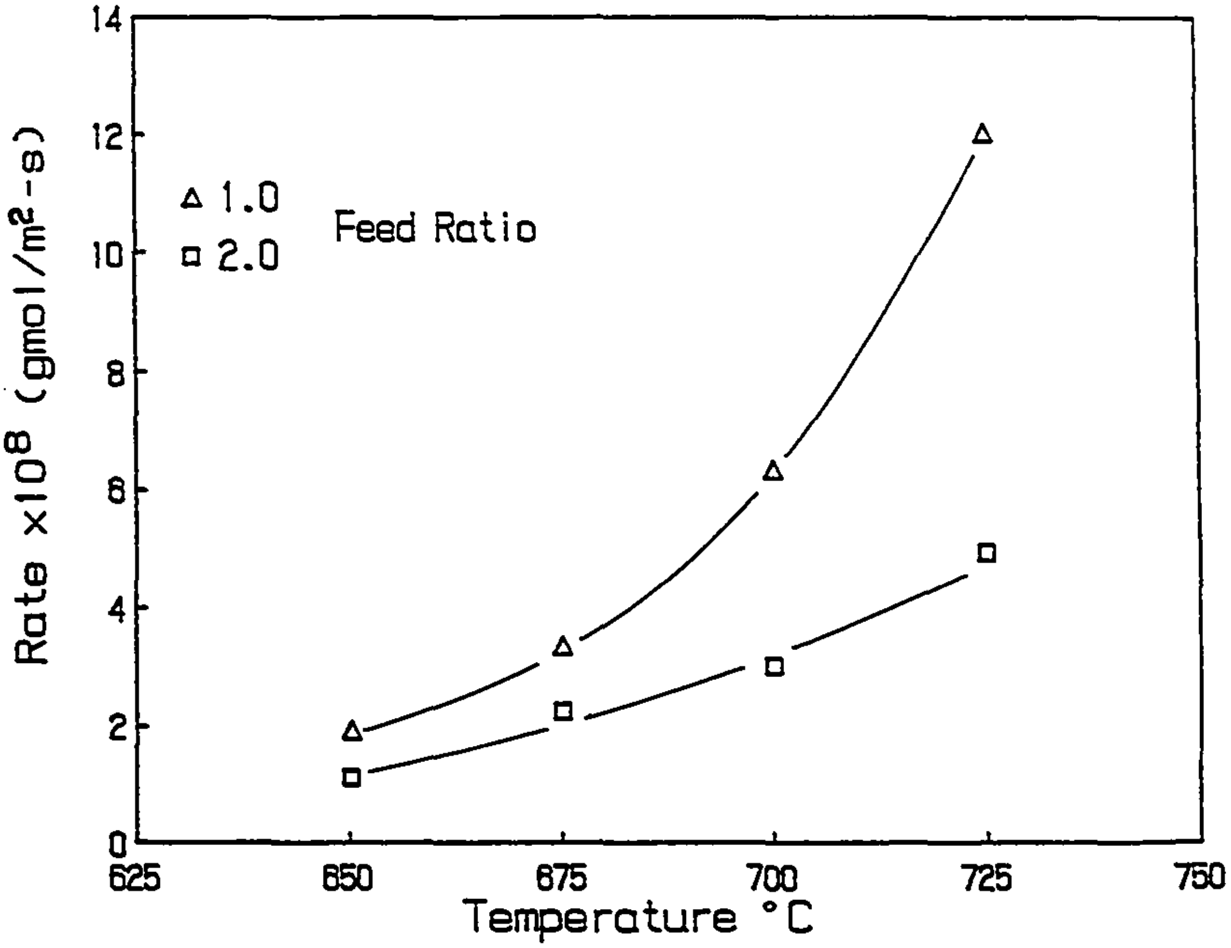


Figure 5.11 Effect of temperature on activity at two feed ratios using 15% Mo/Al_2O_3

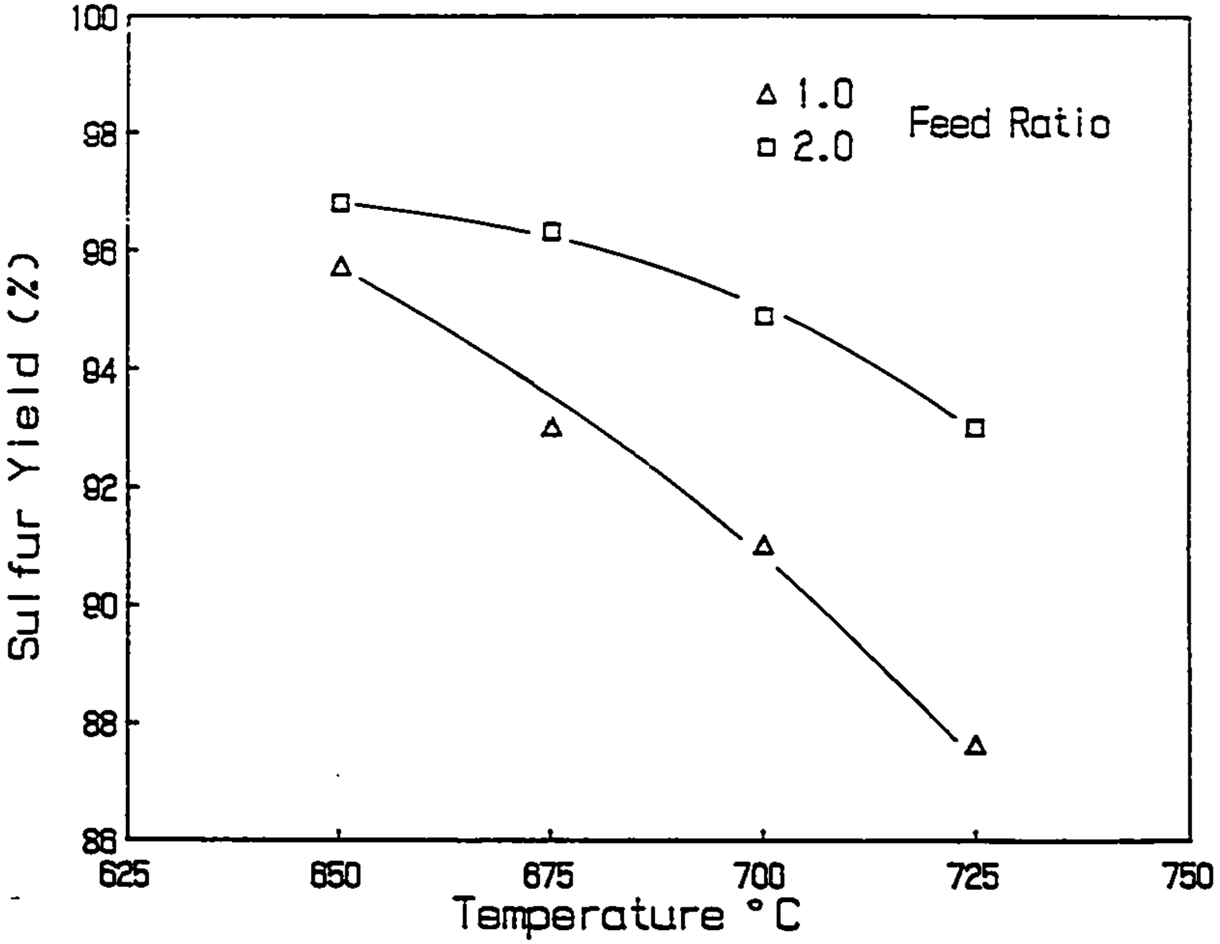


Figure 5.12 Effect of temperature on sulphur yield at two feed ratios using 15% Mo/Al_2O_3

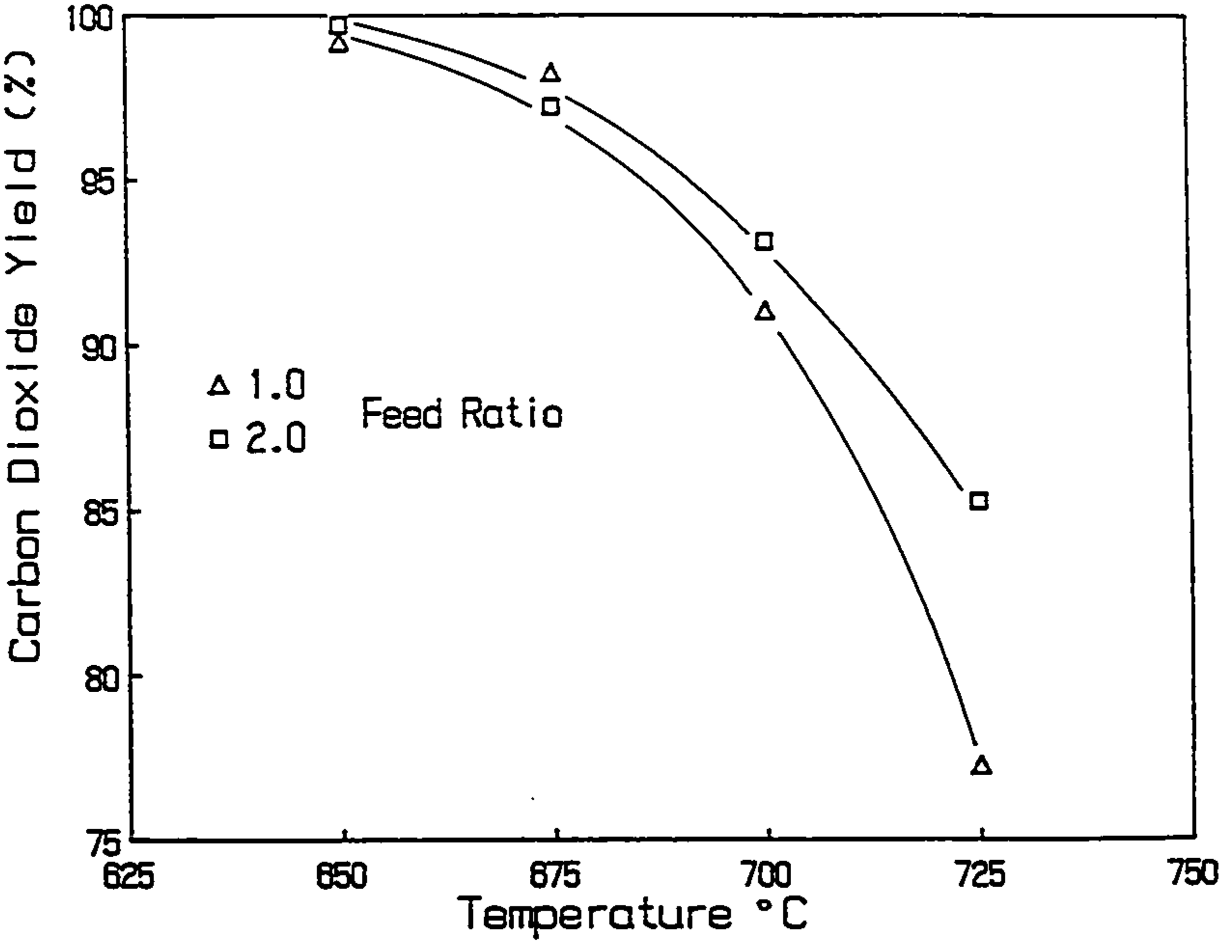


Figure 5.13 Effect of temperature on carbon dioxide yield at two feed ratios using 15% Mo/Al_2O_3

5.4.4 Analysis of Co-Mo/Al_2O_3 Catalyst

As was stated in the literature survey, the addition of cobalt to supported molybdenum catalysts increased the activity for hydrodesulphurization reactions. Tables 5.6a and 5.6b show results comparing the activity and yields of sulphur and CO_2 for 5% Co-15% Mo/Al_2O_3 and 15% Mo/Al_2O_3 when used for the reduction of SO_2 with CH_4 at a feed ratio of 1.0 and temperatures of 700 and 725°C.

Generally, the activity of the cobalt containing catalyst was found to be 20% lower than the supported molybdenum catalyst itself. Both sulphur and CO_2 yields did not significantly change with the addition of cobalt; however, in all cases, sulphur yields were marginally higher with cobalt while CO_2 yields were marginally lower.

One of the reasons cited in the literature for the beneficial effect of cobalt on HDS catalysts is its ability to maintain the even distribution of MoS_2 over the support surface and prevent MoS_2 crystallization (Massoth, 1977). However, pure crystalline MoS_2 has been shown to be an active catalyst for the reduction of SO_2 with CH_4 (Mulligan and Berk, 1989). Therefore, a possible reason for the lower activity of the cobalt catalyst is that it inhibits the formation of MoS_2 crystal clusters on the support surface.

Table 5.6a

Effect of Cobalt on Activity and Yields of Sulphur and CO_2

(T = 700°C)

Catalyst	Activity x 10^8 ($gmol/m^2$-s)	Sulphur Yield (%)	CO_2 Yield (%)
15% Mo/Al_2O_3	6.3	92.6	91.0
5% Co-15% Mo/Al_2O_3	5.1	93.7	87.3

Table 5.6b

Effect of Cobalt on Activity and Yields of Sulphur and CO_2

(T = 725°C)

Catalyst	Activity x 10^8 ($gmol/m^2$-s)	Sulphur Yield (%)	CO_2 Yield (%)
15% Mo/Al_2O_3	12.0	87.6	77.2
5% Co-15% Mo/Al_2O_3	9.8	89.5	73.5

Sarlis and Berk (1990), who also investigated the effect of cobalt, reported that a 3.5% CoO-14% MoO_3/Al_2O_3 catalyst was more active than a 10% MoO_3/Al_2O_3 catalyst. They concluded that cobalt enhanced the performance of the supported molybdenum catalyst. In fact, as was shown in this work, higher Mo loadings result in higher activity (Figure 5.2); therefore the increased activity of the cobalt containing catalyst was due to its higher molybdenum content and not the presence of cobalt.

Since there were no problems encountered with the stability of the supported molybdenum catalyst, and the addition of cobalt did not improve the characteristics and performance of the catalyst, the addition of cobalt was concluded to be undesirable for the reduction of SO_2 with CH_4.

5.4.5 Effect of Catalyst Support

In the following section, a combination SiO_2-Al_2O_3 support is compared with an alumina support. There are two reasons for selecting a silica-alumina support for high temperature reactions. Firstly, silica-alumina has a more stable structure than alumina itself which has many transition phases. Secondly, SiO_2-Al_2O_3 has a much higher surface area after conditioning at high temperature. In fact, the surface area is almost twice as high as that of alumina (Table 5.4). In this section, the catalytic behaviour of a 15% Mo/SiO_2-Al_2O_3 catalyst and a 15% Mo/Al_2O_3 catalyst is compared.

The first aspect of catalyst performance to be considered is that of activity. For both catalysts, the results are plotted in Figure 5.14. The 15% Mo/SiO_2-Al_2O_3 catalyst has an activity approximately 1/10 that of the 15% Mo/Al_2O_3 catalyst. Although the surface area is twice as high for the SiO_2-Al_2O_3 support, at least five times the amount of catalyst would be required in an industrial application in order to obtain a similar SO_2 conversion.

The yields of elemental sulphur and carbon dioxide are plotted versus temperature in Figures 5.15 and 5.16 respectively. In the case of sulphur yield, results are 3-4% higher than with the alumina support. Likewise, in the case of carbon dioxide yield, results are higher with the SiO_2-Al_2O_3 support at the higher temperatures, particularly at 725°C where the CO_2 yield is 91% compared to 77% found with the alumina support. It should be noted that when the SiO_2-Al_2O_3 pellets were used without molybdenum on its surface, the CO_2 yield at 700°C was found to be only 12% as compared to 95% with the 15% Mo loading. This could be due to the fact that SiO_2-Al_2O_3 is a hydrocarbon cracking catalyst and therefore, large amounts of elemental carbon, CO, and COS were produced as opposed to CO_2.

