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**CH₄-Olefin Coupling Using
Supported- Nickel and Solid Superacid Catalysts**

by

Bruce Gordon Anderson

A thesis submitted in partial fulfillment
of the requirements for the degree of

Doctor of Philosophy
in
Chemistry

Department of Chemistry
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August, 1993

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Dedication:

This thesis is dedicated to the late Gordon R. Anderson (December 23, 1923 - August 4, 1988). The memory of his unfailing strength, perserverance and zest for life has been a great source of inspiration to me during the course of this work, as it doubtlessly will be in everything that I will ever do.

This one's for you Dad.

Table of Contents:

	page:
Dedication	i
Table of Contents	ii
Abstract	vi
Acknowledgements	x
List of Abbreviations and Terminology	xi
 Chapter 1: Introduction	 1
Natural Gas Reserves	1
Present Uses of Natural Gas	2
Reactivity of Methane	3
Thermodynamics and Kinetics	3
Thermodynamics of Direct Methane Coupling	4
Methane Conversion Strategies	7
Established Technologies	7
Steam Reforming	7
The Fischer- Tropsch Process	8
Methanol Synthesis	9
Mobil's Methanol-to-Gasoline (MTG) Process	9
More Recent Methane Conversion Strategies	10
Current Research in Homogeneous CH ₄ Conversion	10
Heterogeneous CH ₄ Conversion	11
Oxidative Coupling of Methane	12
Methane Coupling with Unsaturated Compounds	14
Thermodynamics of Methane Coupling with Unsaturated Compounds	14
Previous Research Involving CH ₄ Coupling with Unsaturated Compounds	17
Using Supported Transition Metal Catalysts	17
Using Superacid Catalysts	18
 Chapter 2: Reactions of Methane and Propylene over Ni/SiO₂ and CH₄-activated Ni/SiO₂.	 25
Reactions of Olefins	26
Thermodynamics of Various Reactions Involving Propylene	26
Homologation	30
Experimental	32
Materials	32
Apparatus	33

	page:
Chapter 2: Reactions of Methane and Propylene over Ni/SiO₂ and CH₄-activated Ni/SiO₂ (continued).	
Gas Chromatographic Analysis	37
Catalyst Preactivation	39
Hydrogen Reduction	39
Standard Methane Preactivation Protocol	41
Propylene/ (Methane or Helium) Reactions	41
Results and Discussion	43
Control Experiments over H ₂ Reduced Ni/SiO ₂	43
Effects of CH ₄ in C ₃ H ₆ /CH ₄ Feed Gas	43
Effects of Contact Time	45
Effects of Residual H ₂ on the C ₃ H ₆ /CH ₄ Reaction	46
Effects of Residual H ₂ on the C ₃ H ₆ /He Reaction	48
Experiments over Methane-Preactivated NiO/SiO ₂	51
Preactivation of NiO/SiO ₂ with pure CH ₄	51
Carbon Deposition During C ₃ H ₆ /CH ₄ and C ₃ H ₆ /He Reactions	52
Effects of CH ₄ Preactivation Temperature	52
The Role of CH ₄ During Preactivation	58
Effects of Reaction Temperature on the C ₃ H ₆ /CH ₄ Reaction	65
Effects of CH ₄ in C ₃ H ₆ /CH ₄ Feed Gas at 350°C	69
Effects of Contact Time	71
A Comparison of CH ₄ -preactivation versus H ₂ Reduction of NiO/SiO ₂ Catalysts on C ₃ H ₆ /CH ₄ Reactions at 350°C	74
Conclusions	77
Chapter 3: Characterization of ZrO₂/SiO₂	80
Introduction	80
Acidity and Basicity in Solids	80
Coordinative Unsaturation	80
Enhancement of Surface Acidity in Binary Oxide Mixtures	82
Zirconium Dioxide	86
Zirconia/Silica	86
Temperature Programmed Desorption (TPD)	89
Experimental	92
Catalyst Preparation	92
Temperature Programmed Desorption (TPD) Experiments	93
Infrared Spectroscopy	95
Powder X-ray Diffraction Analysis	96
Results and Discussion	97
Infrared Spectra of the hydroxyl stretching region	97