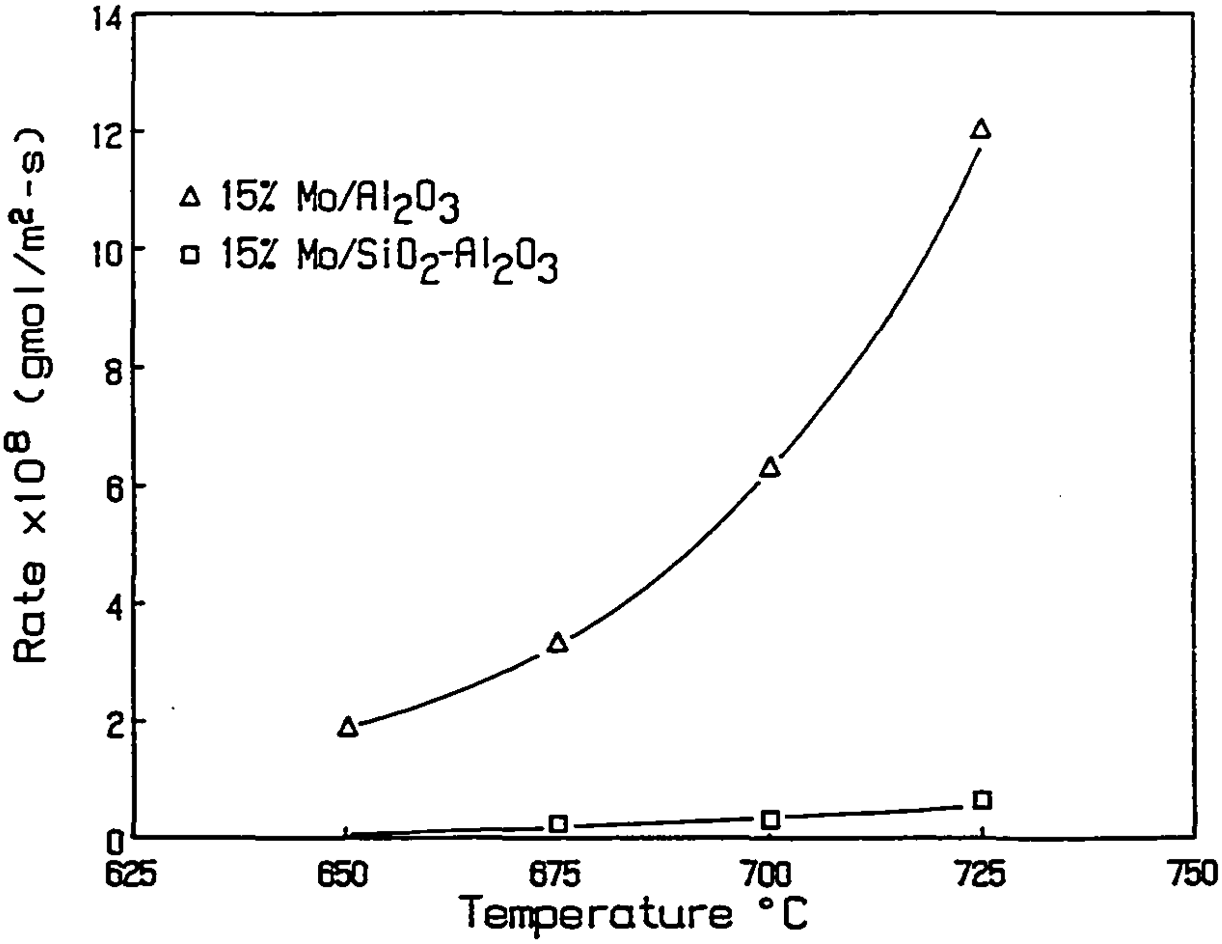


Figure 5.14 Effect of catalyst support material on the rate of SO_2 consumption

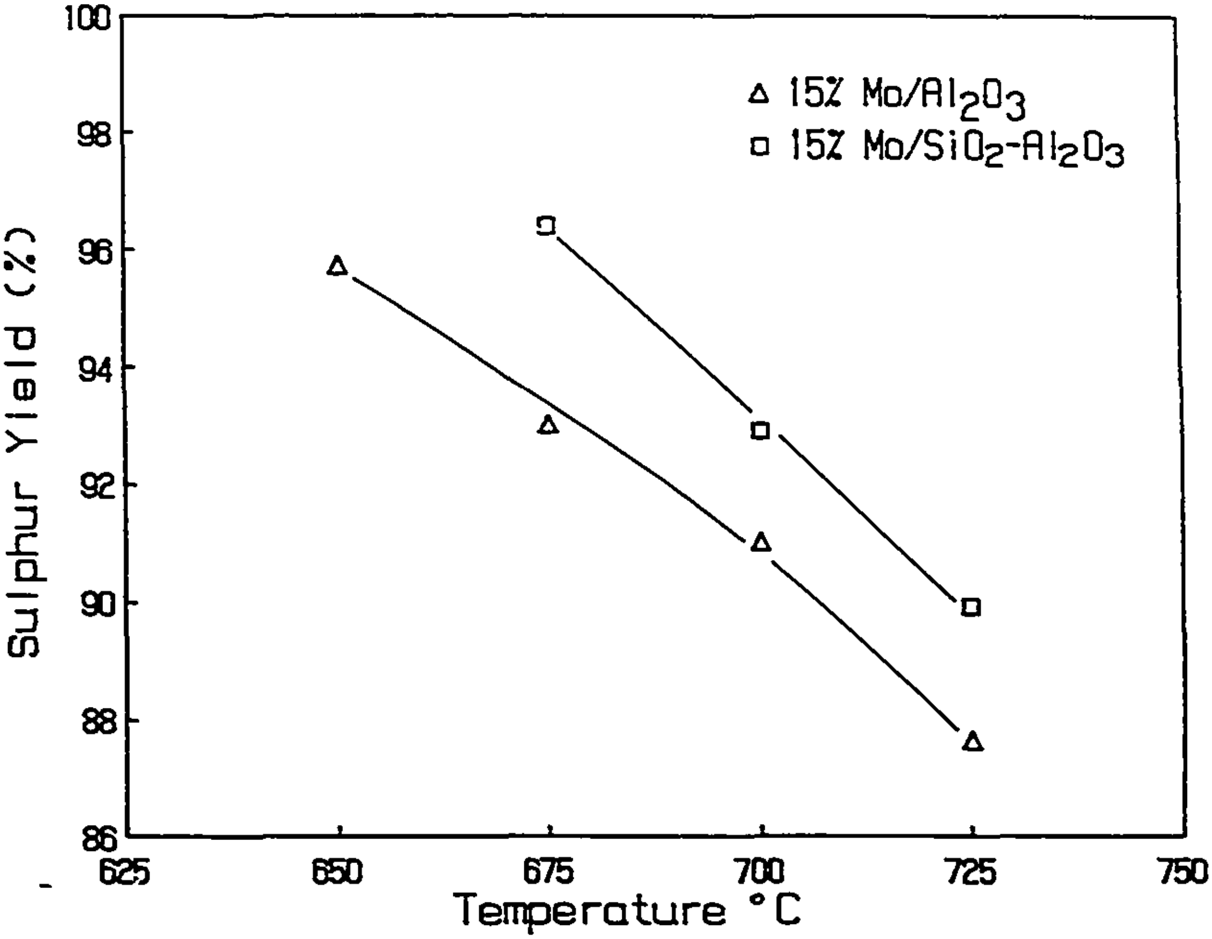


Figure 5.15 Effect of catalyst support material on sulphur yield

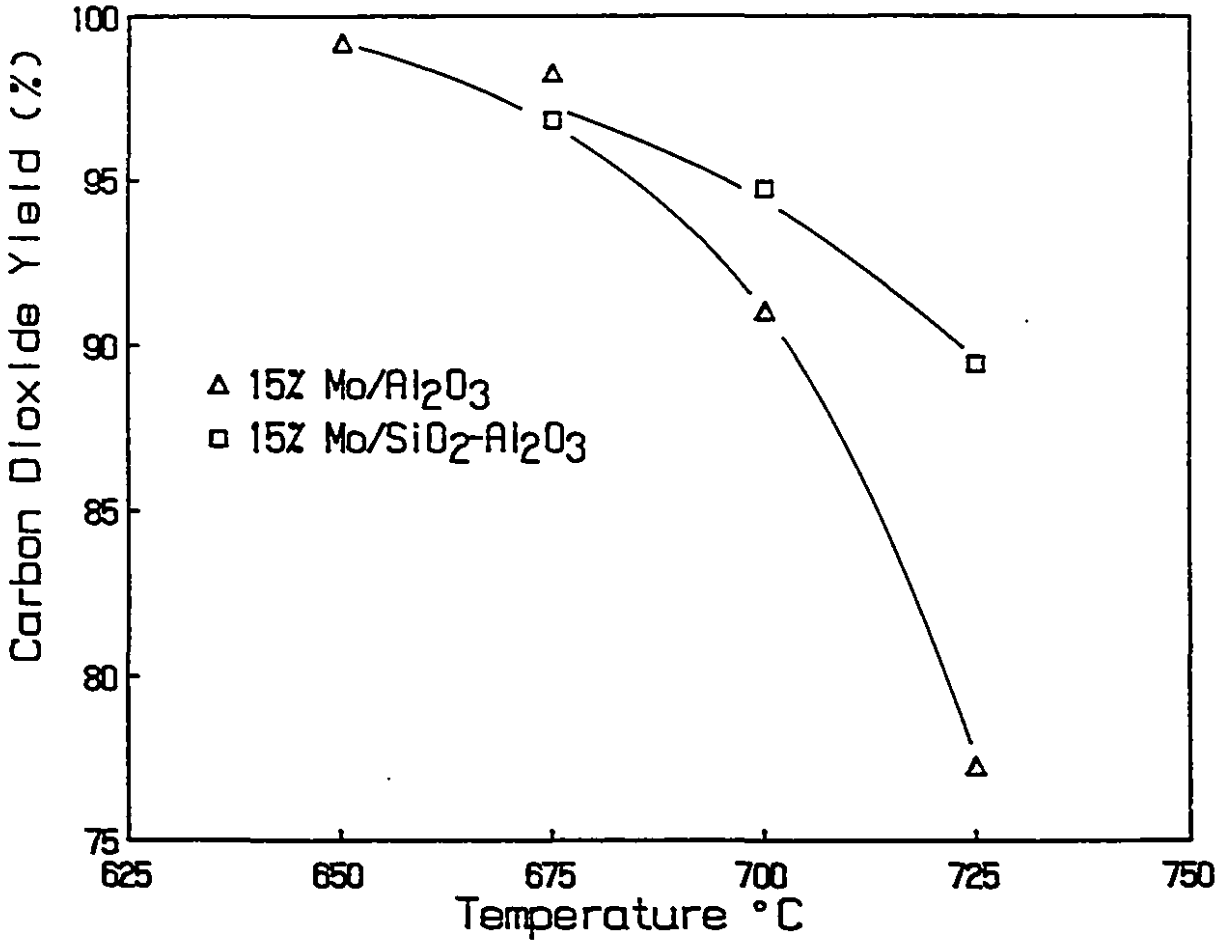


Figure 5.16 Effect of catalyst support material on carbon dioxide yield

The conclusion from this comparison between supports is that there is a significant synergistic effect between the molybdenum and the surface of the support material. Clearly, neither the active sulphide phase nor the support act independently of each other. Since the activity was significantly higher for the alumina supported catalysts, the silica-alumina support will no longer be considered and the remainder of this study will focus on the alumina supported catalysts.

5.5 Integral Conversion Results

As stated above, all results presented thus far were determined from experiments where the conversions were less than 20%. For an industrial process; however, conversions as high as 100%, are required. Therefore, integral conversion results are presented in Tables 5.7 and 5.8 for the 15% Mo/Al_2O_3 catalyst and alumina. Conversions of SO_2, for both catalysts, were approximately 30% and 100% at 650 and 700°C, respectively. The higher conversions for these experiments in comparison to the differential experiments were obtained by simply increasing the catalyst loading in the reactor. Again, the two catalysts are compared with respect to their activities, and to the yields of sulphur and CO_2 for a molar feed ratio of 1.0 at the temperatures of 650 and 700°C.

Table 5.7

Reaction Rates of Sulphur Species
(Rates x 10^9 gmol/m^2-s)

	15% Mo/Al_2O_3		Alumina	
	650°C	700°C	650°C	700°C
SO_2	10.6	26.4	8.74	28.2
[S]	9.54	14.1	8.24	8.07
H_2S	0.90	11.9	0.39	19.3
COS	0.03	0.39	0.11	0.83

Table 5.8

Yields of Sulphur and Carbon Dioxide

	Sulphur Yield (%)		CO_2 Yield	
	650°C	700°C	650°C	700°C
15% Mo/Al_2O_3	91.1	53.4	99.4	97.7
Alumina	94.3	28.9	88.5	91.7

The rates of SO_2 consumption of both catalysts are comparable to each other at both temperatures with the rates with alumina being slightly higher at 700°C. It is also seen that the sulphur yields for both catalysts decrease significantly with the increase in temperature. A comparison of the two catalysts shows that, at 700°C, the sulphur yield obtained with 15% Mo/Al_2O_3 was 25% higher than that of alumina. The higher rate of consumption of SO_2 with alumina at this temperature, therefore, was the result of the increased production of H_2S and not that of elemental sulfur. Clearly, if reasonably high sulphur yields are to be maintained, the reaction temperature must be kept below 700°C.

The rate of COS production increased approximately by an order of magnitude with the increase in temperature for both catalysts; however, these rates remain relatively low compared to those of H_2S. Temperature had little effect on the CO_2 yields for either catalyst. However, the supported molybdenum catalyst results were at least 6% higher than the CO_2 yields obtained with alumina and remained above 97%, even with the high conversions.

5.6 Summary

The catalyst preparation procedure was found to be repeatable and effective in producing catalysts with the desired quantity, and uniform distribution of molybdenum. All molybdenum loadings (i.e. 5, 10, and 15% Mo) showed higher activities, and higher sulphur and CO_2 yields than alumina. The 5 and 10% Mo/Al_2O_3 catalysts were similar in all three aspects of catalyst performance considered. However, the 15% Mo/Al_2O_3 catalyst was found to have activity 1.5 to 2 times those of the other loadings, higher sulphur yields, and comparable CO_2 yields. This catalyst was also found to be stable under the severe reaction conditions. The major side product was H_2S but its rate of production could be minimized by keeping the reaction temperature below 700°C. Increasing the molar feed ratio of SO_2 to CH_4 from 1.0 to 2.0 was found to improve the sulphur yield by up to 4%, but had no effect on the CO_2 yield, and decreased the rate of SO_2 consumption by 50% at 725°C.

The addition of cobalt to the alumina supported molybdenum catalyst had a detrimental effect on its performance. Although sulphur and CO_2 yields were relatively unaffected by the addition of cobalt, the activity was reduced by 20%. In the case of support material, the 15% Mo/Al_2O_3 catalyst was concluded to be superior because of its ten-fold increase in activity over the 15% Mo/SiO_2-Al_2O_3 catalyst despite the higher surface area and higher yields of elemental sulphur and CO_2 of the silica-alumina supported catalyst.

CHAPTER 6

EFFECT OF SULPHIDATION PROCEDURE

The objective of this chapter is to compare the method of catalyst sulphidation using H_2S with the method using SO_2 and CH_4. In this chapter, experimental results obtained for alumina supported catalysts which were sulphided using either H_2S or SO_2 and CH_4 will be presented. The experimental results are compared with the results of a thermodynamic analysis of these heterogeneous systems.

6.1 Catalyst Evaluation Criteria

The two sulphidation procedures will be evaluated on the basis of molybdenum retention, sulphur to molybdenum ratio, and the ratio of MoS_2 to Al_2O_3 support expressed as grams MoS_2 per 100 g Al_2O_3. The first criterion is a measure of the removal of molybdenum from the support surface as molybdena species may volatilize at the high temperatures used in this study. The second criterion is a measure of the degree of sulphidation of the molybdenum remaining on the surface. Since X-ray diffraction analysis of the sulphided catalysts showed that the only sulphide formed is MoS_2, a S/Mo ratio of 2.0 would indicate complete sulphidation. The last criterion is a measure of support surface coverage. Okamato <u>et al</u>. (1977) report that a maximum 10-15% Mo content in the form of MoO_3 remains well dispersed in a monolayer coverage of a 180 m^2/g Al_2O_3 support surface. Based on this result and considering the conversion of MoO_3 to MoS_2 and a support surface area of 135 m^2/g of Al_2O_3 in the present work, approximately 15 g of MoS_2 are required per 100 g Al_2O_3 in a monolayer coverage.

6.2 Catalysts Sulphided with H_2S

6.2.1 Experimental Results and Discussion

The supported MoO_3/Al_2O_3 catalysts prepared as described in section 4.1 were sulphided using a 12% H_2S in argon mixture at 600°C. During the sulphidation procedure, the exit gas was analyzed. In addition to argon and unreacted H_2S, SO_2 was also found. In fact, during the first 5 minutes, the only sulphur bearing gaseous component was SO_2 as all of the H_2S was initially consumed. Subsequently, some unreacted H_2S appeared, and the SO_2 content decreased.

In the following two hours of sulphidation, as much as 0.1% of the reaction exit flow was found to be SO_2. Sulphidation was assumed to be complete when the SO_2 concentration was negligible and no further change was found in the H_2S concentration. During this procedure, elemental sulphur accumulated at the cold reactor exit. Normally, 5 hours were required for the completion of the procedure.

Table 6.1 shows the composition of 5, 10, and 15% Mo/Al_2O_3 catalyst following sulphidation. The only components were MoS_2, MoO_2, and Al_2O_3; no MoO_3 was detected in any of the samples (see Section 5.1.3). These results indicate that in the experiments, the MoO_3 was not completely sulphided but rather some was partially reduced to MoO_2.

In chapter 5, it was noted that the 5 and 10% Mo/Al_2O_3 catalysts had similar catalytic behaviour with respect to activity and selectivity. It was also noted that the 15% loading had the highest activity and yields of sulphur and carbon dioxide which were also similar to those obtained with pure crystalline MoS_2.

These results may be explained by the data on molybdenum retention, sulphur to molybdenum ratio, and grams of MoS_2 per 100 g Al_2O_3 support shown in Table 6.2 for the H_2S sulphided catalysts. Firstly, under the sulphiding conditions used in the preparation, no molybdenum was removed from any of the catalysts. Secondly, the sulphur to molybdenum ratio increased with increasing molybdenum loading. This suggests that as the molybdenum loading was

Table 6.1

Composition of the Mo/Al_2O_3 Catalysts with Various Molybdenum Loadings Sulphided with H_2S

	MoS_2	MoO_2	Al_2O_3
5% Mo/Al_2O_3	4.5%	2.6%	92.9%
10% Mo/Al_2O_3	10.3%	4.2%	85.5%
15% Mo/Al_2O_3	17.0%	4.2%	78.8%

Table 6.2

Molybdenum and Sulphur Content of the Catalysts Sulphided with H_2S

	Molybdenum Retention	S/Mo	$\frac{MoS_2}{100g\ Al_2O_3}$
5% Mo/Al_2O_3	100%	1.14	4.8 g
10% Mo/Al_2O_3	100%	1.33	12.0 g
15% Mo/Al_2O_3	100%	1.53	21.6 g

increased more Mo having bulk properties was available for sulphidation. This explanation is consistent with the observations of LoJacono et al. (1973) and is further supported by the previous kinetic data which showed that the 15% Mo/Al_2O_3 catalyst behaved in a manner similar to that of pure crystalline MoS_2.

It was found that the ratio of MoS_2 to Al_2O_3 also increased with increasing molybdenum loading. This is not surprising considering that there was more molybdenum available and that, as was previously stated, the molybdenum was sulphided to a greater degree. However, these data are significant when compared to the quantity of MoS_2 required for monolayer coverage. As calculated above, approximately 15 g of MoS_2 per 100 g of Al_2O_3 is the expected limit for monolayer coverage. Therefore, both the 5% and 10% Mo catalysts have only sufficient MoS_2 to allow for simple monolayer coverage. On the other hand, the 15% Mo/Al_2O_3 catalyst has 21.6 g MoS_2/100 g Al_2O_3 which is 50% more MoS_2 than is theoretically required for simple monolayer coverage. Therefore, this catalyst has a sufficient MoS_2 content to cover the alumina surface and allow for some MoS_2 crystallization.

6.2.2 Thermodynamic Analysis

The thermodynamic analysis was performed using the software package F*A*C*T which is based on free energy minimization. For the thermodynamic analysis, the only components that were present in the initial mixture were solid MoO_3 and gaseous H_2S and argon. No restriction was placed on possible products. The analyses were performed using a temperature of 600°C and a large excess of gaseous reactant (1000 moles gas per mole of MoO_3) in order to simulate the laboratory experiments.

Table 6.3 shows that the gaseous products present at equilibrium consist primarily of H_2S, H_2, S_2, H_2O, SO_2, while the only solid products are MoO_2, and MoS_2. No MoO_3 was found at equilibrium, consistent with the experimental data. The sulphidation of MoO_3 is limited almost exclusively by the availability of sulphur. Since one mole of MoO_3 was used in the analysis, theoretically two moles of atomic sulphur would be required to produce one mole of MoS_2. In fact, as shown in Table 6.3, when an excess of atomic sulphur was introduced into the system in the form of H_2S, complete sulphidation is achieved. When sulphur is not in excess, MoO_2 is the only oxidized molybdenum component. In this case, the mole fractions of elemental sulphur S_2, and SO_2 remain constant with increasing initial H_2S

Table 6.3

Equilibrium Composition of the MoO_3 - H_2S - Ar System at 873 K and Various Initial Concentrations of H_2S

Initial Species Abundance (mol)			Equilibrium Mole Fractions					Moles	
MoO_3	H_2S	Ar	H_2S	H_2	S_2	H_2O	SO_2	MoS_2	MoO_2
1.0	0.5	999.5	1.39×10^{-7}	4.93×10^{-7}	1.77×10^{-7}	4.99×10^{-4}	3.33×10^{-4}	0.083	0.917
1.0	1.0	999.0	2.79×10^{-7}	9.87×10^{-7}	•	9.98×10^{-4}	•	0.332	0.667
1.0	1.5	998.5	4.18×10^{-7}	1.48×10^{-6}	•	1.50×10^{-3}	•	0.583	0.417
1.0	2.0	998.0	5.57×10^{-7}	1.97×10^{-6}	•	2.00×10^{-3}	•	0.833	0.167
1.0	2.5	997.5	6.59×10^{-7}	1.16×10^{-5}	7.23×10^{-5}	2.42×10^{-3}	2.89×10^{-4}	1.00	0
1.0	3.0	997.0	2.80×10^{-4}	2.49×10^{-5}	2.81×10^{-4}	2.69×10^{-3}	1.52×10^{-3}	1.00	0

abundance until complete sulphidation of MoO_2 to MoS_2 occurs.

This thermodynamic analysis was repeated for various concentrations of H_2S ranging from 0.05% to 12% and for temperatures ranging from 25°C to 650°C (Tables 6.4 and 6.5). In all cases, as long as sulphur was in excess, MoS_2 was the only solid product. In the laboratory sulphidation was observed even at 25°C.

A possible mechanism consistent with the above observations consists of first the decomposition of H_2S to H_2 and sulphur. Hydrogen then reduces MoO_3 to MoO_2 which is then sulphided to MoS_2 with elemental sulphur producing SO_2. This mechanism can be summarized by the following reactions.

$$H_2S \dashrightarrow H_2 + 1/2\ S_2 \qquad (6.1)$$

$$MoO_3 + H_2 \dashrightarrow MoO_2 + H_2O \qquad (6.2)$$

$$MoO_2 + S_2 \dashrightarrow MoS_2 + SO_2 \qquad (6.3)$$

Both experimentally and thermodynamically, there is no MoO_3 observed indicating that the reduction with hydrogen, (reaction 6.2), goes to completion. The fact that the mole fractions of S_2 and SO_2 remain constant until the complete sulphidation of MoO_2 to MoS_2 is consistent with reaction 6.3.

In contrast to the thermodynamic calculations, complete sulphidation was never achieved in the experiments. This is

Table 6.4

Equilibrium Composition of the MoO_3 - H_2S - Ar System at 298 K and Various Initial Concentrations of H_2S

Initial Species Abundance (mol)			Equilibrium Mole Fractions					Moles	
MoO_3	H_2S	Ar	H_2S	H_2	S_2	H_2O	SO_2	MoS_2	MoO_2
1.0	0.5	999.5	7.05×10^{-15}	1.29×10^{-17}	6.29×10^{-20}	4.99×10^{-4}	3.33×10^{-4}	0.083	0.917
1.0	1.0	999.0	1.41×10^{-14}	2.59×10^{-17}	•	9.98×10^{-4}	•	0.332	0.667
1.0	1.5	998.5	2.11×10^{-14}	3.88×10^{-17}	•	1.50×10^{-3}	•	0.583	0.417
1.0	2.0	998.0	2.82×10^{-14}	5.17×10^{-17}	•	2.00×10^{-3}	•	0.833	0.167
1.0	2.5	997.5	1.91×10^{-9}	2.70×10^{-15}	1.06×10^{-14}	2.50×10^{-3}	2.49×10^{-4}	1.00	0
1.0	3.0	997.0	1.38×10^{-7}	1.95×10^{-13}	1.06×10^{-14}	3.00×10^{-3}	6.91×10^{-8}	1.00	0

Table 6.5

Equilibrium Composition of the MoO_3 - H_2S - Ar System at 923 K and Various Initial Concentrations of H_2S

Initial Species Abundance (mol)			Equilibrium Mole Fractions					Moles	
MoO_3	H_2S	Ar	H_2S	H_2	S_2	H_2O	SO_2	MoS_2	MoO_2
1.0	0.5	999.5	8.73×10^{-7}	9.93×10^{-7}	4.11×10^{-7}	4.99×10^{-4}	3.33×10^{-4}	0.083	0.917
1.0	1.0	999.0	6.55×10^{-7}	1.99×10^{-6}	•	9.98×10^{-4}	•	0.332	0.667
1.0	1.5	998.5	4.37×10^{-7}	2.97×10^{-6}	•	1.50×10^{-3}	•	0.583	0.417
1.0	2.0	998.0	2.18×10^{-7}	3.97×10^{-6}	•	2.00×10^{-3}	•	0.833	0.167
1.0	2.5	997.5	5.75×10^{-5}	1.92×10^{-5}	7.66×10^{-5}	2.42×10^{-3}	2.89×10^{-4}	1.00	0
1.0	3.0	997.0	2.51×10^{-4}	4.22×10^{-5}	2.99×10^{-4}	2.71×10^{-3}	1.46×10^{-4}	1.00	0

probably due to the fact that some of the molybdenum was bound to the support surface and was not easily sulphided. As described earlier, as the molybdenum loading was increased, more molybdenum having bulk properties was available and thus a greater degree of sulphidation was observed. However, the thermodynamic analysis assumes that there is no support surface effect on the molybdenum and complete sulphidation is possible.

Finally, the equilibrium volatilities of the possible molybdenum compounds MoO_3, MoO_2 and MoS_2, were also examined. MoO_3 was the only compound found to be volatile even at temperatures in excess of 750°C used in experimentation. This demonstrates one of the primary advantages in using H_2S as a sulphiding agent for MoO_3. The reaction can proceed at a reasonable rate even at relatively low temperatures. This is important because while MoS_2 and MoO_2 are not volatile at any of the reaction temperatures used, MoO_3 is volatile and can be removed from the support surface over time, particularly at temperatures in excess of 750°C. Because MoO_3 is sulphided, or at least reduced to MoO_2 before it can be removed, 100% Mo retention is achieved for all catalyst loadings.

6.3 Sulphidation Using SO_2 and CH_4

6.3.1 Experimental Results and Discussion

When SO_2 is reduced with methane, the sulphur bearing products include elemental sulphur, H_2S, and COS, as well as unreacted SO_2. As stated in the literature survey, oxidized HDS catalysts are known to become sulphided under SO_2 reduction conditions. In order to investigate the activity of alumina supported MoO_3 and to assess the degree of sulphidation using this method, the following preliminary experiment was performed. A sample of oxidized 15% Mo/Al_2O_3 catalyst was charged to the reactor and using a feed of 25% SO_2, 25% CH_4, and 50% Ar and a temperature of 700°C, the transient conversion of SO_2 was followed until steady state was achieved. The reactor was then cooled to ambient temperature while it was purged continuously with argon.

A visual examination of the catalyst bed showed that the originally yellowish-white pellets (MoO_3) became black during the reaction indicating the presence of MoS_2. The reaction was restarted after 15 hours using the same reaction conditions and the same catalyst pellets in order to determine if the initial increase in activity was due to catalyst conditioning or molybdenum sulphidation. The transient conversion of SO_2 was again recorded. The results are plotted in Figure 6.1.

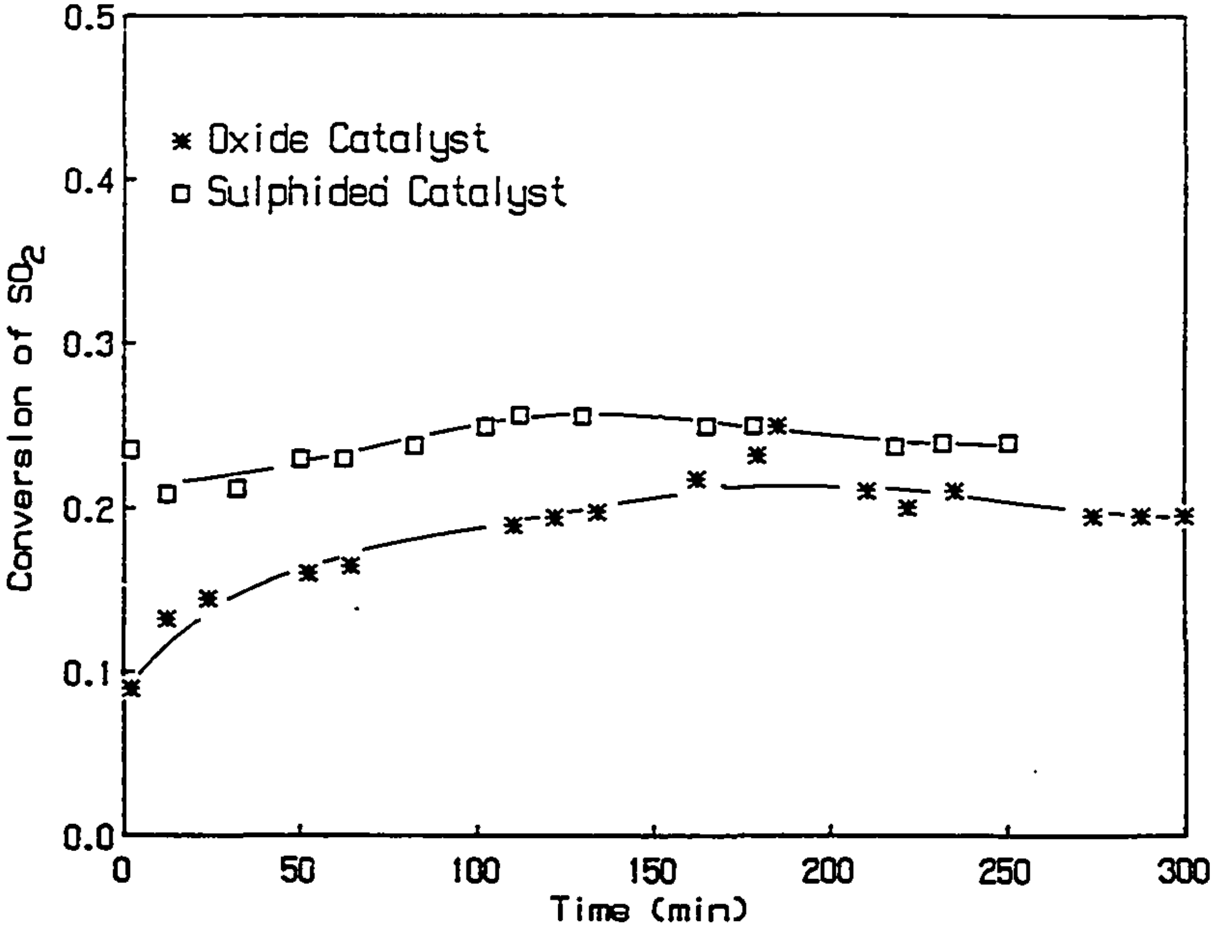


Figure 6.1 Transient conversion of SO_2 as a function of time using a 15% Mo/Al_2O_3 catalyst (SO_2/CH_4 feed ratio = 1, temperature = 700°C)

As can be seen, the initial activity of the oxidized catalyst is relatively low. Sulphur dioxide conversion is only 9%. The conversion gradually increases to a steady state value of 21%. Once sulphided, the catalyst activity is stabilized. In the case of the sulphided catalyst, conversion varies by less than 2% and reaches a steady state value of 22%. These results show that the SO_2 reduction system does sulphide an oxidized catalyst and that the sulphided catalysts are significantly more active than are their oxidized forms.

In order to investigate the effect of temperature on the sulphidation of an oxidized 15% Mo/Al_2O_3 catalyst using SO_2 and CH_4, sulphidation experiments were run using various temperatures and a feed composition of 25% SO_2, 25% CH_4, and 50% Ar. The experiments were run for approximately 5 to 6 hours, which was the required time to achieve steady state.

The steady state composition of the reactor exit gases are given in Table 6.6 for the temperatures of 650, 700, and 750°C. In all cases, there was unreacted SO_2 and CH_4 present at steady state. In fact, at 650°C, over 21% of the exit gas was SO_2. Elemental sulphur was present at all temperatures, as was H_2S, CO_2, H_2O, and inert argon. Carbonyl sulphide and CO were present only at the higher temperatures and only at mole fractions of 0.5% or less. On

Table 6.6

Steady State Exit Gas Composition for SO_2/CH_4 Sulphidation of 15% Mo/Al_2O_3 Catalysts at Various Temperatures

	650°C	700°C	750°C
SO_2	21.1%	19.0%	8.8%
CH_4	23.1%	21.1%	14.4%
S_2	1.6%	2.4%	6.0%
H_2S	0.1%	0.3%	1.7%
COS	0.0%	0.1%	0.4%
CO_2	1.7%	2.3%	6.3%
H_2O	3.5%	5.8%	14.8%
CO	0.0%	0.0%	0.5%
Ar	48.9%	49.0%	47.1%

the other hand, the elemental sulphur mole fraction for all temperatures is greater than 1.6%.

Table 6.7 shows the steady state composition of three 15% Mo/Al_2O_3 catalysts sulphided at the temperatures of 650, 700, 750°C. In all cases, significant quantities of MoO_2 remain (c.f. Table 6.1). Although, greater sulphidation is achieved as the temperature is increased, the quantity of MoS_2 is significantly less than when the 15% Mo/Al_2O_3 was sulphided using H_2S.

The molybdenum retention, S/Mo ratio, and MoS_2 content, are presented in Table 6.8 for the three catalysts sulphided during the reduction of SO_2. At 750°C, the Mo retention is only 87.4%, indicating that some MoO_3 is removed before it is reduced. As expected, the S/Mo ratio is a strong function of temperature with almost twice the degree of sulphidation at 750°C as at 650°C. Therefore, while the highest temperature tested allows for a more complete sulphidation of the molybdenum, there is less molybdenum remaining on the surface to be sulphided and hence, there is little increase in the MoS_2 content at 750°C in comparison to 700°C. As shown previously, this decrease in the molybdenum content is due to the loss of MoO_3 by volatilization.

Table 6.7

Composition of the 15% Mo/Al_2O_3 Catalysts Sulphided with SO_2/CH_4 at Various Temperatures

	MoS_2	MoO_2	Al_2O_3
650°C	8.0%	11.5%	80.5%
700°C	12.0%	8.3%	79.7%
750°C	13.1%	5.2%	81.7%

Table 6.8

Molybdenum and Sulphur Content of the 15% Mo/Al_2O_3 Catalysts Sulphided with SO_2/CH_4 at Various Temperatures

	Molybdenum Retention	S/Mo	$\frac{MoS_2}{100g\ Al_2O_3}$
650°C	100%	0.71	9.9 g
700°C	100%	1.07	15.1 g
750°C	87.4%	1.34	16.0 g

6.3.2 Thermodynamic Analysis

The thermodynamic analysis for this system consists of the determination of the equilibrium composition of the SO_2/CH_4 system in the absence and presence of MoO_3. Firstly, at temperatures greater than 650°C, at least 99% of the elemental sulphur produced in the reduction of SO_2 with CH_4 is present in its diatomic form, S_2, while the bulk of the remaining sulphur is present as S_3. Secondly, elemental sulphur, H_2S, and COS, which are products of the reaction, are all sulphiding agents. MoO_3 then should be completely sulphided to MoS_2 with any of these sulphiding agents, even at concentrations as low as 0.1%, provided the reaction is run for a sufficient length of time.

In addition, the thermodynamic analysis of the SO_2-MoS_2 system showed that SO_2 can be a mild oxidizing agent for MoS_2, following the reaction:

$$MoS_2 + SO_2 \dashrightarrow MoO_2 + 3/2\ S_2 \qquad (6.4)$$

Figure 6.2 is a plot of equilibrium mole fractions of elemental sulphur in a system containing initially solid MoS_2 in a gaseous atmosphere of 25% SO_2 and 75% Ar. For a given temperature, any mole fraction of S_2 in excess of the equilibrium value, as was the case with all experiments

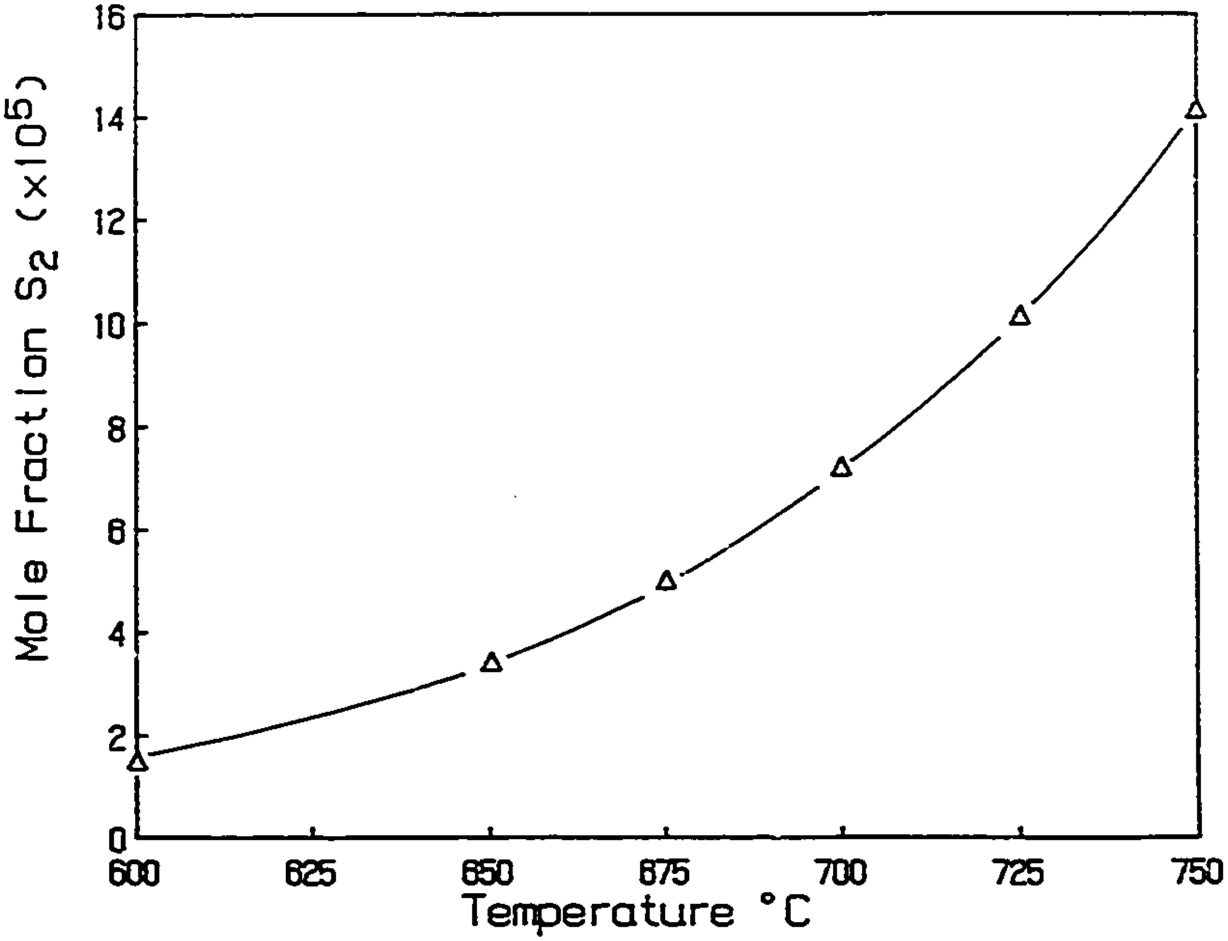


Figure 6.2 Effect of temperature on the equilibrium mole fraction of elemental sulphur over MoO_2 and MoS_2 (mole fraction of SO_2 = 25%)

(Table 6.6), will ensure that no MoO_2 will form. This result indicates that once a molybdenum catalyst has been sulphided, it can not be oxidized back to MoO_2, provided the mole fraction of sulphur is maintained above the equilibrium level for a given temperature. Furthermore, if the mole fraction of S_2 is maintained below the equilibrium value, MoS_2 is oxidized to MoO_2 and not MoO_3. In any case, if any MoO_3 had been formed in the experiments, it would have been removed from the surface and resulted in decreased values of Mo retention.

Since complete sulphidation was never observed when supported molybdenum catalysts were sulphided using SO_2 and CH_4, the explanation that some of the molybdenum interacts with the support surface applies. However, since the degree of sulphidation was affected significantly by temperature, and that a more complete molybdenum sulphidation was observed when 12% H_2S was used as opposed to the lower concentrations of sulphiding agents present in the SO_2-CH_4 system, also points to a kinetic effect.

6.4 Comparison of Sulphidation Methods

The rates of SO_2 consumption for various catalysts are plotted versus temperature in Figure 6.3. The catalysts considered in the figure are the 10 and 15% Mo/Al_2O_3 sulphided using H_2S and a 15% Mo/Al_2O_3 catalyst sulphided

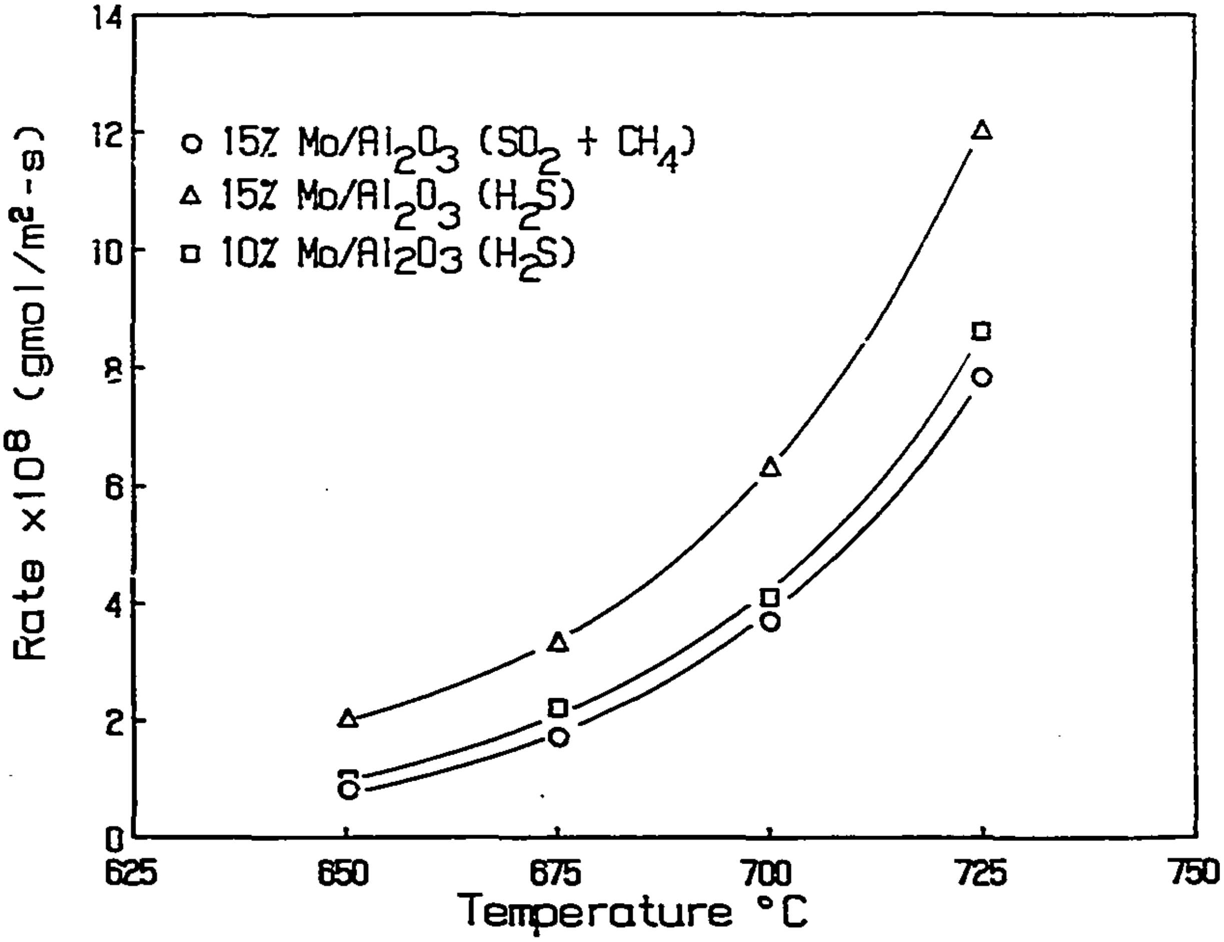


Figure 6.3 Effect of temperature on activity for various catalysts sulphided using H_2S or SO_2 and CH_4

using SO_2 and CH_4 at 700°C. It is found that the H_2S sulphided 15% Mo/Al_2O_3 catalyst is at least 1.5 times more active than the other two catalysts. In fact, the other two catalysts behave in a similar manner to each other. By examining the MoS_2 content, it can be seen that when an oxidized 15% Mo/Al_2O_3 catalyst is sulphided using SO_2 and CH_4, there is insufficient MoS_2 produced to allow for some MoS_2 crystallization in addition to monolayer coverage of the support surface. This is the same case as for the H_2S sulphided 10% Mo/Al_2O_3 catalyst. This results in these two catalysts having similar catalytic performance which is inferior to that of the H_2S sulphided 15% Mo/Al_2O_3.