	page:
Chapter 3: Characterization of ZrO₂/SiO₂ (continued)	
Thermal Stability of hydroxyl groups	98
Effect of water on hydroxyl groups	101
D ₂ O exchange of surface hydroxyl groups	101
NH ₃ Adsorption on SiO ₂	104
Infrared Spectrum of NH ₃ on SiO ₂	104
NH ₃ Adsorbed on Zirconia	106
Ammonia adsorption on ZrO ₂ /SiO ₂	108
FTIR Results of NH ₃ on ZrO ₂ /SiO ₂	115
Effects of NH ₃ Contact Time on TPD Spectra	119
Effects of Activation Temperature on NH ₃ TPD Spectra	120
Blank Experiments	121
Other TPD Experiments	121
TPD of Pyridine on ZrO ₂ /SiO ₂	124
Pyridine Poisoning Experiments	128
Infrared spectroscopy of pyridine adsorbed on ZrO ₂ /SiO ₂	130
Results of X-ray Diffraction Analysis	133
Conclusions	136
Chapter 4: Characterization of Sulphate-Promoted ZrO₂/SiO₂	138
Introduction	138
Experimental	145
Preparation of Sulphate-promoted Zirconia-Silica	145
Results	146
FTIR Characterization of sulphate-promoted ZrO ₂ /SiO ₂	146
Effect of activation temperature on sulphate species	149
Adsorption of ammonia on sulphated ZrO ₂ /SiO ₂	151
Adsorption of pyridine on sulphated ZrO ₂ /SiO ₂	156
TPD of Ammonia on sulphated ZrO ₂ /SiO ₂	159
TPD of Pyridine on sulphated ZrO ₂ /SiO ₂	161
Gravimetric ammonia adsorption measurements	163
X-ray Diffraction Analysis of sulphated ZrO ₂ /SiO ₂	165
Conclusions	166
Chapter 5: Reactions of Methane and Ethylene (or Propylene) over Sulphate-Promoted ZrO₂/SiO₂:	168
Sulphate-Promoted ZrO ₂ -SiO ₂ as a Catalyst for the CH ₄ /Olefin Coupling Reaction	172
Experimental	174
Materials	174
Apparatus	175

	page:
Chapter 5: Reactions of Methane and Ethylene (or Propylene) over Sulphate-Promoted ZrO₂/SiO₂ (continued):	
Catalyst Activation	175
Gas Chromatographic Analysis	176
Reaction Conditions	176
Results and Discussion	178
Reactions Using Methane/Ethylene Mixtures	179
Directions for Further Study	186
 Appendix 1: Development of a Flow Reactor System with an On-line Mass Spectrometer Detector:	 190
Description of Mass Spectrometer Detection System	190
Calibration of the Mass Spectrometer System	193
Calibration using Static Gas Mixtures	194
Calibration of Flowing Gas Mixtures	196
Determination of the Sensitivity of the Flow System with Mass Spectrometer Detector	197
System Evaluation by Analysis of the Hydrogenation of Propylene over 1.0% Pt/Al ₂ O ₃	198
References	201

Abstract:

The development of technologies for the conversion of natural gas, which is predominantly methane, into higher molecular weight compounds, such as gasoline-range hydrocarbons for combustion, or into ethylene, higher olefins, and aromatics for use by the chemical industry, is of great importance given the depleting supply of crude oil. In this thesis, we have investigated the coupling of methane with olefins, such as ethylene and propylene using silica-supported nickel and sulphate-promoted zirconia-silica catalysts.

A fixed-bed flow reactor system was used to conduct experiments in which mixtures of methane and propylene were reacted over a CH_4 -preactivated Ni/SiO_2 catalyst, typically at 350°C . Experiments were also conducted over H_2 -reduced Ni/SiO_2 . Reaction parameters such as: methane preactivation conditions; reaction temperature; contact time; and feed gas composition were also varied and their effects on the resultant product spectra were analyzed in order to understand the processes involved.