6.5 Summary

It has been shown that the sulphidation procedure has an effect on the performance of alumina supported molybdenum catalysts used for the reduction of SO_2 with CH_4. Alumina supported molybdenum catalysts sulphided with 12% H_2S are superior to those sulphided under SO_2 and CH_4 reaction conditions. The higher activity found with H_2S sulphided catalysts, can be attributed to a higher degree of molybdenum sulphidation resulting in an increase in MoS_2 content. While elemental sulphur, COS, and H_2S, which are all products of the reduction of SO_2 with CH_4, act as sulphiding agents for MoO_3, they are not present in sufficiently high concentrations to allow for the same degree of sulphidation found when 12% H_2S is used. In addition, sulphidation using SO_2 and CH_4 at 750°C results in molybdenum removal from the surface.

CHAPTER 7

REACTION MECHANISM AND RATE LAW

The objective of this chapter is to determine the rate law and reaction mechanism for the reduction of SO_2 with CH_4 using the developed catalyst under conditions where no by-products are formed. The stoichiometry of this reaction is the same as reaction 2.11 and is written as follows.

$$2\ SO_2 + CH_4 \longrightarrow CO_2 + S_2 + H_2O \qquad (7.1)$$

In the previous two chapters, it was determined that the 15% Mo/Al_2O_3 catalyst sulphided using H_2S was the most effective of the catalysts tested according to the criteria used. In this chapter, this catalyst is studied in order to determine the kinetics of the reduction of SO_2 with CH_4. In addition, the effects of mass transfer resistances were determined. Finally, the activity of the sulphided 15% Mo/Al_2O_3 catalyst is compared to that of bauxite.

7.1 Evaluation of Mass Transfer Resistances

To ensure that the intrinsic rates were obtained, the effects of both external film and internal pore diffusion were determined under the conditions outlined in the following sections for the H_2S sulphided 15% Mo/Al_2O_3 catalyst.

7.1.1 External Film Diffusion

External mass transfer resistances are affected by the gas flow rate. A series of experiments was designed to determine the range of gas flow rates necessary to eliminate external mass transfer limitations. The range of the total feed flow rates was limited by the equipment set-up to between 4.0 and 8.3 cm^3/s. Within this range, the external mass transfer coefficient, k_m, is estimated by correlations to increase by a factor of 1.5 (see Appendix D) (Smith, 1981). Therefore, for reactions which are controlled by external mass transfer, the observed rate would change by a factor of 1.5 within this range of flow rates according to equation 7.2.

$$r(i) = k_m(C_b - C_s) \qquad (7.2)$$

where r(i) is the rate of reaction of species i; k_m is the mass transfer coefficient per unit area of catalyst; and C_b and C_s are the bulk and surface concentrations of reactants.

The integrated form of the mass balance for species i for a fixed bed reactor operating under plug flow conditions, is given by:

$$\left(\frac{1}{C(i)_f}\right)\left(\frac{\Delta M}{Q_f}\right) = \int_0^x \frac{dx}{r(i)} \qquad (7.3)$$

where M is the mass of catalyst (g); r(i) is the rate of production of species i (mol/g·s); Q_f is the total volumetric feed rate (cm^3/s); $C(i)_f$ is the concentration of species i in the feed (mol/cm^3); and x is the conversion of species i.

The feed concentration of i, which in this case represents that of SO_2, is fixed. Therefore, if $\Delta M/Q_f$ is held constant for various inlet volumetric flow rates, and conversion is found to be constant, then the rate expression must not change if the equation is to hold. This is the case where there are no external mass transfer limitations.

For these experiments, a constant feed gas composition of 25% SO_2, 25% CH_4, and 50% Ar and a temperature of 725°C was used. The results plotted in Figure 7.1 show that conversion varied by less than 2% over the entire range of flow rates. Therefore, it is concluded that for the reaction temperatures used, the flow rates within the range tested are all above the threshold for external film diffusion.

7.1.2 Internal Pore Diffusion

To investigate the degree of internal mass transfer limitations on the reaction, the following experiment was performed. Using the same catalyst as above, SO_2 consumption rates were determined over the temperature range of 650 to 725°C. The pellets were then removed and

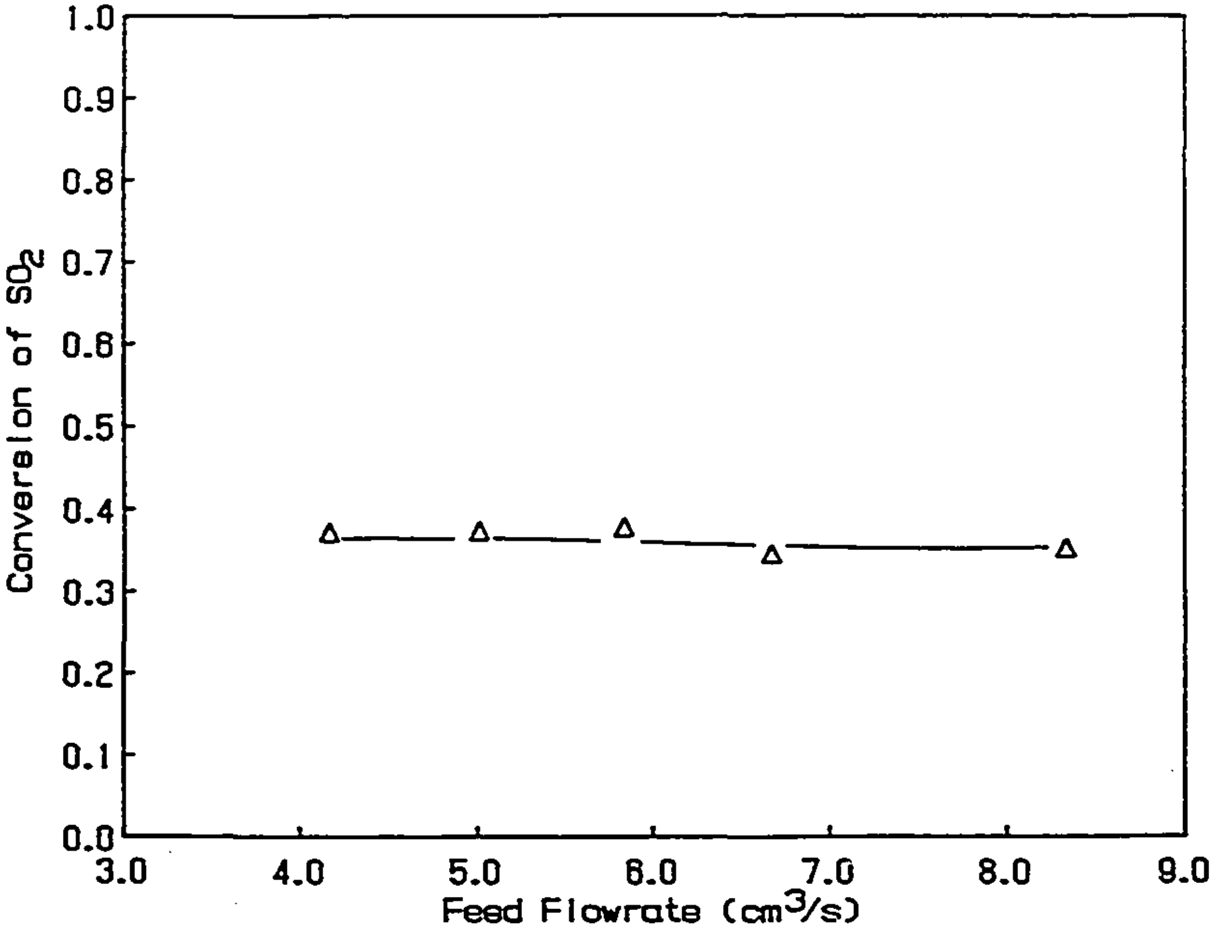


Figure 7.1 Effect of flow rate on conversion of sulphur dioxide at constant $\Delta M/Q_f$

pulverized into a fine powder. The SO_2 consumption rates were then determined over the same temperature range. The results are plotted in Figure 7.2. There is no significant difference between the reaction rates for this catalyst in the pellet and powder forms, indicating no internal mass transfer limitations.

These results, combined with the external mass transfer analysis results, indicate that the observed reactions are not under mass transfer control.

7.2 Development of the Reaction Rate Model

Heterogeneous catalytic reactions which are not diffusion limited can be modelled by a sequence of three steps, adsorption of reactants, surface reaction, and desorption of products (Fogler, 1992). The slowest of these steps controls the overall rate of reaction and is known as the rate-limiting step. The reaction rate model is developed by assuming that one of the steps is rate limiting, and then comparing the model to the data. When the rates predicted by the model follow those determined experimentally, the rate-limiting step and the reaction mechanism are assumed to be correct.

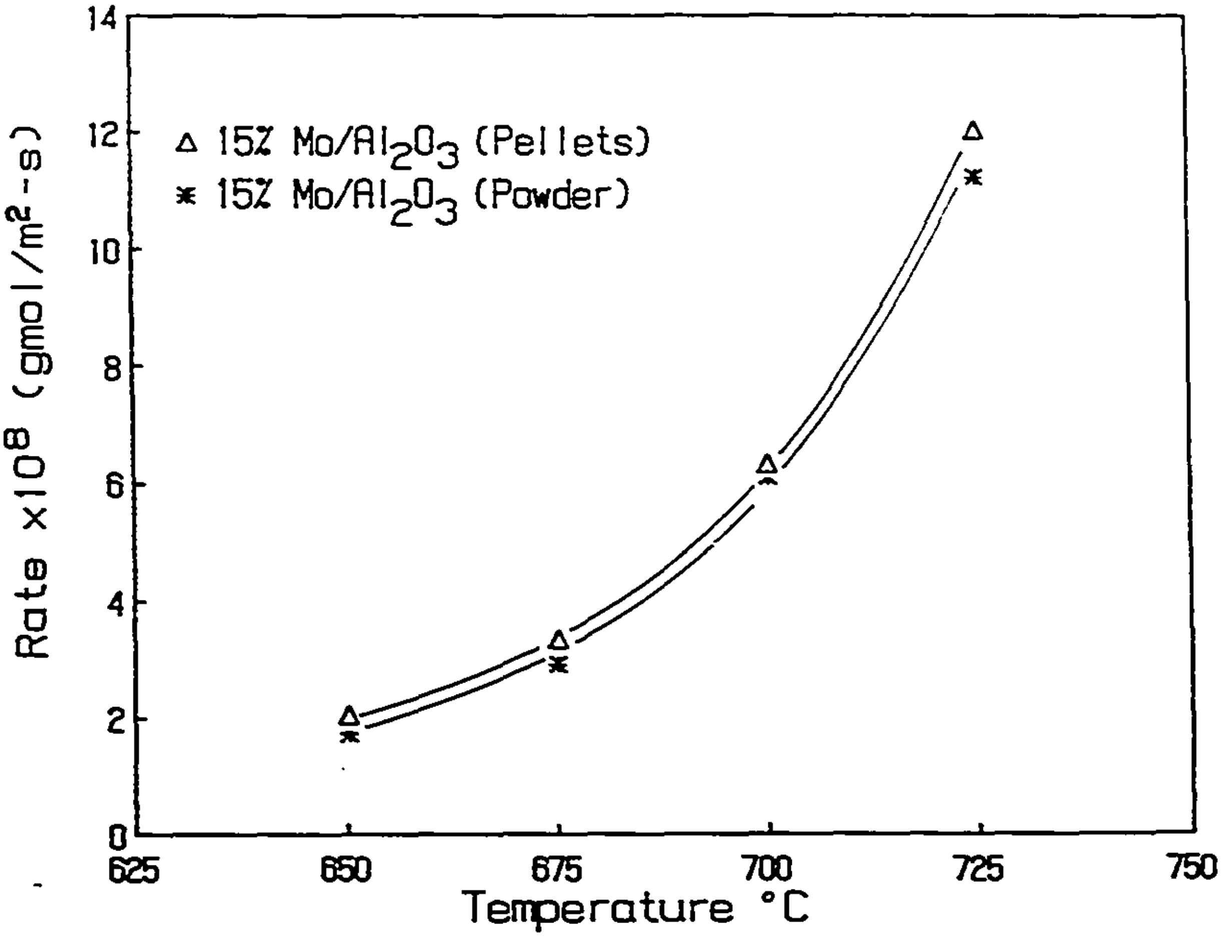


Figure 7.2 Comparison of SO_2 consumption rates for 15% Mo/Al_2O_3 catalysts in pellet and powder form

7.2.1 Kinetic Experiments

Kinetic experiments were performed in order to obtain the necessary data for determining the reaction mechanism and establishing a rate law. Experimental conditions were selected to minimize by-product formation. This was done in order to simplify the analysis. The yields of elemental sulphur and CO_2 were maintained at, or above 95% for all runs. In addition, differential behaviour of the reactor was maintained for all reaction conditions by varying the quantity of catalyst loaded in the reactor.

For all experiments, the total feed flow rate was approximately 6.3 cm^3/s and the total pressure was 1 atm. Temperatures of 600, 625, and 650°C were investigated. Sulphur dioxide partial pressures in the feed gas were varied between 0.1 and 0.8 atm, and methane partial pressures were varied between 0.1 and 0.5 atm. In all cases, the balance of the feed gas was argon.

The rates of CH_4 consumption as a function of methane partial pressure at various temperatures are shown in Figures 7.3 and 7.4 for constant SO_2 partial pressures of 0.2 and 0.5 atm, respectively. Rate data were not obtained at partial pressures above 0.5 atm at 625 and 650°C, and 0.3 atm at 650°C because of high production of by-products. All rate data sheets for all runs are included in Appendix E.

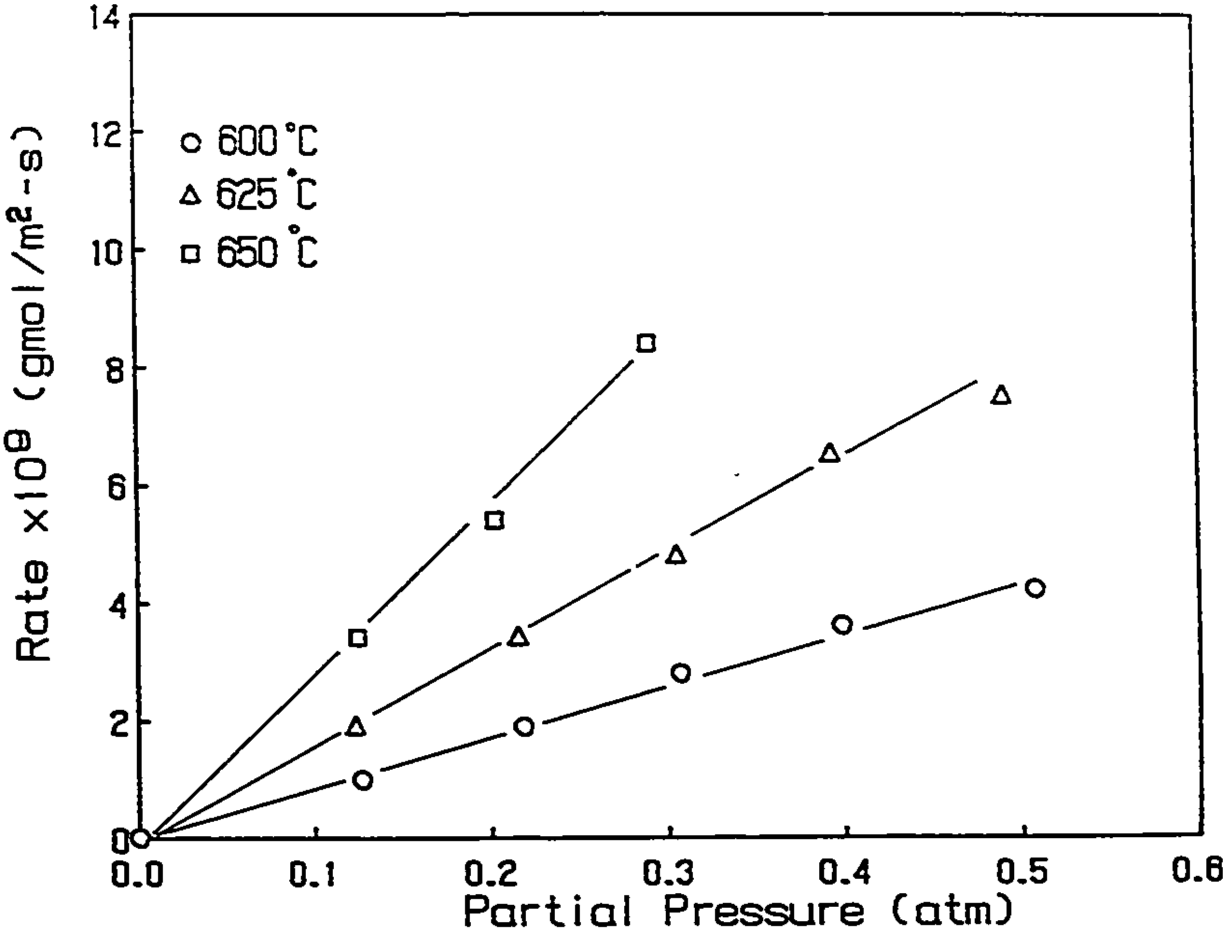


Figure 7.3 Effect of methane partial pressure on the rate of methane consumption using 15% Mo/Al_2O_3 catalyst at various temperatures (sulphur dioxide partial pressure = 0.2 atm)

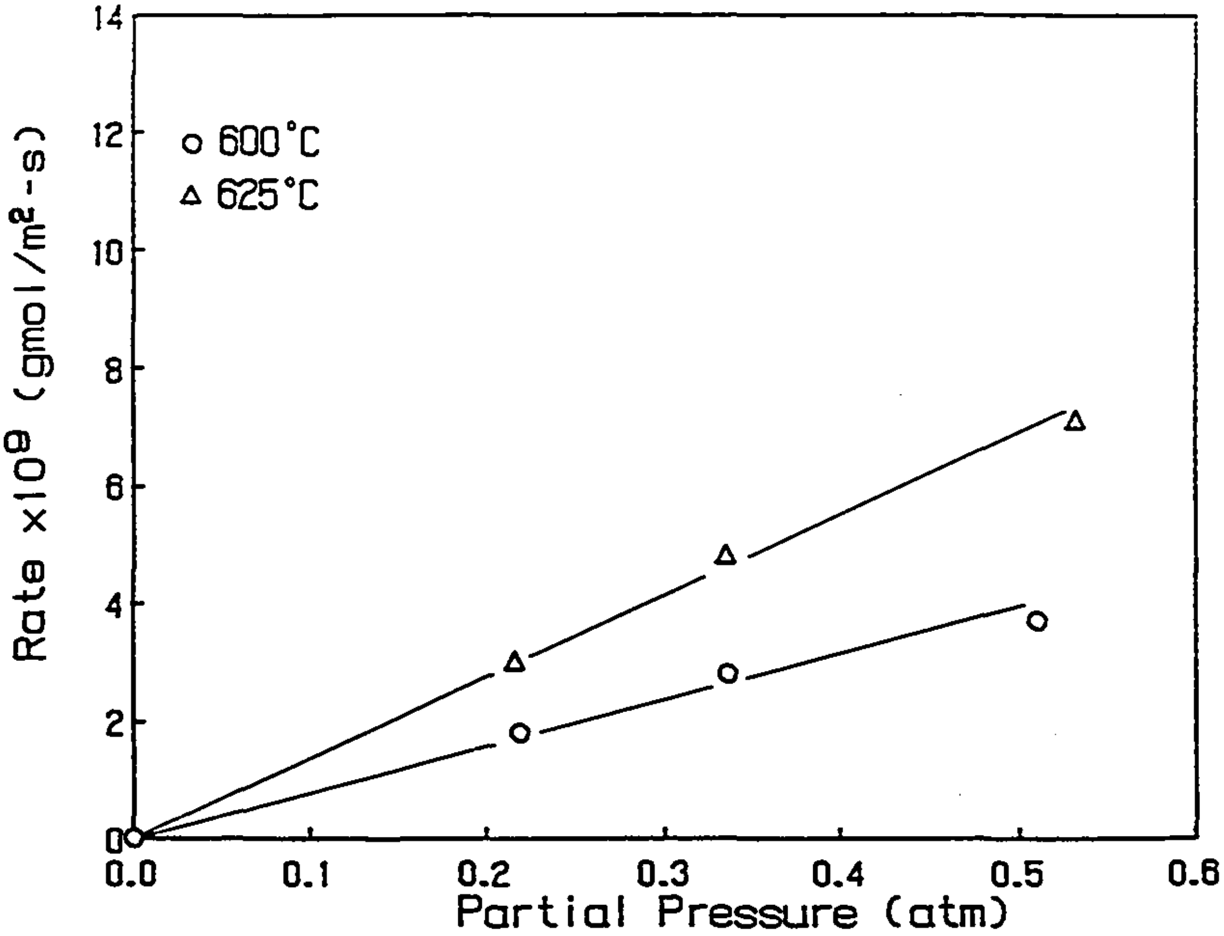


Figure 7.4 Effect of methane partial pressure on the rate of methane consumption using 15% Mo/Al_2O_3 catalyst at various temperatures (sulphur dioxide partial pressure = 0.5 atm)

In all cases, there is essentially a linear relationship between the rate of methane consumption and methane partial pressure indicating that the adsorption of CH_4 on the catalyst surface could be the controlling step.