Control experiments over hydrogen-reduced Ni/SiO_2 in which propylene was co-fed with helium rather than with methane resulted in increased propylene conversions and in an increase of the yields of propane, C_2 's and C_4 's. It was concluded that the production of C_4 's was due to homologation or metathesis reactions, rather than to methane coupling.

Variation of the temperature of the methane preactivation treatment from 350°C to 600°C revealed an increased CH_4 conversion from approximately 1% at 350°C to 60% at 600°C . Subsequent reaction of $\text{C}_3\text{H}_6/\text{CH}_4$ mixtures over these catalysts at 350°C revealed that there was virtually no activity over the former catalyst and very little over the latter.

However, catalysts activated between 400°C and 500°C showed very similar activities. These results suggest that insufficient reduction of NiO occurred at 350°C (no activity was observed over a NiO/SiO₂ catalyst that had not been preactivated) and that preactivation at 600°C led to excessive carbon deposition. At intermediate temperatures sufficient reduction occurred without excessive carbon deposition.

Experiments in which helium was co-fed with propylene rather than methane over CH₄-preactivated catalysts suggested that the same processes were responsible for C₄ production over CH₄-reduced NiO/SiO₂ and hydrogen-reduced NiO/SiO₂ *ie* propylene homologation and/or metathesis. There was no evidence to support a mechanism by which CH_x species, formed by the dissociative adsorption of methane either during activation or during reaction, coupled with propylene to produce C₄'s. Rather, dissociatively adsorbed methane only served to block metal sites at which reactions could otherwise occur.

Sulphate-promoted zirconia-silica, a solid superacid, has previously been used as a catalyst for the coupling of CH₄ and ethylene to form hydrocarbons in the C₃ to C₇ range. The lifetime of these catalysts was severely limited due to fouling caused by oligomerization of ethylene. In an effort to alleviate this problem, zirconia was dispersed on silica prior to sulphation. Prior to use as a catalyst, the surface properties of sulphate-promoted zirconia-silica, and the precursor material, zirconia-silica were characterized by: Fourier Transform Infrared spectroscopy (FTIR); Temperature Programmed Desorption (TPD); X-ray Diffraction (XRD); and gravimetric ammonia adsorption measurements.

Zirconia-silica, like many binary oxide mixtures, possesses enhanced surface acidity relative to its parent components. TPD experiments using NH₃ found that samples of 5, 10,

and 20 wt. % $\text{ZrO}_2/\text{SiO}_2$, previously activated by evacuation at 450°C , contained a similar amount of surface acid sites, $260\ \mu\text{mole/g}$ sample. XRD analysis revealed no peaks due to crystalline phases following calcination at 450°C , suggesting that these materials were amorphous, even with zirconia loadings as high as 20 wt. %. Infrared spectroscopy using NH_3 as a probe of the surface acid sites was slightly ambiguous as to whether both Lewis and Bronsted acid sites were formed because of the presence of a broad band at $1460\ \text{cm}^{-1}$ which is often assigned to the asymmetric deformation mode of the ammonium ion. However, the fact that this peak could be removed by evacuation at 100°C , coupled with its breadth, suggested that this peak was due to a weaker interaction such as hydrogen-bonding between ammonia and surface hydroxyl groups. Infrared studies using pyridine as a probe molecule revealed that only Lewis acid sites were formed.

Infrared analysis of 10 wt. % $\text{ZrO}_2/\text{SiO}_2$ with sulphate loadings ranging from 100 to $1000\ \mu\text{mole/g}$ revealed that the nature of the surface sulphate species was dependent on the temperature of activation. For low activation temperatures, *eg.* 200°C , a hydrogensulphate species, which possessed Bronsted acidity, was formed by an interaction with surface hydroxyl groups. At 500°C activation, the adsorbed sulphate existed as a bidentate species coordinated to Zr^{4+} .

IR analysis using NH_3 as a probe revealed that both Lewis and Bronsted acid sites existed after 500°C activation. The amount of each type of acid site appeared to increase with increased sulphate loading. Similar experiments using pyridine supported this conclusion.