The rates of CH_4 consumption as a function of SO_2 partial pressure at various temperatures are shown in Figures 7.5 and 7.6 for constant CH_4 partial pressures of 0.2 and 0.5 atm, respectively. The reaction rates are not strongly affected by changes in the SO_2 partial pressure even at partial pressures as high as 0.8 atm. In fact, there is a slight decline in the rate of methane consumption with increasing SO_2 partial pressure. This indicates that SO_2 does not participate in the rate-controlling step other than by possibly hindering adsorption of CH_4 to a slight degree.

7.2.2 Development of Model

A possible mechanism for the reduction of SO_2 with CH_4 over a 15% Mo/Al_2O_3 catalyst based on the experimental data includes the following steps each of which is an elementary reaction with its own equilibrium and rate constants. In this case it is assumed that CH_4 is the adsorbed species.

1. Adsorption of CH_4 on the surface

$$CH_4 + E \underset{k_{-a}}{\overset{k_a}{\Longleftrightarrow}} CH_4 \cdot E \qquad (7.4)$$

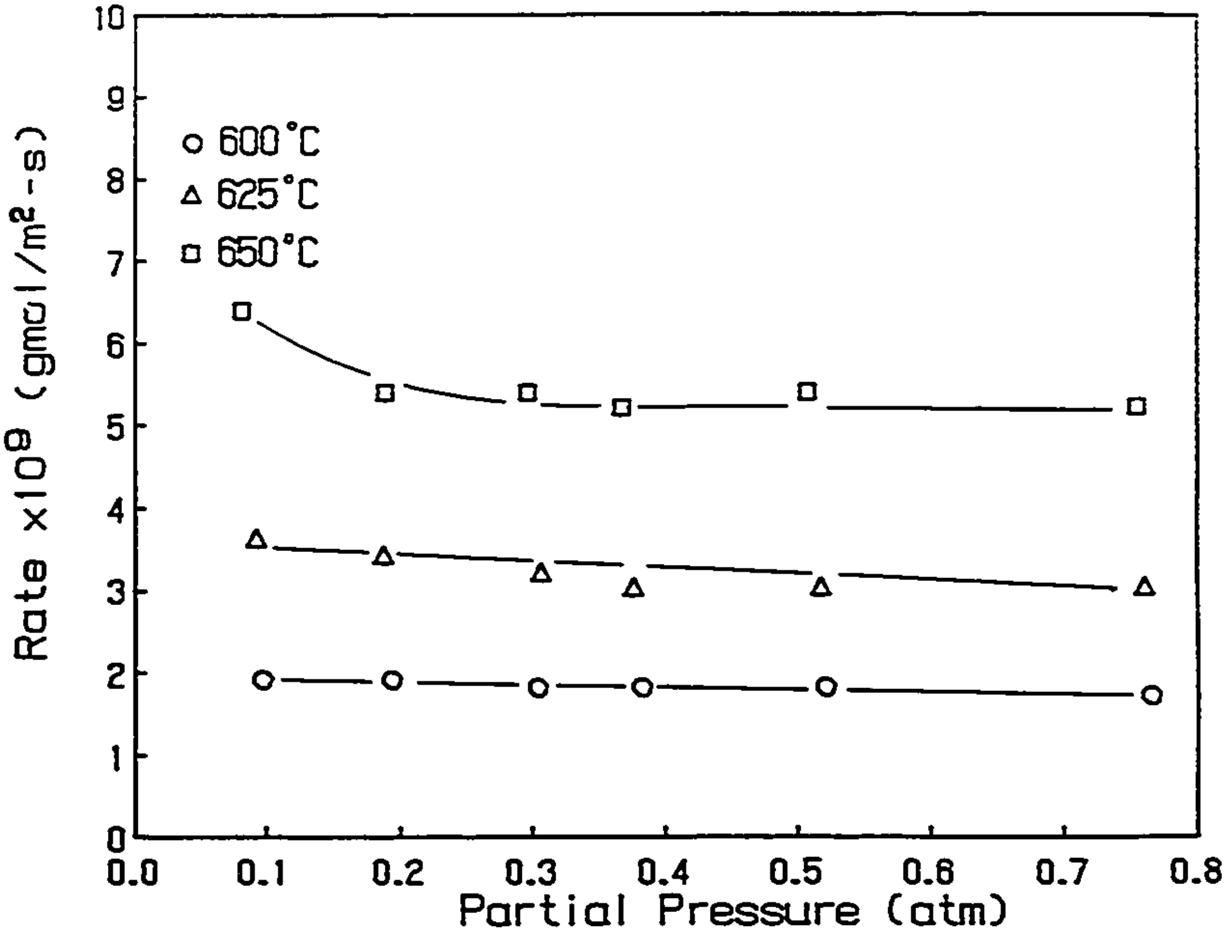


Figure 7.5 Effect of sulphur dioxide partial pressure on the rate of methane consumption using 15% Mo/Al_2O_3 catalyst at various temperatures (methane partial pressure = 0.2 atm)

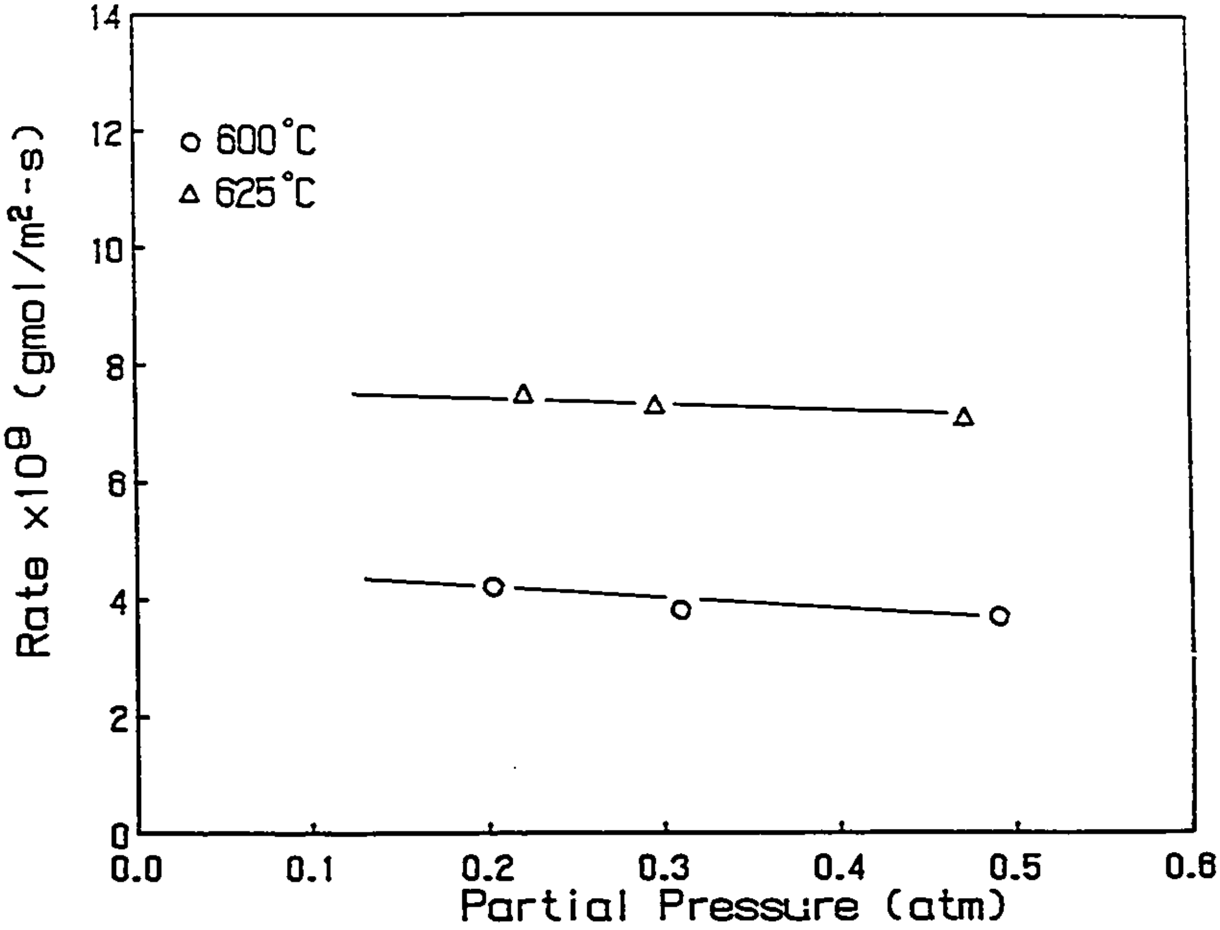


Figure 7.6 Effect of sulphur dioxide partial pressure on the rate of methane consumption using 15% Mo/Al_2O_3 catalyst at various temperatures (methane partial pressure = 0.5 atm)

2. Surface Reaction with SO_2

$$SO_2 + CH_4\cdot E \overset{k_r}{\underset{k_{-r}}{\Longleftrightarrow}} C\cdot E + D_{(g)} \qquad (7.5)$$

3. Desorption of products

$$C\cdot E \overset{k_d}{\underset{k_{-d}}{\Longleftrightarrow}} C_{(g)} + E \qquad (7.6)$$

In these equations, E denotes an active site on the catalyst surface; $CH_4\cdot E$ is an activated complex; $C\cdot E$ represents all absorbed products; and $D_{(g)}$, all possible products from the surface reaction which are not adsorbed.

By developing and combining the rate equations for reactions 7.4 to 7.6 (see Appendix F), and knowing that the equilibrium constant for the reaction is large (> 1.95×10^{12} at 600°C), the following expression for the reduction of SO_2 with CH_4 is obtained assuming that the adsorption of CH_4 is the rate limiting step.

$$r(CH_4) = \frac{k\ P_{CH_4}}{1 + K\ P_{SO_2}} \qquad (7.7)$$

Equation 7.7 is similar to the single-site expression developed by Helmstrom and Atwood (1978) shown in section 2.5.1 where the rate of methane consumption is proportional to the methane partial pressure and inversely proportional to $1 + KP_{SO_2}$. It should be noted that since the rate expression predicts a finite rate as the SO_2 partial pressure approaches zero, the controlling step must change at concentrations below the range used in this study.

A similar analysis can be performed assuming that SO_2 is the adsorbed species:

1. Adsorption of SO_2 on the surface

$$SO_2 + E \underset{k_{-a}}{\overset{k_a}{\Longleftrightarrow}} SO_2\cdot E \qquad (7.8)$$

2. Surface Reaction with CH_4

$$CH_4 + SO_2\cdot E \underset{k_{-r}}{\overset{k_r}{\Longleftrightarrow}} C\cdot E + D_{(g)} \qquad (7.9)$$

3. Desorption of products

$$C\cdot E \underset{k_{-d}}{\overset{k_d}{\Longleftrightarrow}} C_{(g)} + E \qquad (7.10)$$

In these equations, E denotes an active site on the catalyst surface; $SO_2\cdot E$ is an activated complex; $C\cdot E$ represents all absorbed products; and $D_{(g)}$, all possible products from the surface reaction which are not adsorbed.

In this case, a rate law can be developed using a procedure similar to that shown in Appendix F. The resulting expression has the following form.

$$r(CH_4) = \frac{k\ P_{SO_2}}{1 + K\ P_{CH_4}} \qquad (7.11)$$

Since the partial pressure of SO_2 appears in the numerator, it is clear from the experimental data that this rate expression is not valid.

Rate expressions can also be developed where either the surface reaction or the desorption of products is the rate determining step (Appendix F). If the surface reaction were controlling the overall rate, changes in the partial pressures of both CH_4 and SO_2 would affect the reaction rate. In addition, if the desorption of products were the rate determining step, the observed rate would be a function of the partial pressures of CH_4 and SO_2 as well as the partial pressures of all possible reaction products which are not adsorbed. Therefore, it is concluded that the rate expression which was developed based on the assumption that the adsorption of methane is the rate limiting step, is the most representative of the data.

To evaluate the individual constants, equation 7.7 was linearized and the constants were evaluated by linear regression analysis. The temperature dependence of the constants were then determined and may be expressed by the following Arrhenius-type equations:

$$k = 9.75 \exp[-36000/RT] \quad (\mathrm{gmol/m^2\text{-}s}) \tag{7.12}$$

$$K = 1.43\mathrm{x}10^{-7} \exp[26200/RT] \quad (\mathrm{atm^{-1}}) \tag{7.13}$$

From the expression for the reaction rate constant, the activation energy is 36.0 kcal per mole of CH_4.

7.3 Model Evaluation

The above model has been developed based on the assumption that the adsorption of methane is the controlling step in the reaction mechanism. In order to determine the validity of this assumption, the experimental data are compared with rates predicted by the model. The results are presented in Table 7.1 for various concentrations of reactants and for reaction temperatures of 600, 625 and 650°C. The residuals were then determined at each of the experimental data points and were found to be randomly distributed with respect to temperature and partial pressures of SO_2 and CH_4. Therefore, the model does represent the experimental data indicating that the assumption that the rate limiting step is the adsorption of CH_4 is valid.

Although this expression gives the rate of consumption of CH_4 under various reaction conditions, it is also valid for the determination of the rate of consumption of SO_2 or the rates of production of elemental sulphur, CO_2, and H_2O because the rates of all these species are related by stoichiometry according to equation 7.1 when no by-products are formed.

Table 7.1

Comparison of Predicted and Experimental Rates of CH_4 Consumption (gmol/m^2-s) x 10^9

$P(CH_4)$ (atm)	$P(SO_2)$ (atm)	T (K)	Experimental Rate	Predicted Rate	Residuals (x 10^9)
0.126	0.222	873	0.97	1.09	-0.12
0.222	0.097	"	1.96	2.04	-0.08
0.217	0.193	"	1.91	1.90	0.01
0.211	0.303	"	1.85	1.76	0.09
0.307	0.207	"	2.88	2.67	0.21
0.122	0.208	898	1.87	1.96	-0.09
0.218	0.091	"	3.64	3.63	0.01
0.214	0.187	"	3.47	3.46	0.01
0.211	0.306	"	3.22	3.28	-0.06
0.305	0.196	"	5.03	4.91	0.12
0.124	0.201	923	3.40	3.52	-0.12
0.211	0.082	"	6.42	6.15	0.27
0.202	0.188	"	5.47	5.74	-0.27
0.206	0.296	"	5.63	5.72	-0.09
0.290	0.184	"	8.49	8.25	0.24

7.4 Catalyst Comparison

As stated earlier, a rate model was published by Helmstrom and Atwood (1978) for the reduction of SO_2 with CH_4 using a bauxite catalyst. This model is used to compare the reaction rates obtained with bauxite with those obtained with the newly developed catalyst. The results of this comparison are shown in Table 7.2. For comparison, the rates of methane consumption are reported on a catalyst weight basis as opposed to a surface area basis, since no surface area data were supplied by Helmstrom and Atwood in their study.

From the data in Table 7.2, it is clear that there is a distinct advantage in using the newly developed catalyst. The rates of CH_4 consumption (and all other reaction rates) are between 13.0 and 39.9 times higher with the 15% Mo/Al_2O_3 catalyst when compared with the bauxite catalyst. The higher ratios of the reaction rates are found at the higher SO_2 partial pressures. This indicates that while the reaction mechanism for the reduction of SO_2 with CH_4 may be the same for the two catalysts, the adsorption of SO_2 on the bauxite surface is more extensive than on the surface of the 15% Mo/Al_2O_3 catalyst. This is important because if the reduction of SO_2 to elemental sulphur is to be used in an

Table 7.2

Comparison of CH_4 Consumption Rates for the 15% Mo/Al_2O_3 Catalyst and Bauxite (gmol/g-s) x 10^8

$P(CH_4)$ (atm)	$P(SO_2)$ (atm)	T (K)	15% Mo/Al_2O_3 (r_1)	Bauxite (r_2)	r_1/r_2
0.126	0.222	873	11.0	0.43	25.5
0.222	0.097	"	22.3	1.72	13.0
0.217	0.193	"	21.8	0.86	25.3
0.211	0.303	"	21.1	0.53	39.8
0.307	0.207	"	32.8	1.13	29.0
0.122	0.208	898	21.3	0.78	27.3
0.218	0.091	"	41.4	3.12	13.3
0.214	0.187	"	39.5	1.52	26.0
0.211	0.306	"	36.7	0.92	39.9
0.305	0.196	"	57.3	2.07	27.7

industrial process, high concentrations of SO_2 will have to be used in order to reduce reactor size. These high SO_2 concentrations will seriously inhibit the reaction if bauxite is used and will have only a marginal effect on the rates if the 15% Mo/Al_2O_3 catalyst is used.

7.5 Summary

In this chapter, it was established that there were no external film diffusion or internal pore diffusion limitations on the reactions using the H_2S sulphided 15% Mo/Al_2O_3 catalyst. A model was developed for the reduction of SO_2 with CH_4 for temperatures ranging from 600 to 650°C under reaction conditions where the only products were CO_2, H_2O and elemental sulphur. The adsorption of methane was found to be the rate limiting step in the mechanism. However, SO_2 which also adsorbs on the catalyst surface had an inhibiting effect on the reaction rates. The reaction rates using the 15% Mo/Al_2O_3 catalyst were compared with calculated rates from a previously developed single-site model using bauxite. Although, the reaction mechanisms were found to be similar, the reaction rates obtained with the 15% Mo/Al_2O_3 catalyst were 13 to 40 times higher than those with the bauxite catalyst with the highest values found at the highest SO_2 partial pressures. This was attributed to a higher degree of SO_2 adsorption on the bauxite catalyst.

CHAPTER 8

CONCLUSIONS, ORIGINAL CONTRIBUTIONS AND RECOMMENDATIONS

The primary objective of this thesis was to develop a catalyst for the reduction of sulphur dioxide with methane. Supported molybdenum catalysts were studied using various loadings of molybdenum, different support materials such as alumina and silica-alumina, and with the addition of cobalt, a known promoter for hydrodesulphurization reactions. The catalysts were evaluated on the basis of activity and elemental sulphur and carbon dioxide yields using a tubular plug flow reactor. A study was also included where the methods of sulphidation of alumina supported molybdenum catalysts employing H_2S or SO_2 and CH_4 were compared. Finally, a kinetic study was performed under the conditions of differential conversion and minimal by-product formation with the objective of determining the rate law and reaction mechanism.

8.1 Conclusions from the Catalyst Development Study

The main conclusions that can be drawn from the catalyst development study include the following.

(1) Among H_2S sulphided catalysts, all molybdenum loadings (i.e. 5, 10 and 15% Mo) showed higher activities, and higher sulphur and CO_2 yields than alumina alone. The 5

and 10% Mo/Al_2O_3 catalysts were similar in all three aspects of catalyst performance considered. However, the 15% Mo/Al_2O_3 catalyst was found to have activity 1.5 to 2 times those of the other loadings, higher sulphur yields, and comparable CO_2 yields.

(2) Generally, higher activities were observed with higher loadings of molybdenum. However, among the H_2S sulphided catalysts considered, the 15% molybdenum loading can be considered to be an optimum loading since increasing the loading above this level to 21% did not increase activity. In fact, the 15% molybdenum loading showed an activity equivalent to that of pure crystalline MoS_2.

(3) The major by-product of the reduction of SO_2 with CH_4 when catalyzed by the supported molybdenum catalysts was H_2S, however, its rate of production can be minimized by maintaining the reaction temperature below 700°C.

(4) The product distribution using alumina supported molybdenum catalysts was different from when alumina was used. While H_2S was the major by-product observed with the supported molybdenum catalysts, COS was the major sulphur bearing by-product when alumina was the catalyst. In addition, when alumina was used, CO accounted for as much as 30% of the carbon bearing products while no elemental carbon was found at any temperature. On the other hand, no CO was

detected at any temperature using supported molybdenum catalysts while some elemental carbon production was observed particularily at temperatures in excess of 700°C. These results indicate that there is a different mechanism involved when supported molybdenum catalysts are used.

(5) Increasing the molar feed ratio of SO_2 to CH_4 from 1.0 to 2.0 improved the sulphur yield by up to 4%, but had no effect on the CO_2 yield, and decreased the rate of SO_2 consumption by 50% at 725°C.

(6) The H_2S sulphided 15% Mo/Al_2O_3 catalyst was found to have a constant chemical composition and specific surface area indicating that it was stable under the severe reaction conditions.

(7) The addition of cobalt to the 15% Mo/Al_2O_3 catalyst had a detrimental effect on its performance. Although sulphur and CO_2 yields were relatively unaffected by the addition of cobalt, the activity was reduced by 20%. Consequently, for the reduction of SO_2 with CH_4 it is concluded that cobalt should not be added to the alumina supported molybdenum catalyst.

(8) Large quantities of elemental carbon, CO, and COS were produced when silica-alumina was used as a catalyst. When molybdenum was supported on this material, yields of

elemental sulphur and CO_2 were higher than when the 15% Mo/Al_2O_3 catalyst was used. However, the activity of the 15% Mo/SiO_2-Al_2O_3 catalyst was 10% that of the 15% Mo/Al_2O_3 catalyst. From these results, it was concluded that alumina is a better catalyst support material for this reaction system. However, the results also indicate that neither the molybdenum phase nor the support material act independently of each other but rather the catalyst performance is a result of the interaction between the two phases.

8.2 Conclusions from the Sulphidation Study

The main conclusions that can be drawn from the sulphidation study include the following.

(1) Alumina supported molybdenum catalysts sulphided with 12% H_2S are superior to those sulphided under SO_2 and CH_4 reaction conditions.

(2) The higher activity found with H_2S sulphided catalysts can be attributed to a higher degree of molybdenum sulphidation resulting in an increase in MoS_2 content. Both oxides of molybdenum are less active for the reduction of SO_2 with CH_4 than MoS_2.

(3) The H_2S sulphided 15% Mo/Al_2O_3 catalyst is the most active of the supported molybdenum catalysts because

its MoS_2 content exceeds the level which can remain in a well dispersed monolayer, resulting in significant MoS_2 crystal formation not found with the other molybdenum loadings. This catalyst, therefore, has characteristics, such as activity, which are similar to pure unsupported crystalline MoS_2.

(4) From the experimental results and thermodynamic calculations, it was determined that the mechanism for MoO_3 sulphidation using H_2S includes three steps. In the first step H_2S decomposes to hydrogen and elemental sulphur. The hydrogen then reduces the MoO_3 to MoO_2. In the third step, elemental sulphur reacts with the MoO_2 produced in the second step to form MoS_2.

(5) While elemental sulphur, COS, and H_2S, which are all products of the reduction of SO_2 with CH_4, act as sulphiding agents for MoO_3, they are not present in sufficiently high concentrations to allow for the same degree of sulphidation found when 12% H_2S is used.

(6) Following either sulphidation procedure, some molybdenum remains in the oxide form as MoO_2 and not MoO_3. The reduction of MoO_3 to MoO_2 was found to be fast and therefore no molybdenum was removed from the support surface except at 750°C where some MoO_3, which is more volatile than MoO_2, was removed before reduction to MoO_2.

8.3 Conclusions from the Mechanism Study

The main conclusions which can be drawn from the kinetic and mechanism study include the following.

(1) In the case where the only products from the reduction of SO_2 with CH_4 in the temperature range of 600 to 650°C are elemental sulphur, CO_2 and H_2O, the adsorption of methane was found to be the rate limiting step. However, SO_2 which also adsorbs on the catalyst surface had an inhibiting effect on the reaction rates.

(2) When compared to the results calculated using a previously published single-site model developed for a bauxite catalyst, the H_2S sulphided 15% Mo/Al_2O_3 was found to be 13 to 40 times more active with the highest values found at the highest SO_2 partial pressures. This effect is attributed to a higher degree of SO_2 adsorption on the bauxite surface which "poisons" active sites.

8.4 Original Contributions

The reduction of sulphur dioxide to form elemental sulphur has been extensively studied in the past. However, the published work is far from complete.

Much of the work that has been performed in the past with the objective of optimizing the SO_2 reduction system for the production of elemental sulphur has focused on the choice of reducing agent and the manipulation of parameters such as reactant concentration, reactor temperature and pressure, reactor configuration.

The present work contributes a body of knowledge to the field of SO_2 reduction by focusing on the development of a catalyst for the reduction of SO_2 with CH_4. Numerous catalysts were examined and it was shown how the design of the catalyst including the loading of molybdenum and support material affect the reaction system at various temperatures and reactant feed concentrations.

Other information claimed to be new findings are:

1) Alumina supported molybdenum sulphide catalyst are stable under the severe reaction conditions including temperatures above 500°C.

2) The optimum molybdenum loading as determined by maximized activity and yields of elemental sulphur and CO_2 is 15%. Increasing the molybdenum loading above this level does not improve catalyst performance for this reaction system.

3) The addition of cobalt decreased the activity of the developed catalyst below that of pure crystalline MoS_2 because the role of cobalt in supported molybdenum catalysts appears to be to maintain molybdenum dispersion and hinder MoS_2 crystal formation.

4) Alumina supported oxidized molybdenum catalysts can be sulphided using SO_2 and CH_4 although the sulphidation was found to be more complete when 12% H_2S is used.

5) A rate law was developed for the reduction of SO_2 with CH_4 using the newly developed catalyst. The reaction was found to be methane adsorption limited.

8.5 Recommendations for Further Research

The following is a list of recommendations for future research which might be taken into consideration in order to further the body of knowledge in the field of catalytic reduction of SO_2 with CH_4.

1) Although a basic understanding of the reaction mechanism has been obtained from this work, it may be necessary to study the more general case where some by-products are formed. In some processes using this catalyst, higher temperatures may be required which will result in a different product distribution than that studied here.

2) Since the adsorption of both SO_2 and CH_4 ultimately determines the reaction rates, a complete adsorption study using the sulphided 15% Mo/Al_2O_3 catalyst could be performed in order to gain a better understanding of the influence of various parameters on the performance of the catalyst.

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APPENDIX A

CALIBRATION OF GAS FLOW METERS

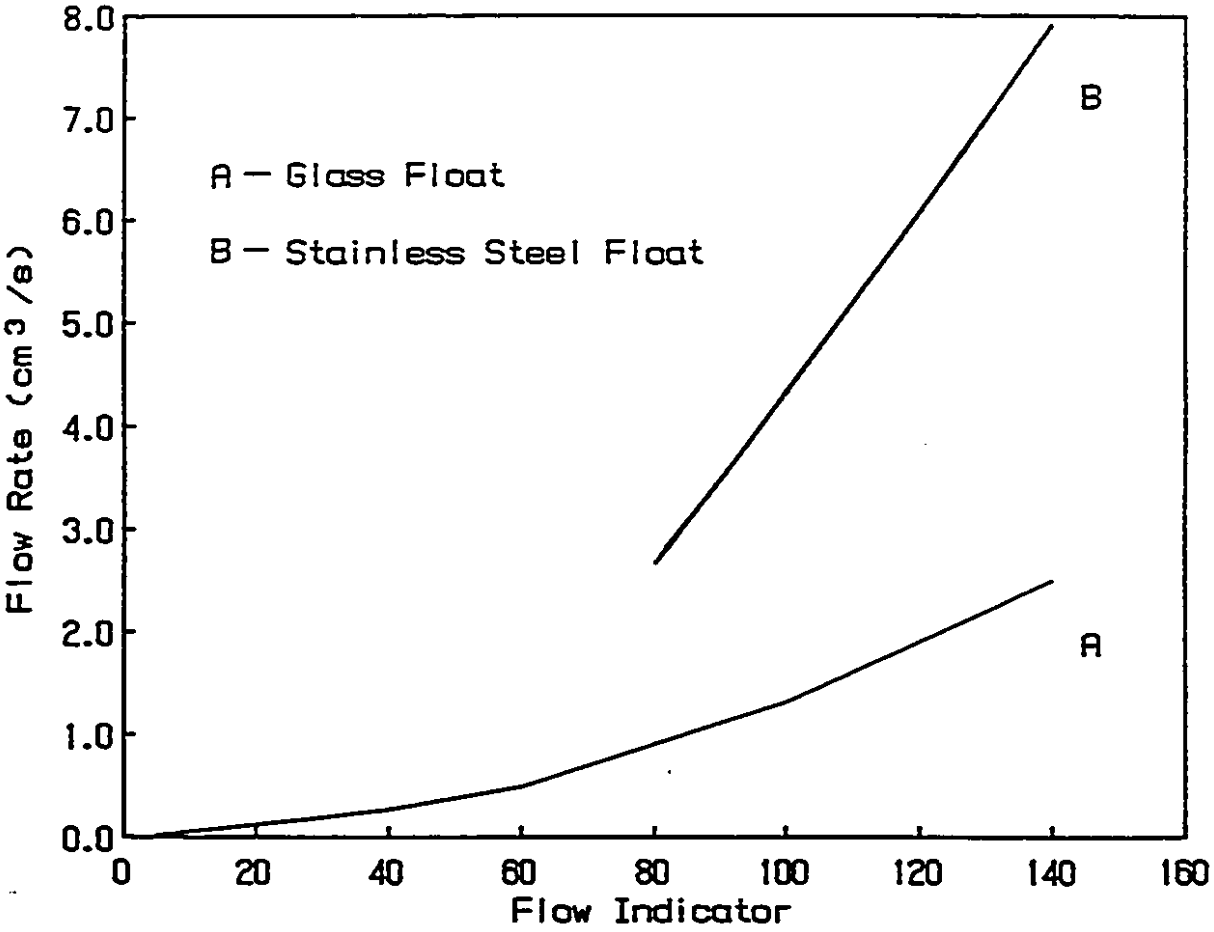

Figure A.1 Calibration of the Ar flow meter (Pressure = 1 atm, Temperature = 20°C)

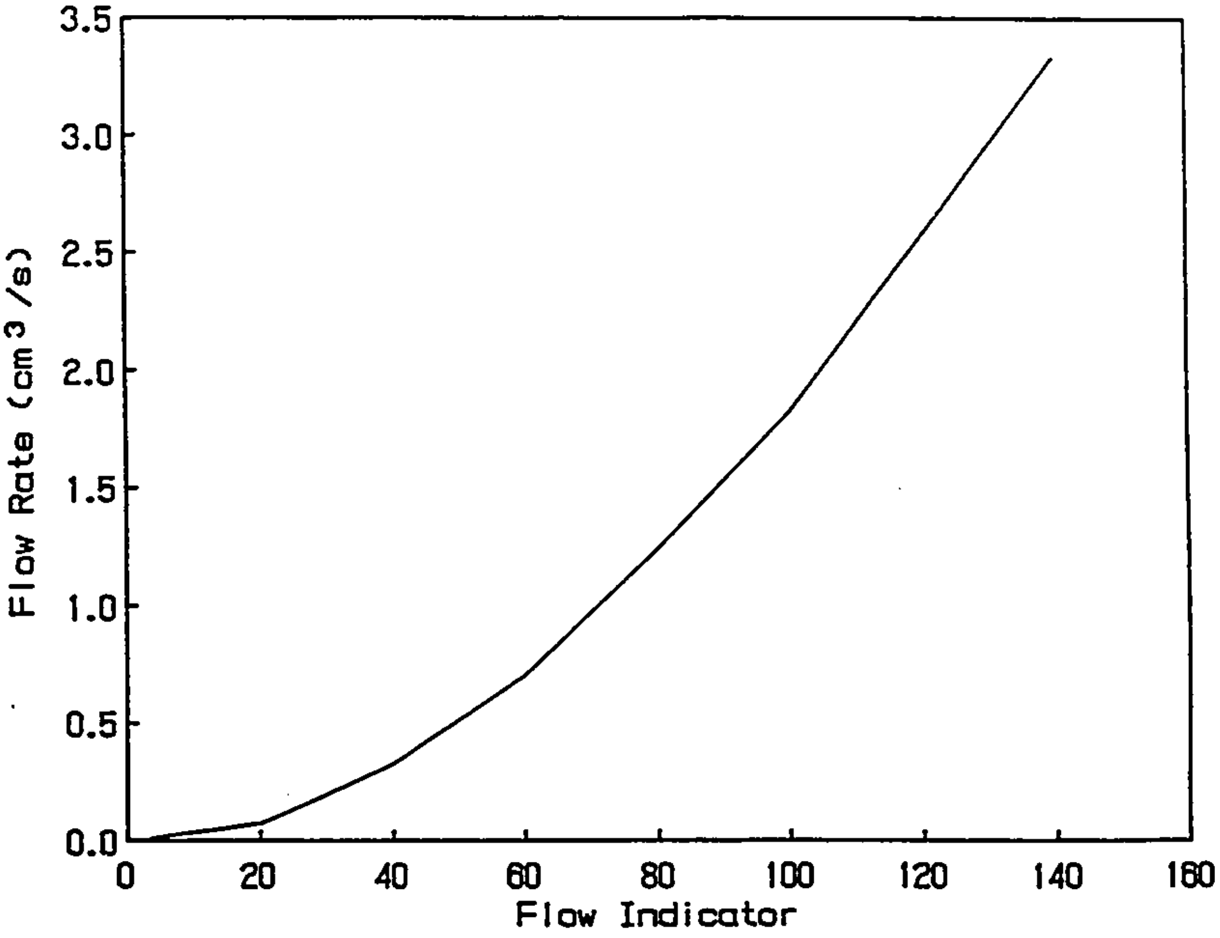

Figure A.2 Calibration of the SO_2 flow meter

(Pressure = 1 atm, Temperature = 20°C)

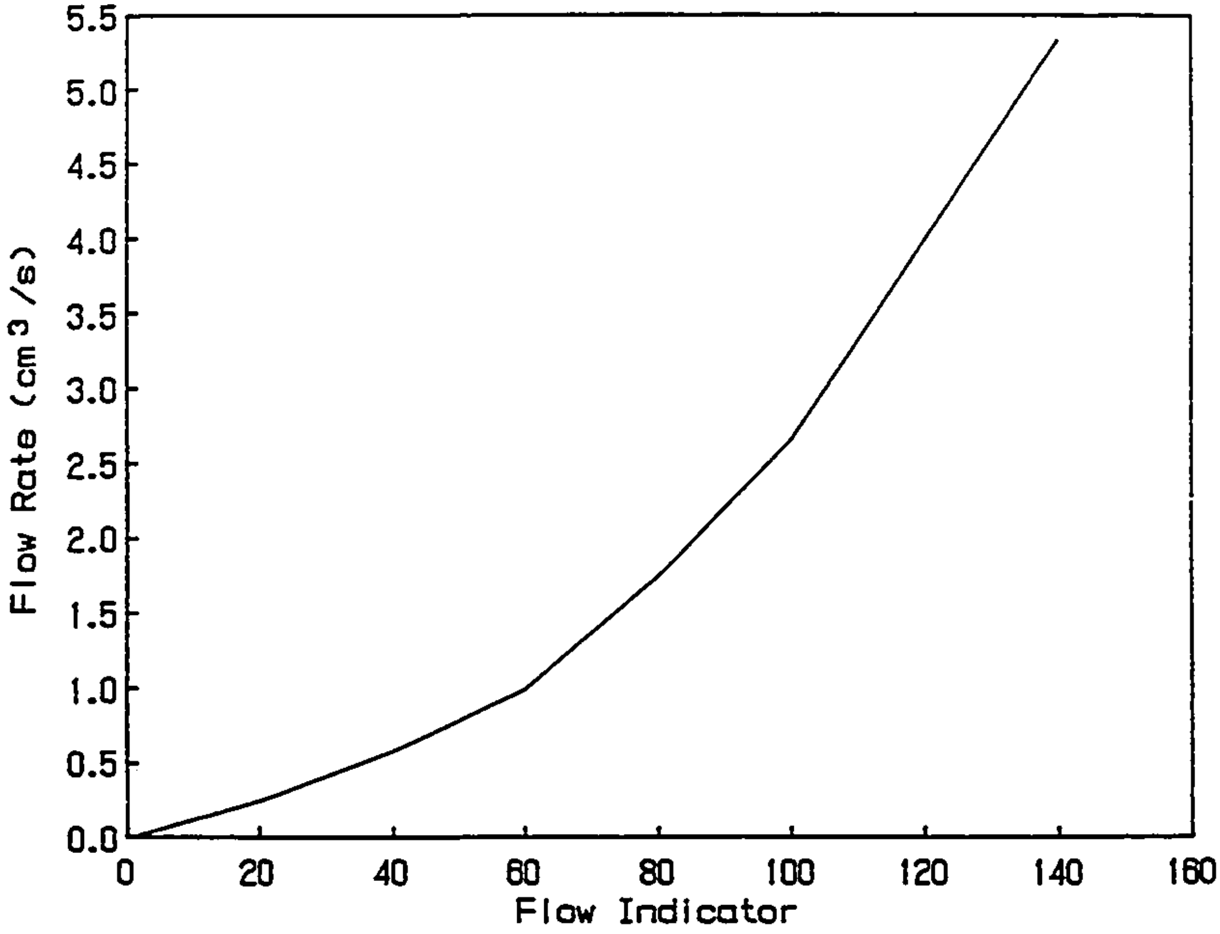

Figure A.3 Calibration of the CH_4 flow meter

(Pressure = 1 atm, Temperature = 20°C)

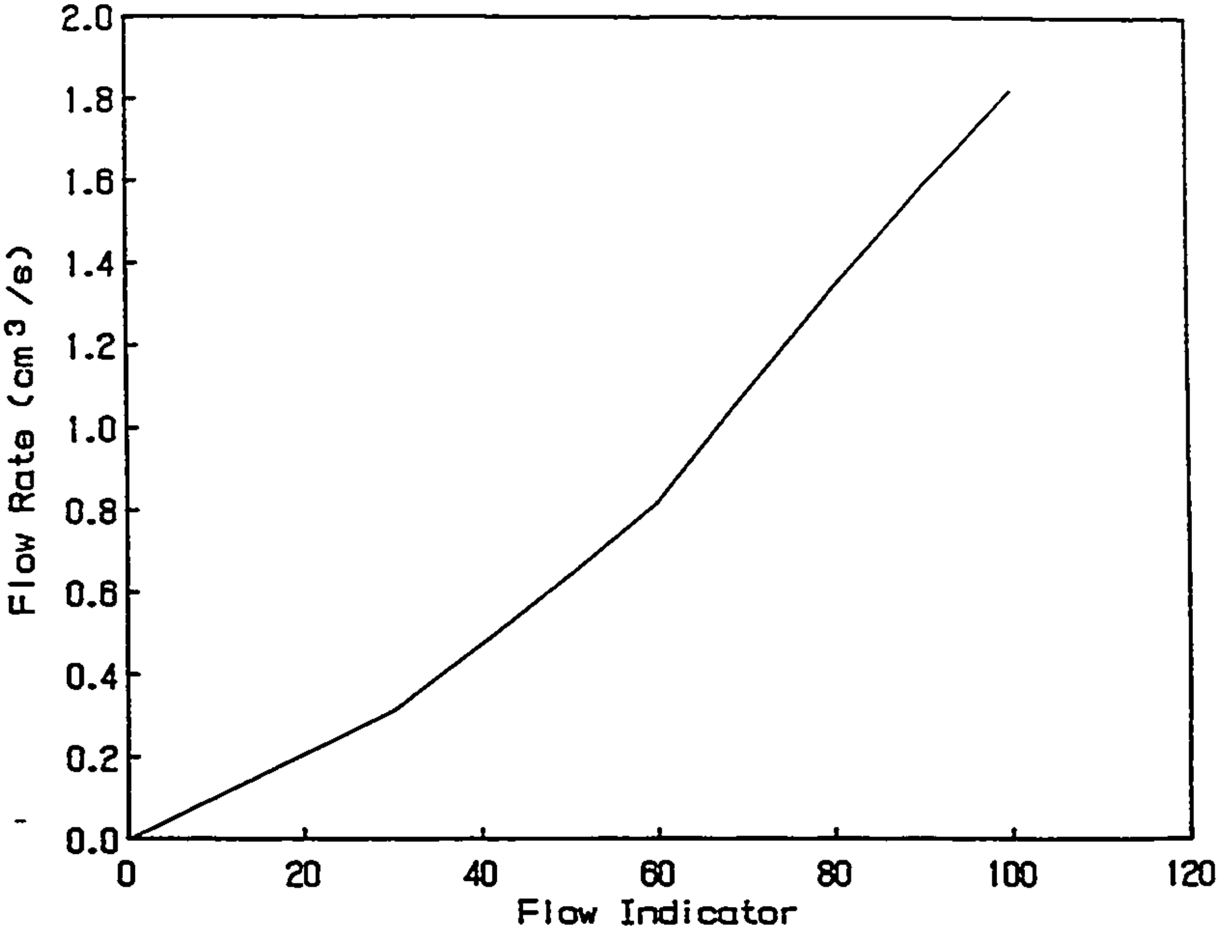

Figure A.4 Calibration of the H_2S flow meter

(Pressure = 1 atm, Temperature = 20°C)