TPD of NH_3 on $1500\ \mu\text{mole/g}$ 10 wt. % $\text{ZrO}_2/\text{SiO}_2$, activated at 450°C , revealed that

in addition to a peak at 240°C, which was assigned to Lewis acid sites on $\text{ZrO}_2/\text{SiO}_2$, a peak which began at 410°C and continued to the temperature of activation was observed. This peak was attributed to NH_3 desorption from very strong, perhaps superacidic sites. Direct measurement of the number of these sites by TPD was hampered by the fact that not all ammonia was desorbed prior to reaching the original activation temperature. The number of these sites was estimated to be between 118 and 190 $\mu\text{mole/g}$ sample.

The acidity of 10 wt. % $\text{ZrO}_2/\text{SiO}_2$ with various loadings of sulphate was measured by gravimetric ammonia adsorption following evacuation at various temperatures. The amounts of irreversibly adsorbed ammonia were found to increase with increased sulphate loading at 25, 100, and 200°C. Attempts to measure the amount of irreversible adsorption at temperatures greater than 200°C were hampered by weight loss due to sulphate. Thus, precise measurement of the number of acid sites at high temperature was not possible.

Sulphate-promoted $\text{ZrO}_2/\text{SiO}_2$, previously activated by evacuation at 500°C, was tested as a catalyst for the coupling of methane and ethylene (or propylene) in a fixed-bed reactor at atmospheric pressure and at temperatures ranging from 225 to 275°C. All experiments were hampered by rapid deactivation of the catalyst (within 35 minutes on stream) due to oligomerization. Only minute quantities of propane were detected. Reactions of methane alone showed that it also interacted strongly with the catalyst, leading to deactivation.

Acknowledgements:

I would like to thank my supervisors, Dr. Yoshimitsu Amenomiya and Dr. Barry Morrow for their patient and unselfish direction during the course of this work.

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Lastly, I would like to thank: my mother, Joan; my sister, Cheryl; my extended family, Carole and Len Fisher, and especially my love and best friend, Michele. Your support and encouragement made this possible.

List of Abbreviations and Terminology:

C1 Chemistry: A term commonly used to refer to chemical processes involving methane.

Gas Hourly Space Velocity (GHSV):

Volume of feed gas/ unit time/ unit volume of catalyst.

$[\text{time}]^{-1}$

Contact Time: $(\text{Space Velocity})^{-1}$

A measure of the length of time that a reactant is in contact with the catalyst. For a plug flow reactor it is approximated by the ratio of the volumetric flow rate of the feed gas to the catalyst bed volume.

W/F : Weight of catalyst/ total flow rate of feed gas $[\text{mg min/ mL}]$

The terms defined below are used frequently throughout this thesis:

- (1) C_2 's refers to ethane, ethylene, and acetylene.
- (2) C_4 's refers to iso- C_4H_{10} , n- C_4H_{10} , and the four butene isomers

(1-butene, isobutene, cis-2-butene, and trans-2-butene).

- (3) **Conversion** is defined as the ratio of the amount of a reactant consumed to the initial amount present. Conversions were calculated based on quantitative gas chromatographic analyses of the initial reactant and the product effluent streams as described later.
- (4) **Selectivity to C_x (S_x)** is defined as the ratio of the amount of reactant converted to form a particular product, C_x , to the total amount of reactant consumed.

Hence, the **yield of C_x (Y_x)** is the product of the conversion and the selectivity to C_x . Conversion, selectivity and yield are all expressed as percentages.

Chapter 1

Introduction:

Natural Gas Reserves:

Natural gas, which is predominantly methane, is an abundant resource. World reserves are greater than 10^{14} m³ [1]. At current rates of consumption these reserves will last for sixty years, compared with thirty years for crude oil reserves [1].

Canada possesses significant proven natural gas reserves, estimated at 2.4×10^{12} m³ or 2.2 % of the world's total [2]. It has been estimated that Canada's remaining discoverable reserves are as high as 18.33×10^{12} m³. This represents 17.6 % of the estimated amount of natural gas remaining on the planet [2].

In spite of the abundance of this non-renewable resource, natural gas has not been used to its full potential to date. There are several reasons for this. The foremost reason is the continued availability of affordable petroleum sources such as crude oil. Secondly, the majority of the world's natural gas reserves are located in remote areas such as Siberia and the Middle East [1]. As a result, large capital investment is necessary to transport the gas from wellhead to the consumer. Natural gas is transported by pressurized pipeline at 8 MPa or by ship as liquefied natural gas (LNG) at -162°C [2]. In addition to the high transportation costs

natural gas has a low energy content per unit volume, which further deters its use. As a result , "in many places in the world, abundant natural gas is now being flared because it is too costly to transport to the site of conversion or utilization as a fuel. This is a profligate waste by any standard" [3].

There are increasing environmental restrictions on the flaring of natural gas, which produces carbon dioxide, a known "green-house" gas.

Present Uses of Natural Gas:

Presently combustion of natural gas as a fuel for domestic and industrial use accounts for 93 % of the world's annual consumption. The remaining 7 % is used by the chemical industry; most of this methane is used as a source of hydrogen for ammonia synthesis or for the production of methanol, higher alcohols, and hydrocarbons [1].

There now exist considerable incentives to develop technologies for converting natural gas, or methane, into more easily transportable chemicals such as methanol or liquid hydrocarbons [1]. The projected depletion of the world's crude oil reserves has also provided incentive to develop alternate sources of petrochemical building blocks such as ethylene, higher olefins, and aromatic hydrocarbons. Technologies for the direct conversion of methane to these products are currently being developed. "Methane's eventual competitiveness with petroleum refining on a large scale seems to depend on development of direct methane

conversion by catalytic means. In addition, there is an incentive to develop a direct methane conversion process for production of ethylene and higher olefins to meet a rising demand for these raw materials" [3].

Interestingly, some authors feel that existing methane conversion technologies, such as ethylene production by oxidative coupling, have already advanced to the point where they are economically attractive compared with conventional ethylene production from crude oil [4], while others feel that "all research projects in C1 chemistry should be re-evaluated in light of economic constraints..." [5].

Reactivity of Methane:

Thermodynamics and Kinetics:

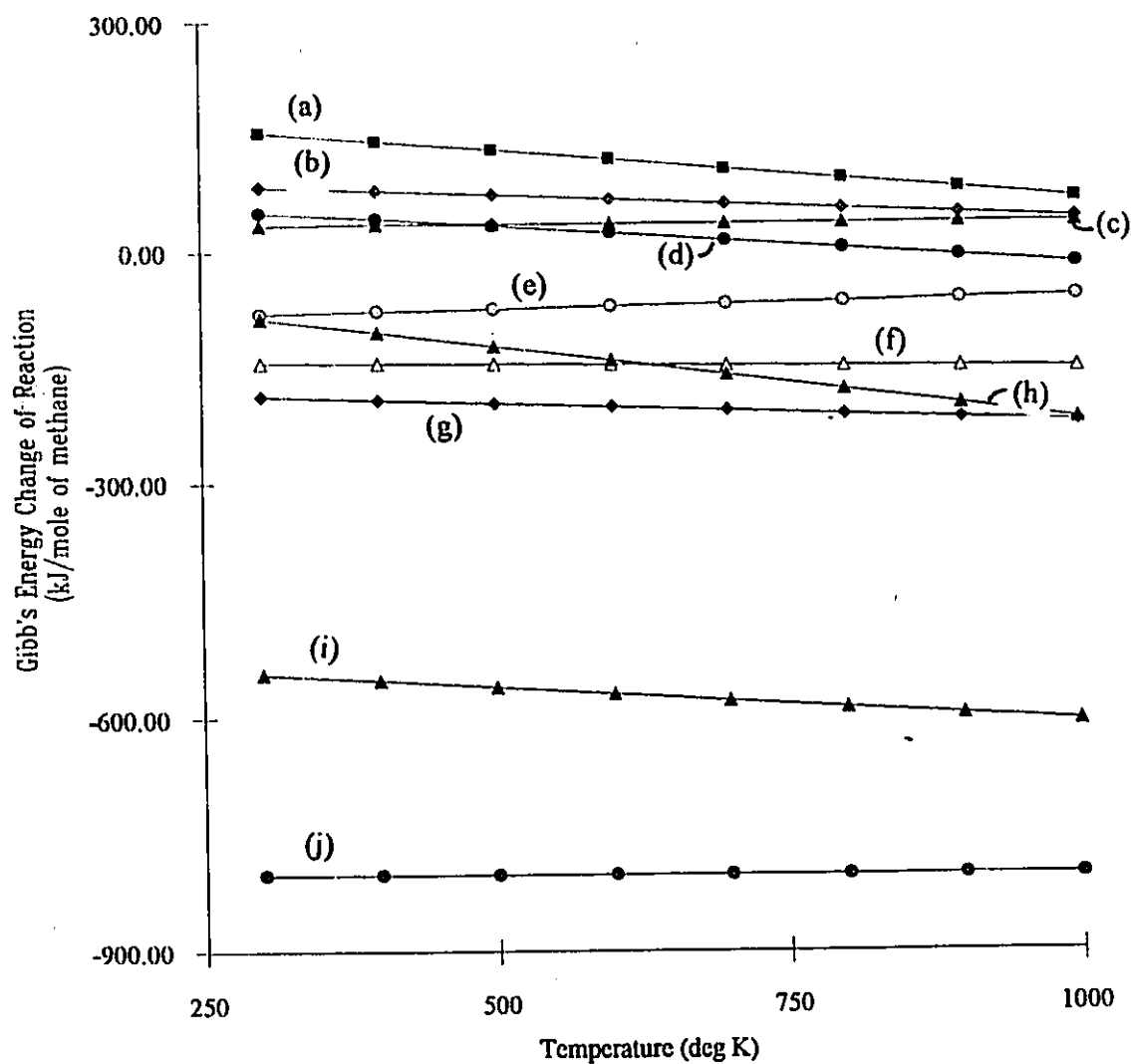
Methane is thermodynamically the most stable hydrocarbon. The stability of the methane molecule is reflected in the large, negative Gibb's energy of formation from its elements (-50.67 kJ/mol @ 300 K) and by the large dissociation energy of the $\text{CH}_3\text{-H}$ bond (435 kJ/mol). The bond dissociation energy of the C-H bond in methane is higher than that of the C-H bond in methyl or methylenic groups in higher alkanes. It is higher than the C-C bond strength present in all other hydrocarbons [5].

In addition to its stability methane demonstrates low chemical reactivity thus requiring the use of forcing conditions *ie.* extremely high temperatures in order to obtain sufficient rates of reaction. Under such conditions free-radical processes dominate and control of selectivity to desired products becomes problematic; for example, partial rather than complete chlorination or oxidation products are difficult to isolate.

Thermodynamics of Direct Methane Coupling:

As a result of the great stability of the methane molecule a price must be paid in terms of energy input in order to transform it into any higher molecular weight hydrocarbon by direct coupling. As is shown in Figure 1.1, the direct dehydrogenative coupling reactions, in which two methane molecules react to form ethane, ethylene, or acetylene (reactions a-c) all possess large positive Gibb's energies of reaction. For example, the Gibb's energy of reaction to form ethane is approximately 34 kJ/mole CH_4 over the temperature range 298 K to 1000 K; the Gibb's energy of the reactions to form ethylene or acetylene are even larger. As a result, temperatures in excess of 1500 K are used in the industrial production of acetylene from CH_4 . The data used in all thermodynamic calculations in this thesis were taken from Stull *et al.* [6].

Figure 1.1: Gibb's Energy Change for Reactions Involving Methane as a function of Temperature.



legend:

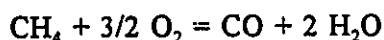
- | | | |
|--|--|--|
| (a) $2 \text{CH}_4 = \text{C}_2\text{H}_2 + 3 \text{H}_2$ | (b) $2 \text{CH}_4 = \text{C}_2\text{H}_4 + 2 \text{H}_2$ | (c) $2 \text{CH}_4 = \text{C}_2\text{H}_6 + \text{H}_2$ |
| (d) $\text{CH}_4 = \text{graphite} + 2 \text{H}_2$ | (e) $2 \text{CH}_4 + 1/2 \text{O}_2 = \text{C}_2\text{H}_6 + \text{H}_2\text{O}$ | (f) $2 \text{CH}_4 + \text{O}_2 = \text{C}_2\text{H}_4 + 2 \text{H}_2\text{O}$ |
| (g) $2 \text{CH}_4 + 3/2 \text{O}_2 = \text{C}_2\text{H}_2 + 3 \text{H}_2\text{O}$ | (h) $\text{CH}_4 + 1/2 \text{O}_2 = \text{CO} + 2 \text{H}_2$ | (i) $\text{CH}_4 + 3/2 \text{O}_2 = \text{CO} + 2 \text{H}_2\text{O}$ |
| (j) $\text{CH}_4 + 2 \text{O}_2 = \text{CO}_2 + 2 \text{H}_2\text{O}$ | | |

Figure 1.1 also shows that methane becomes unstable with respect to its elements, graphite and hydrogen, at approximately 800 K (reaction d). As a result, significant amounts of methane are lost due to pyrolysis during attempts to form C₂ hydrocarbons at temperatures beyond this point.

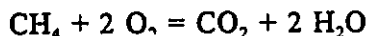
A dramatic decrease in the Gibbs energy of reaction is obtained if an oxidizing agent, such as molecular oxygen, is reacted with methane to form ethane and water *ie.*

$2 \text{CH}_4 + 1/2 \text{O}_2 = \text{C}_2\text{H}_6 + \text{H}_2\text{O}$ (see Figure 1.1, reaction e). The Gibbs energy change for this reaction is -80 kJ/mole CH₄ at 298 K. This reaction, commonly known as oxidative coupling of methane, has been the subject of considerable research over the past decade as will be discussed later.

Although addition of oxygen makes the formation of ethane thermodynamically easier, the complete oxidation of methane to carbon monoxide or to carbon dioxide is even more facile. The Gibbs energy change for the combustion reaction (reaction i):



is -544 kJ/mole CH₄ at 298 K and for the reaction (reaction j):



is -801 kJ/mole CH₄ at 298 K. Therefore the tendency towards complete oxidation is very large; selectivity to partially oxidized products, such as ethane or ethylene (reactions e and f), remains the most challenging problem facing this approach.

Methane Conversion Strategies:

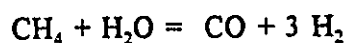
Established Technologies:

The conversion of natural gas, predominantly methane, to higher molecular weight hydrocarbons for use as petrochemical feedstocks or as combustible fuels has long been of interest. The continued depletion of the world's oil supplies and societies' continued reliance on petroleum products has only served to increase the need for such technologies.

Most methane conversion technologies that have been developed to date rely on multistep processes and few are economically feasible, except under special circumstances such as readily available methane or where dictated by geopolitical conditions. Many require that methane first undergo a process of steam-reforming to "synthesis gas", a mixture of carbon monoxide and hydrogen, before further processing is possible.

Steam Reforming of Methane:

Steam reforming of methane to form synthesis gas has been carried on an industrial scale since the 1930's and therefore is very much an established technology. This process is however, both energy and capital intensive. The process can be generally represented by the equation:

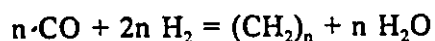


and is generally carried out over a supported nickel catalyst at temperatures near 700°C [7-9]. Once produced, the synthesis gas may be converted into gasoline-range hydrocarbons via the Fischer-Tropsch (FT) process or into methanol, as an end product, or the methanol may be further reacted to gasoline-range hydrocarbons via Mobil's H-ZSM5 zeolite-catalyzed methanol-to-gasoline (MTG) process.

The Fischer-Tropsch Process:

The Fischer-Tropsch Process was developed by the Axis Powers during World War II as a means of supplying their war machine with much needed gasoline in light of embargos that existed at that time. Since this process relies on synthesis gas as a starting material it is only economically feasible today in countries where petroleum supplies are scarce but coal or natural gas is abundant. The only large scale plants currently operating are in South Africa.

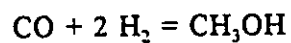
The FT process may be represented by the general equation:



The primary products of this process are linear terminal olefins, but these may undergo further reaction before leaving the catalyst bed. The FT process is an established technology and a great deal of research has been conducted; an excellent review of this process has been written by Dry [10].