APPENDIX B

GAS CHROMATOGRAPH TEMPERATURE PROGRAM

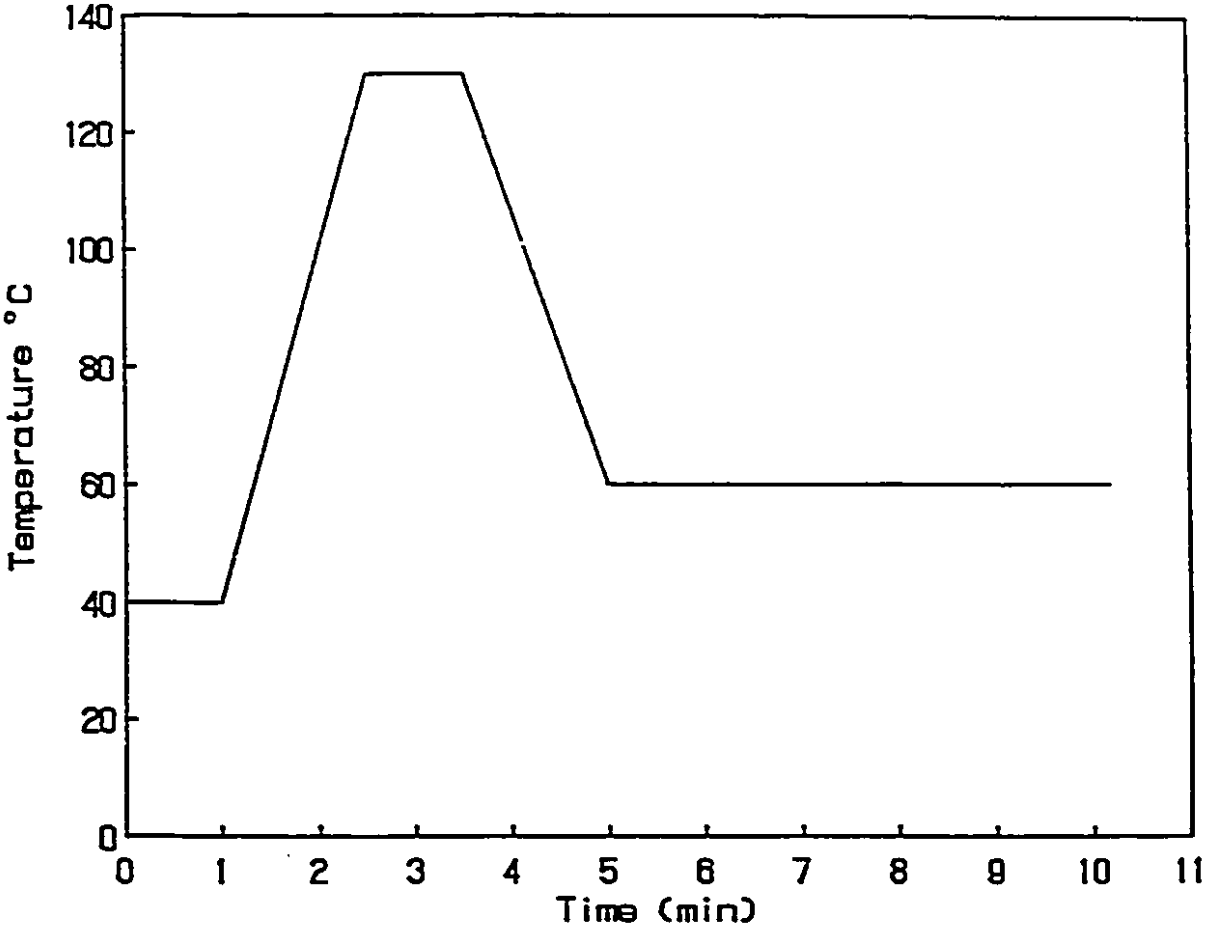

Figure B.1 Gas chromatograph temperature program

APPENDIX C

CATALYST COMPOSITION SAMPLE CALCULATION

The catalyst samples were analyzed for composition according to the procedures outlined in sections 4.2.3 to 4.2.5. In the case of the 15% Mo/Al_2O_3 sulphided with H_2S, the major components which were identified by x-ray diffraction analysis were MoS_2, MoO_2, and Al_2O_3. The sulphur content was 6.8%, and the molybdenum concentration in the resulting solution analyzed by atomic absorption spectroscopy was 13.4 ppm.

Calculation of moles of molybdenum in original catalyst sample:

$$13.4 \text{ ppm} = 13.4 \times 10^{-6} \text{ g Mo/g solution} \qquad \text{(C.1)}$$

Assuming a solution density of 1.0 g/cm^3:

$$13.4 \text{ ppm} = 13.4 \times 10^{-4} \text{ g Mo/100 cm}^3 \text{ solution} \qquad \text{(C.2)}$$

This solution had been diluted from 10 to 100 cm^3, therefore, the original solution of 100 cm^3 aqua regia which was used to digest the original catalyst sample of 0.1 g contained 10 times the above quantity of molybdenum.

$$(13.4 \times 10^{-4} \text{ g Mo/100 cm}^3)(100/10)/(96 \text{ g/mol Mo})$$
$$= 1.39 \times 10^{-4} \text{ mol Mo in sample} \qquad \text{(C.3)}$$

Calculation of moles of sulphur in original catalyst sample:

$$(0.068 \text{ g S/ g catalyst})(0.1 \text{ g catalyst})/32 \text{ g/mol S}$$

$$= 2.13 \times 10^{-4} \text{ mol S in sample} \quad (C.4)$$

Since the only sulphur bearing component was MoS_2, the quantity of MoS_2 was calculated directly from the sulphur content.

$$\text{mol } MoS_2 = (\text{mol S})/2 = 1.06 \times 10^{-4} \text{ mol } MoS_2 \quad (C.5)$$

$$\text{g } MoS_2 = (\text{mol } MoS_2) \times 160 \text{ g/mol} = 1.70 \times 10^{-2} \text{ g} \quad (C.6)$$

The moles of MoO_2 was calculated by difference from the total moles of molybdenum and the moles of MoS_2.

$$\text{mol } MoO_2 = (\text{mol Mo}) - (\text{mol } MoS_2)$$

$$= 3.30 \times 10^{-5} \text{ mol } MoO_2 \quad (C.7)$$

$$\text{g } MoO_2 = (\text{mol } MoO_2) \times 128 \text{ g/mol} = 4.22 \times 10^{-3} \text{ g} \quad (C.8)$$

The quantity of alumina was then calculated by difference between the total mass of catalyst sample (0.1 g) and the total of the masses of MoS_2 and MoO_2 calculated above.

$$\text{g } Al_2O_3 = 0.1 \text{ g} - 1.70 \times 10^{-2} \text{ g} - 4.22 \times 10^{-3} \text{ g}$$

$$= 7.88 \times 10^{-2} \text{ g } Al_2O_3 \quad (C.9)$$

The overall composition was then calculated directly from the calculated masses of MoS_2, MoO_2, and Al_2O_3.

$$MoS_2 = 17.0\%$$

$$MoO_2 = 4.2\%$$

$$Al_2O_3 = 78.8\%$$

APPENDIX D

EFFECT OF FLOW RATE ON MASS TRANSFER COEFFICIENT

The total flow rates examined in the external film diffusion experiments outlined in section 7.1.1 ranged from 4.0 to 8.3 cm^3/s. The effect of this change in flow rate on the external mass transfer coefficient has been estimated using correlations from Smith (1981).

The mass transfer coefficient can be estimated from the j-factor which is a function of the Stanton and Schmidt numbers:

$$j_d = \left(\frac{k_m \rho}{G}\right)\left(\frac{a_m}{a_t}\right)\left(\frac{\mu}{\rho D}\right)^{0.67} \qquad \text{(D.1)}$$

For Reynold's numbers greater than 10, the j-factor can be estimated from the following correlation:

$$j_d = \frac{0.455}{\varepsilon_B}\left(\frac{d_p G}{\mu}\right)^{-0.407} \qquad \text{(D.2)}$$

where k_m = mass transfer coefficient

G = mass velocity based on the cross-sectional area of the empty reactor

a_m = effective mass transfer area of pellets

a_t = total external area of pellets

d_p = diameter of catalyst pellet

μ = viscosity of the gas

ρ = density of the gas

D = molecular diffusivity of species being transferred

ε_B = void fraction of the bed

Combining equations D.1 and D.2, the mass transfer coefficient, k_m, can be written as a function of mass velocity.

$$k_m = \left(\frac{0.455}{\varepsilon_B}\right)\left(\frac{1}{\rho}\right)\left(\frac{a_t}{a_m}\right)\left(\frac{d_p}{\mu}\right)^{-0.407}\left(\frac{\mu}{\rho D}\right)^{-0.67} G^{0.6} \qquad \text{(D.3)}$$

If all other variables are kept constant, k_m is proportional to $G^{0.6}$ according to equation D.3. In addition, in the case where pressure is constant, the mass flow rate is proportional to the volumetric flow rate. Therefore, if the gas flow rate is increased by a factor of 2.08 (8.3/4), the mass transfer coefficient will increase by a factor of approximately 1.5.

APPENDIX E

REACTION RATE MODEL DATA SHEETS

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.50  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 600.000 C
FEED FLOWRATE : 375.000 CM3/MIN
FEED RATIO (SO2/CH4) :    .501
FEED COMPOSITION (YSO2,YCH4) :    .207        .413


CHROMATOGRAPH RUN     784

EXIT FLOWRATE =  365.90 CM3/MIN

YSO2 AVG =  .189   YCH4 AVG =  .398

XSO2 =      .144   XCH4     =  .041

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2                .171                  .7567D-08
CH4                .383                  .3740D-08
H2S                .001                  .2164D-09
CO2                .012                  .3612D-08
CO                 .000                  .0000D+00
COS                .000                  .0000D+00
H2O                .030                  .7910D-08
SULPHUR            .028                  .7350D-08
H2                 .000                  .0000D+00
C                  .000                  .1280D-09

YIELD S =     .9714D+00      YIELD CO2 =  .9658D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 625.000 C
FEED FLOWRATE : 384.600 CM3/MIN
FEED RATIO (SO2/CH4) :    .501
FEED COMPOSITION (YSO2,YCH4) :    .207        .413


CHROMATOGRAPH RUN     789

EXIT FLOWRATE =  357.10 CM3/MIN

YSO2 AVG =  .183   YCH4 AVG =  .392

XSO2 =      .202   XCH4     =  .065

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2                .159                   .1365D-07
CH4                .371                   .6828D-08
H2S                .002                   .6825D-09
CO2                .022                   .6568D-08
CO                 .000                   .0000D+00
COS                .000                   .0000D+00
H2O                .031                   .1416D-07
SULPHUR            .030                   .1297D-07
H2                 .000                   .0000D+00
C                  .000                   .2570D-09

YIELD S =     .9500D+00      YIELD CO2 =  .9619D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 600.000 C
FEED FLOWRATE : 365.900 CM3/MIN
FEED RATIO (SO2/CH4) :    .695
FEED COMPOSITION (YSO2,YCH4) :    .221         .318


CHROMATOGRAPH RUN     796

EXIT FLOWRATE =  361.40 CM3/MIN

YSO2 AVG =  .207   YCH4 AVG =  .308

XSO2 =      .087   XCH4     =  .025

COMPONENT      MOLE FRACTION       REACTION RATE (GMOL/M2-S)

SO2                .192                   .5858D-08
CH4                .298                   .2879D-08
H2S                .001                   .1529D-09
CO2                .010                   .2792D-08
CO                 .000                   .0000D+00
COS                .000                   .0000D+00
H2O                .029                   .6132D-08
SULPHUR            .023                   .5705D-08
H2                 .000                   .0000D+00
C                  .000                   .0000D+00

YIELD S =    .9739D+00      YIELD CO2 =  .9698D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 625.000 C
FEED FLOWRATE : 375.000 CM3/MIN
FEED RATIO (SO2/CH4) :    .665
FEED COMPOSITION (YSO2,YCH4) :    .212        .319


CHROMATOGRAPH RUN     799

EXIT FLOWRATE =  361.40 CM3/MIN

YSO2 AVG =  .196   YCH4 AVG =  .305

XSO2 =      .124   XCH4     =  .054

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2                .179                  .1026D-07
CH4                .291                  .5033D-08
H2S                .001                  .8714D-09
CO2                .016                  .4800D-08
CO                 .000                  .0000D+00
COS                .000                  .2148D-10
H2O                .027                  .1092D-07
SULPHUR            .024                  .9739D-08
H2                 .000                  .0000D+00
C                  .000                  .0000D+00

YIELD S =     .9468D+00     YIELD CO2 =  .9537D+00
```

```
          REACTOR CONDITIONS
          ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 625.000 C
FEED FLOWRATE : 375.000 CM3/MIN
FEED RATIO (SO2/CH4) :    .901
FEED COMPOSITION (YSO2,YCH4) :    .200        .222


CHROMATOGRAPH RUN     806

EXIT FLOWRATE =  361.40 CM3/MIN

YSO2 AVG =  .187   YCH4 AVG =  .214

XSO2 =      .112   XCH4     =  .046

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2                .174                    .7149D-08
CH4                .207                    .3471D-08
H2S                .001                    .2631D-09
CO2                .012                    .3435D-08
CO                 .000                    .0000D+00
COS                .000                    .0000D+00
H2O                .021                    .7428D-08
SULPHUR            .020                    .6887D-08
H2                 .000                    .0000D+00
C                  .000                    .0000D+00

YIELD S =     .9632D+00      YIELD CO2 =  .9897D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 600.000 C
FEED FLOWRATE : 370.300 CM3/MIN
FEED RATIO (SO2/CH4) :    .901
FEED COMPOSITION (YSO2,YCH4) :    .201        .221


CHROMATOGRAPH RUN     810

EXIT FLOWRATE =  365.90 CM3/MIN

YSO2 AVG =  .193   YCH4 AVG =  .217

XSO2 =      .061   XCH4     =  .022

COMPONENT      MOLE FRACTION       REACTION RATE (GMOL/M2-S)

SO2               .186                    .3882D-08
CH4               .213                    .1912D-08
H2S               .000                    .6208D-10
CO2               .007                    .1888D-08
CO                .000                    .0000D+00
COS               .000                    .0000D+00
H2O               .013                    .3988D-08
SULPHUR           .012                    .3791D-08
H2                .000                    .0000D+00
C                 .000                    .0000D+00

YIELD S =     .9767D+00      YIELD CO2 =  .9875D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 600.000 C
FEED FLOWRATE : 379.700 CM3/MIN
FEED RATIO (SO2/CH4) :   1.454
FEED COMPOSITION (YSO2,YCH4) :    .317        .218


CHROMATOGRAPH RUN     819

EXIT FLOWRATE =  370.40 CM3/MIN

YSO2 AVG =  .303   YCH4 AVG =  .211

XSO2 =      .046   XCH4     =  .028

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2                .290                     .3793D-08
CH4                .203                     .1850D-08
H2S                .000                     .6208D-10
CO2                .006                     .1790D-08
CO                 .000                     .0000D+00
COS                .000                     .0000D+00
H2O                .024                     .4006D-08
SULPHUR            .022                     .3756D-08
H2                 .000                     .0000D+00
C                  .000                     .6000D-09

YIELD S =     .9903D+00      YIELD CO2 =  .9674D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 625.000 C
FEED FLOWRATE : 379.700 CM3/MIN
FEED RATIO (SO2/CH4) :   1.454
FEED COMPOSITION (YSO2,YCH4) :    .317        .218


CHROMATOGRAPH RUN     824

EXIT FLOWRATE =  365.90 CM3/MIN

YSO2 AVG =  .301   YCH4 AVG =  .211

XSO2 =      .050   XCH4     =  .033

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2               .294                   .6370D-08
CH4               .204                   .3217D-08
H2S               .001                   .1561D-09
CO2               .011                   .3184D-08
CO                .000                   .0000D+00
COS               .000                   .0000D+00
H2O               .020                   .6372D-08
SULPHUR           .020                   .6214D-08
H2                .000                   .0000D+00
C                 .000                   .0000D+00

YIELD S =     .9755D+00      YIELD CO2 =  .9897D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 650.000 C
FEED FLOWRATE : 379.700 CM3/MIN
FEED RATIO (SO2/CH4) :   1.454
FEED COMPOSITION (YSO2,YCH4) :    .317        .218


CHROMATOGRAPH RUN     827

EXIT FLOWRATE =  357.10 CM3/MIN

YSO2 AVG =  .296   YCH4 AVG =  .206

XSO2 =      .091   XCH4     =  .070

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2                .274                  .1143D-07
CH4                .193                  .5630D-08
H2S                .001                  .4023D-09
CO2                .019                  .5602D-08
CO                 .000                  .0000D+00
COS                .000                  .2754D-10
H2O                .035                  .1166D-07
SULPHUR            .035                  .1103D-07
H2                 .000                  .0000D+00
C                  .000                  .0000D+00

YIELD S =     .9648D+00      YIELD CO2 =  .9951D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 600.000 C
FEED FLOWRATE : 379.700 CM3/MIN
FEED RATIO (SO2/CH4) :   1.817
FEED COMPOSITION (YSO2,YCH4) :    .387        .213


CHROMATOGRAPH RUN     893

EXIT FLOWRATE =  375.00 CM3/MIN

YSO2 AVG =  .383   YCH4 AVG =  .212

XSO2 =      .010   XCH4     =  .009

COMPONENT      MOLE FRACTION       REACTION RATE (GMOL/M2-S)

SO2                .379                  .3570D-08
CH4                .211                  .1741D-08
H2S                .000                  .1139D-09
CO2                .006                  .1723D-08
CO                 .000                  .0000D+00
COS                .000                  .0000D+00
H2O                .005                  .3694D-08
SULPHUR            .004                  .3436D-08
H2                 .000                  .0000D+00
C                  .000                  .0000D+00

YIELD S =     .9625D+00      YIELD CO2 =  .9894D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 625.000 C
FEED FLOWRATE : 379.700 CM3/MIN
FEED RATIO (SO2/CH4) :   1.817
FEED COMPOSITION (YSO2,YCH4) :    .387        .213


CHROMATOGRAPH RUN     840

EXIT FLOWRATE =  370.40 CM3/MIN

YSO2 AVG =  .376   YCH4 AVG =  .208

XSO2 =      .039   XCH4     =  .032

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2                 .365                 .6096D-08
CH4                 .202                 .3018D-08
H2S                 .000                 .1490D-09
CO2                 .010                 .3005D-08
CO                  .000                 .0000D+00
COS                 .000                 .0000D+00
H2O                 .015                 .6182D-08
SULPHUR             .014                 .5947D-08
H2                  .000                 .0000D+00
C                   .000                 .0000D+00

YIELD S =     .9755D+00      YIELD CO2 =  .9957D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 650.000 C
FEED FLOWRATE : 379.700 CM3/MIN
FEED RATIO (SO2/CH4) :   1.817
FEED COMPOSITION (YSO2,YCH4) :    .387          .213


CHROMATOGRAPH RUN     844

EXIT FLOWRATE =  365.90 CM3/MIN

YSO2 AVG =  .368   YCH4 AVG =  .203

XSO2 =      .067   XCH4     =  .060

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2                .349                  .1049D-07
CH4                .194                  .5219D-08
H2S                .001                  .3563D-09
CO2                .018                  .5193D-08
CO                 .000                  .0000D+00
COS                .000                  .2593D-10
H2O                .025                  .1059D-07
SULPHUR            .024                  .1013D-07
H2                 .000                  .0000D+00
C                  .000                  .0000D+00

YIELD S =     .9660D+00     YIELD CO2 =  .9950D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 625.000 C
FEED FLOWRATE : 389.600 CM3/MIN
FEED RATIO (SO2/CH4) :   2.394
FEED COMPOSITION (YSO2,YCH4) :    .529        .221


CHROMATOGRAPH RUN     854

EXIT FLOWRATE =  379.70 CM3/MIN

YSO2 AVG =  .517   YCH4 AVG =  .215

XSO2 =      .026   XCH4     =  .035

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2                .505                   .6096D-08
CH4                .209                   .2988D-08
H2S                .001                   .1196D-09
CO2                .010                   .2987D-08
CO                 .000                   .0000D+00
COS                .000                   .0000D+00
H2O                .017                   .6218D-08
SULPHUR            .015                   .5976D-08
H2                 .000                   .0000D+00
C                  .000                   .0000D+00

YIELD S =     .9804D+00      YIELD CO2 =  .9996D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 600.000 C
FEED FLOWRATE : 389.600 CM3/MIN
FEED RATIO (SO2/CH4) :   2.394
FEED COMPOSITION (YSO2,YCH4) :    .529        .221


CHROMATOGRAPH RUN     850

EXIT FLOWRATE =  384.60 CM3/MIN

YSO2 AVG =  .521   YCH4 AVG =  .218

XSO2 =      .017   XCH4     =  .017

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2               .514                   .3684D-08
CH4               .215                   .1792D-08
H2S               .000                   .5158D-10
CO2               .006                   .17910-08
CO                .000                   .0000D+00
COS               .000                   .0000D+00
H2O               .010                   .3786D-08
SULPHUR           .009                   .3632D-08
H2                .000                   .0000D+00
C                 .000                   .0000D+00

YIELD S =     .9860D+00      YIELD CO2 =  .9994D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 650.000 C
FEED FLOWRATE : 389.600 CM3/MIN
FEED RATIO (SO2/CH4) :   2.394
FEED COMPOSITION (YSO2,YCH4) :    .529        .221


CHROMATOGRAPH RUN     860

EXIT FLOWRATE =  375.00 CM3/MIN

YSO2 AVG =  .506   YCH4 AVG =  .209

XSO2 =      .052   XCH4     =  .074

COMPONENT      MOLE FRACTION       REACTION RATE (GMOL/M2-S)

SO2               .484                    .1092D-07
CH4               .197                    .5406D-08
H2S               .001                    .2708D-09
CO2               .018                    .5429D-08
CO                .000                    .0000D+00
COS               .000                    .0000D+00
H2O               .029                    .1098D-07
SULPHUR           .028                    .1065D-07
H2                .000                    .0000D+00
C                 .000                    .0000D+00

YIELD S =     .9752D+00      YIELD CO2 =  .9958D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 600.000 C
FEED FLOWRATE : 379.700 CM3/MIN
FEED RATIO (SO2/CH4) :   0.462
FEED COMPOSITION (YSO2,YCH4) :    .104        .225


CHROMATOGRAPH RUN     879

EXIT FLOWRATE =  375.00 CM3/MIN

YSO2 AVG =  .097   YCH4 AVG =  .222

XSO2 =      .127   XCH4      =  .016

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2               .090                    .3974D-08
CH4               .219                    .1958D-08
H2S               .000                    .1706D-09
CO2               .007                    .1947D-08
CO                .000                    .0000D+00
COS               .000                    .0000D+00
H2O               .011                    .4054D-08
SULPHUR           .009                    .3803D-08
H2                .000                    .0000D+00
C                 .000                    .0000D+00

YIELD S =     .9570D+00      YIELD CO2 =  .9945D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 625.000 C
FEED FLOWRATE : 379.700 CM3/MIN
FEED RATIO (SO2/CH4) :   0.462
FEED COMPOSITION (YSO2,YCH4) :    .104        .225


CHROMATOGRAPH RUN     883

EXIT FLOWRATE =  370.40 CM3/MIN

YSO2 AVG =  .091   YCH4 AVG =  .218

XSO2 =      .212   XCH4     =  .045

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2                .078                  .7323D-08
CH4                .211                  .3643D-08
H2S                .002                  .3903D-09
CO2                .012                  .3658D-08
CO                 .000                  .0000D+00
COS                .000                  .0000D+00
H2O                .020                  .7330D-08
SULPHUR            .018                  .6933D-08
H2                 .000                  .0000D+00
C                  .000                  .0000D+00

YIELD S =     .9467D+00      YIELD CO2 =  .9960D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 650.000 C
FEED FLOWRATE : 379.700 CM3/MIN
FEED RATIO (SO2/CH4) :   0.462
FEED COMPOSITION (YSO2,YCH4) :    .104        .225


CHROMATOGRAPH RUN     889

EXIT FLOWRATE =  361.40 CM3/MIN

YSO2 AVG =  .082   YCH4 AVG =  .211

XSO2 =      .286   XCH4     =  .090

COMPONENT      MOLE FRACTION       REACTION RATE (GMOL/M2-S)

SO2               .060                   .1301D-07
CH4               .198                   .6422D-08
H2S               .004                   .8951D-09
CO2               .021                   .6382D-08
CO                .000                   .0000D+00
COS               .000                   .4043D-10
H2O               .035                   .1326D-07
SULPHUR           .033                   .1211D-07
H2                .000                   .0000D+00
C                 .000                   .0000D+00

YIELD S =     .9312D+00     YIELD CO2 =  .9937D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 650.000 C
FEED FLOWRATE : 379.700 CM3/MIN
FEED RATIO (SO2/CH4) :   0.706
FEED COMPOSITION (YSO2,YCH4) :    .221        .313


CHROMATOGRAPH RUN     895

EXIT FLOWRATE =  361.40 CM3/MIN

YSO2 AVG =  .184   YCH4 AVG =  .290

XSO2 =      .272   XCH4     =  .087

COMPONENT       MOLE FRACTION       REACTION RATE (GMOL/M2-S)

SO2                 .146                   .1712D-07
CH4                 .267                   .8497D-08
H2S                 .004                   .1014D-08
CO2                 .027                   .8431D-08
CO                  .000                   .0000D+00
COS                 .000                   .6606D-10
H2O                 .064                   .1738D-07
SULPHUR             .059                   .1611D-07
H2                  .000                   .0000D+00
C                   .000                   .0000D+00

YIELD S =      .9408D+00      YIELD CO2 =  .9922D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 650.000 C
FEED FLOWRATE : 384.600 CM3/MIN
FEED RATIO (SO2/CH4) :   0.958
FEED COMPOSITION (YSO2,YCH4) :    .204         .213


CHROMATOGRAPH RUN     898

EXIT FLOWRATE =  370.40 CM3/MIN

YSO2 AVG =  .189   YCH4 AVG =  .202

XSO2 =      .113   XCH4     =  .063

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2                .173                  .1107D-07
CH4                .191                  .5479D-08
H2S                .002                  .5745D-09
CO2                .018                  .54510-08
CO                 .000                  .0000D+00
COS                .000                  .2870D-10
H2O                .027                  .1124D-07
SULPHUR            .025                  .1050D-07
H2                 .000                  .0000D+00
C                  .000                  .0000D+00

YIELD S =     .9481D+00      YIELD CO2 =  .9948D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 600.000 C
FEED FLOWRATE : 379.400 CM3/MIN
FEED RATIO (SO2/CH4) :   0.418
FEED COMPOSITION (YSO2,YCH4) :    .217        .519


CHROMATOGRAPH RUN     915

EXIT FLOWRATE =  375.00 CM3/MIN

YSO2 AVG =  .203   YCH4 AVG =  .503

XSO2 =      .102   XCH4     =  .034

COMPONENT      MOLE FRACTION       REACTION RATE (GMOL/M2-S)

SO2               .189                    .8700D-08
CH4               .487                    .4286D-08
H2S               .001                    .4463D-09
CO2               .014                    .41980-08
CO                .000                    .0000D+00
COS               .000                    .1922D-10
H2O               .021                    .9004D-08
SULPHUR           .016                    .8254D-08
H2                .000                    .0000D+00
C                 .000                    .0000D+00

YIELD S =     .9487D+00      YIELD CO2 =  .9795D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 625.000 C
FEED FLOWRATE : 384.600 CM3/MIN
FEED RATIO (SO2/CH4) :   0.434
FEED COMPOSITION (YSO2,YCH4) :    .223        .514


CHROMATOGRAPH RUN     918

EXIT FLOWRATE =  365.80 CM3/MIN

YSO2 AVG =  .194   YCH4 AVG =  .489

XSO2 =      .220   XCH4     = .055

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2               .166                   .1609D-07
CH4               .464                   .7922D-08
H2S               .003                   .9251D-09
CO2               .025                   .76200-08
CO                .000                   .0000D+00
COS               .000                   .5011D-10
H2O               .042                   .1694D-07
SULPHUR           .039                   .1516D-07
H2                .000                   .0000D+00
C                 .000                   .2519D-09

YIELD S =     .9425D+00      YIELD CO2 =  .9619D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 600.000 C
FEED FLOWRATE : 384.600 CM3/MIN
FEED RATIO (SO2/CH4) :   1.772
FEED COMPOSITION (YSO2,YCH4) :    .225        .127


CHROMATOGRAPH RUN     903

EXIT FLOWRATE =  379.70 CM3/MIN

YSO2 AVG =  .222   YCH4 AVG =  .126

XSO2 =      .021   XCH4     =  .016

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2               .219                 .1961D-08
CH4               .124                 .9732D-09
H2S               .000                 .5785D-10
CO2               .003                 .9721D-09
CO                .000                 .0000D+00
COS               .000                 .0000D+00
H2O               .005                 .1978D-08
SULPHUR           .005                 .1903D-08
H2                .000                 .0000D+00
C                 .000                 .0000D+00

YIELD S =     .9705D+00     YIELD CO2 =  .9989D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 625.000 C
FEED FLOWRATE : 384.600 CM3/MIN
FEED RATIO (SO2/CH4) :   1.772
FEED COMPOSITION (YSO2,YCH4) :    .225        .127


CHROMATOGRAPH RUN     905

EXIT FLOWRATE =  375.00 CM3/MIN

YSO2 AVG =  .208   YCH4 AVG =  .122

XSO2 =      .112   XCH4     =  .039

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2                .192                  .3796D-08
CH4                .117                  .1866D-08
H2S                .000                  .5276D-10
CO2                .006                  .1865D-08
CO                 .000                  .0000D+00
COS                .000                  .0000D+00
H2O                .037                  .3862D-08
SULPHUR            .035                  .3743D-08
H2                 .000                  .0000D+00
C                  .000                  .0000D+00

YIELD S =     .9861D+00     YIELD CO2 =  .9994D+00
```

```
         REACTOR CONDITIONS
         ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 650.000 C
FEED FLOWRATE : 389.700 CM3/MIN
FEED RATIO (SO2/CH4) :   1.634
FEED COMPOSITION (YSO2,YCH4) :    .214        .131


CHROMATOGRAPH RUN     S11

EXIT FLOWRATE =  370.40 CM3/MIN

YSO2 AVG =  .201   YCH4 AVG =  .124

XSO2 =      .106   XCH4     =  .091

COMPONENT       MOLE FRACTION       REACTION RATE (GMOL/M2-S)

SO2                 .188                  .6878D-08
CH4                 .117                  .3403D-08
H2S                 .001                  .2792D-09
CO2                 .012                  .3391D-08
CO                  .000                  .0000D+00
COS                 .000                  .1416D-10
H2O                 .020                  .6974D-08
SULPHUR             .019                  .6599D-08
H2                  .000                  .0000D+00
C                   .000                  .0000D+00

YIELD S =     .9594D+00     YIELD CO2 =  .9958D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 600.000 C
FEED FLOWRATE : 379.700 CM3/MIN
FEED RATIO (SO2/CH4) :    .626
FEED COMPOSITION (YSO2,YCH4) :    .325        .519


CHROMATOGRAPH RUN     924

EXIT FLOWRATE =  375.00 CM3/MIN

YSO2 AVG =  .308   YCH4 AVG =  .506

XSO2 =      .089   XCH4     =  .032

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2                .290                  .8054D-08
CH4                .492                  .3964D-08
H2S                .001                  .2187D-09
CO2                .013                  .3945D-08
CO                 .000                  .0000D+00
COS                .000                  .1872D-10
H2O                .025                  .8218D-08
SULPHUR            .023                  .7814D-08
H2                 .000                  .0000D+00
C                  .000                  .0000D+00

YIELD S =     .9701D+00      YIELD CO2 =  .9953D+00
```

```
          REACTOR CONDITIONS
          ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 625.000 C
FEED FLOWRATE : 379.700 CM3/MIN
FEED RATIO (SO2/CH4) :    .626
FEED COMPOSITION (YSO2,YCH4) :    .325        .519


CHROMATOGRAPH RUN     930

EXIT FLOWRATE =  365.90 CM3/MIN

YSO2 AVG =  .295   YCH4 AVG =  .496

XSO2 =      .153   XCH4     =  .051

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2                 .265                  .1487D-07
CH4                 .473                  .7339D-08
H2S                 .002                  .8327D-09
CO2                 .024                  .7292D-08
CO                  .000                  .0000D+00
COS                 .000                  .4734D-10
H2O                 .043                  .1516D-07
SULPHUR             .040                  .1404D-07
H2                  .000                  .0000D+00
C                   .000                  .0000D+00

YIELD S =     .9440D+00      YIELD CO2 =  .9936D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 625.000 C
FEED FLOWRATE : 384.600 CM3/MIN
FEED RATIO (SO2/CH4) :   1.408
FEED COMPOSITION (YSO2,YCH4) :    .490        .348


CHROMATOGRAPH RUN     933

EXIT FLOWRATE =  365.90 CM3/MIN

YSO2 AVG =  .465   YCH4 AVG =  .334

XSO2 =      .053   XCH4     =  .035

COMPONENT      MOLE FRACTION       REACTION RATE (GMOL/M2-S)

SO2                .440                   .9761D-08
CH4                .321                   .4806D-08
H2S                .001                   .3621D-09
CO2                .015                   .4789D-08
CO                 .000                   .0000D+00
COS                .000                   .1736D-10
H2O                .042                   .9944D-08
SULPHUR            .036                   .9399D-08
H2                 .000                   .0000D+00
C                  .000                   .0000D+00

YIELD S =     .9629D+00     YIELD CO2 =  .9964D+00
```

```
          REACTOR CONDITIONS
          ******************
AREA OF THE CATALYST : 113.90  M2/G
CATALYST WEIGHT :   8.038 G
REACTOR TEMPERATURE : 600.000 C
FEED FLOWRATE : 384.600 CM3/MIN
FEED RATIO (SO2/CH4) :   1.408
FEED COMPOSITION (YSO2,YCH4) :    .490        .348


CHROMATOGRAPH RUN     935

EXIT FLOWRATE =  370.40 CM3/MIN

YSO2 AVG =  .466   YCH4 AVG =  .336

XSO2 =      .035   XCH4     =  .020

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2                .443                  .5658D-08
CH4                .325                  .2811D-08
H2S                .000                  .4809D-10
CO2                .009                  .2810D-08
CO                 .000                  .0000D+00
COS                .000                  .0000D+00
H2O                .031                  .5696D-08
SULPHUR            .031                  .5611D-08
H2                 .000                  .0000D+00
C                  .000                  .0000D+00

YIELD S =     .9915D+00     YIELD CO2 =  .9996D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 112.50  M2/G
CATALYST WEIGHT :   7.530 G
REACTOR TEMPERATURE : 600.000 C
FEED FLOWRATE : 379.700 CM3/MIN
FEED RATIO (SO2/CH4) :    .421
FEED COMPOSITION (YSO2,YCH4) :    .220        .522


CHROMATOGRAPH RUN     938

EXIT FLOWRATE =  370.40 CM3/MIN

YSO2 AVG =  .202   YCH4 AVG =  .507

XSO2 =      .146   XCH4     =  .034

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2               .183                    .8628D-08
CH4               .491                    .4257D-08
H2S               .001                    .3494D-09
CO2               .013                    .4256D-08
CO                .000                    .0000D+00
COS               .000                    .0000D+00
H2O               .032                    .8744D-08
SULPHUR           .028                    .8279D-08
H2                .000                    .0000D+00
C                 .000                    .0000D+00

YIELD S =     .9595D+00     YIELD CO2 =  .9997D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 112.50  M2/G
CATALYST WEIGHT :   7.530 G
REACTOR TEMPERATURE : 575.000 C
FEED FLOWRATE : 379.700 CM3/MIN
FEED RATIO (SO2/CH4) :    .540
FEED COMPOSITION (YSO2,YCH4) :    .313        .580


CHROMATOGRAPH RUN     943

EXIT FLOWRATE =  375.00 CM3/MIN

YSO2 AVG =  .308   YCH4 AVG =  .573

XSO2 =      .016   XCH4     =  .007

COMPONENT      MOLE FRACTION      REACTION RATE (GMOL/M2-S)

SO2                 .303                   .5214D-08
CH4                 .566                   .2579D-08
H2S                 .000                   .2816D-09
CO2                 .008                   .2564D-08
CO                  .000                   .0000D+00
COS                 .000                   .1492D-10
H2O                 .009                   .5300D-08
SULPHUR             .007                   .4932D-08
H2                  .000                   .0000D+00
C                   .000                   .0000D+00

YIELD S =     .9460D+00      YIELD CO2 =  .9942D+00
```

```
        REACTOR CONDITIONS
        ******************
AREA OF THE CATALYST : 112.50  M2/G
CATALYST WEIGHT :   7.530 G
REACTOR TEMPERATURE : 613.000 C
FEED FLOWRATE : 326.1000 CM3/MIN
FEED RATIO (SO2/CH4) :    .975
FEED COMPOSITION (YSO2,YCH4) :    .268        .275


CHROMATOGRAPH RUN     945

EXIT FLOWRATE =  315.80 CM3/MIN

YSO2 AVG =  .252   YCH4 AVG =  .267

XSO2 =      .089   XCH4     =  .026

COMPONENT      MOLE FRACTION       REACTION RATE (GMOL/M2-S)

SO2               .236                    .6310D-08
CH4               .259                    .3171D-08
H2S               .001                    .1667D-09
CO2               .011                    .3104D-08
CO                .000                    .0000D+00
COS               .000                    .0000D+00
H2O               .026                    .6412D-08
SULPHUR           .024                    .6152D-08
H2                .000                    .0000D+00
C                 .000                    .0000D+00

YIELD S =     .9749D+00      YIELD CO2 =  .9789D+00
```

APPENDIX F

RATE LAW DEVELOPMENT

The following is the development of reaction rate law for the reduction of SO_2 with CH_4 assuming that CH_4 is the adsorbed species. The reaction rates of the elementary reactions 7.4, 7.5, and 7.6 are denoted r_A, r_S and, r_D, respectively can be written as follows

$$r_A = k_A\ (C_v\ P_{CH_4} - C_{M\cdot E}/K_A) \qquad (F.1)$$

$$r_S = k_r\ (C_{M\cdot E}\ P_{SO_2} - C_{C\cdot E}\ P_D/K_r) \qquad (F.2)$$

$$r_D = k_D\ (C_{C\cdot E} - P_C\ C_V/K_d) \qquad (F.3)$$

Where P_{CH_4}, P_{SO_2}, P_D = partial pressures of CH_4, SO_2 and gas phase products, respectively

C_V = surface concentration of vacant sites

$C_{M\cdot E}$, $C_{C\cdot E}$ = surface concentration of adsorbed methane and adsorbed reaction products, respectively

k_A, k_C, k_D, k_r = rate constants for the forward reactions

K_A, K_C, K_D, K_r = equilibrium constants of the reactions

When heterogeneous reactions are carried out at steady state, the rates of adsorption, surface reaction and desorption are equal to one another.

$$r(i) = r_A = r_S = r_D \qquad (F.4)$$

The assumption that the adsorption of methane is the rate-controlling step implies that:

$$\frac{r_S}{k_r} = \frac{r_d}{k_D} = 0 \qquad (F.5)$$

The total concentration of vacant and occupied active sites on the catalyst surface is given by

$$C_t = C_V + C_{M\cdot E} + C_{C\cdot E} + C_{I\cdot E} \qquad (F.6)$$

where C_t = total concentration of active sites

$C_{I\cdot E}$ = Concentration of adsorbed inhibitor

In this case, SO_2 acts as an inhibitor and, therefore, $C_{I\cdot E}$ is given by

$$C_{I\cdot E} = K_I C_V P_{SO_2} \qquad (F.7)$$

By combining equations A.1 to A.7 and knowing that the equilibrium constant for the reaction is large (> 1.95 x 10^{12} at 600°C), the following expression is obtained.

$$r(CH_4) = \frac{k_A C_T \ P_{CH_4}}{1 + K_I \ P_{SO_2}} \qquad (F.8)$$

This expression can be further simplified to

$$r(CH_4) = \frac{k\ P_{CH_4}}{1 + K\ P_{SO_2}} \qquad (F.9)$$

A similar analysis can be performed assuming that SO_2 is the adsorbed species. In this case, the resulting rate expression has the following form.

$$r(CH_4) = \frac{k\ P_{SO_2}}{1 + K\ P_{CH_4}} \qquad (F.10)$$

Additional rate expressions can be developed assuming various rate limiting steps. In the case where the surface reaction between adsorbed CH_4 and SO_2 in the gas phase is rate-limiting, the rate law can be written as:

$$r(CH_4) = \frac{k\ P_{CH_4}P_{SO_2}}{1 + K_1P_{SO_2} + K_2P_{CH_4}} \qquad (F.11)$$

where K_1 and K_2 are the equilibrium adsorption constants for SO_2 and CH_4 respectively.

In the case where the desorption of adsorbed products is rate-limiting, the rate law can be written as:

$$r(CH_4) = \frac{k(P_{CH_4}P_{SO_2}/P_D)}{1 + K_d(P_{CH_4}P_{SO_2}/P_D) + K_1P_{SO_2} + K_2P_{CH_4}} \qquad (F.12)$$

where P_D is the partial pressure of a reaction product which is not adsorbed and, K_d is the equilibrium adsorption constant for the adsorbed product.