Methanol Synthesis:

Methanol synthesis from synthesis gas may be represented by the general equation:



Modern low pressure methanol synthesis technology uses a gaseous mixture of H_2 , CO , and CO_2 over a catalyst containing Cu , ZnO , and Al_2O_3 . Typical reaction conditions are 250°C and 5.0 - 7.1 MPa [7,11].

Mobil's MTG Process:

Mobil Oil has recently industrialized a process whereby methanol is converted to gasoline range hydrocarbons. The MTG process uses an H-ZSM5 zeolite catalyst. Typical MTG operating conditions use a fixed-bed reactor at 385°C and 2.17 MPa. The product consists of approximately 80 wt.% C_5+ hydrocarbons [12,13]. Currently plants are operating in New Zealand and Malaysia.

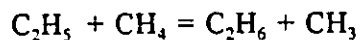
More Recent Methane Conversion Strategies:

Current Research in Homogeneous CH₄ Conversion:

Although the bulk of research into methane conversion strategies is based on the development of heterogeneous catalytic systems and this thesis focusses on strategies of this nature, mention must be made of current research involving homogeneous systems, particularly gaseous systems. Back *et al.* have previously studied the gas phase kinetics of the pyrolysis of CH₄ [14, 15], and C₂H₄ [16] in static reaction vessels at lower temperatures, between 500°C and 800°C. In addition, these authors have studied the rate constants for abstraction of hydrogen from ethylene by methyl and ethyl radicals over the temperature range 350°C to 500°C [17]. Based on these and other data a process for the homogeneous gas phase conversion of methane to higher hydrocarbons was investigated using ethylene as a "sensitizer" [18, 19] at temperatures ranging from 500°C to 575°C and from 650°C to 750°C, respectively. The rationale for this process is as follows:

A "sensitizer" is a substance that induces the decomposition of methane into methyl radicals at lower temperatures, where losses due to carbon formation are lower. In addition, the sensitizer must also induce a chain reaction for the formation of products. Ethylene fulfills the above requirements because ethyl radicals, which are formed during pyrolysis of

ethylene at 500°C [16], are known to react with methane to produce ethane through the reaction:



As a result of the introduction of the above reaction the rate of formation of ethane within the system would be increased. An increase in the rate of formation of ethane was indeed observed [18, 19]. As was pointed out in these studies, homogeneous systems have the advantage that although the rate of conversion of CH_4 is lower than in heterogeneous catalytic reactions the reaction products are all hydrocarbons and no methane is lost to CO_x formation [19].

Heterogeneous CH_4 Conversion:

Technologies for methane conversion to higher hydrocarbons via heterogeneous catalysis incorporate different strategies [7]:

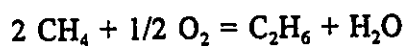
(1) **methane derivatization** in which methane is first converted to an intermediate, as in the FT and the MTG processes mentioned above. Other processes may involve such intermediates as methyl chloride or carbon disulfide [7 and references therein];

(2) direct self-coupling (high-temperature and low temperature)

As discussed previously thermodynamic restrictions require direct dehydrogenative coupling of methane to acetylene, ethylene, or ethane to be carried out at high temperatures, about 1200°C. At these temperatures reactions tend to be homogeneous, free-radical processes. The industrial production of acetylene from CH₄ by homogeneous pyrolysis has been mentioned previously.

Oxidative Coupling of Methane:

Methane can be coupled at lower temperatures (700°C to 900°C) if an oxidant such as oxygen is used. The selective, partial oxidation of methane to C₂ hydrocarbons has been actively researched and several comprehensive reviews exist [2,20-23]. This oxidative condensation, more commonly known as "oxidative methane coupling", involves flowing methane-rich mixtures of methane and oxygen over a catalyst at temperatures ranging from 700°C to 900°C. Alternatively, a batch process may be used in which methane is fed over a reducible oxide "catalyst" forming C₂ hydrocarbons. The reaction can be generally represented by the following equation:



A large number of compounds have been tested as catalysts for oxidative coupling. They include compounds of: the alkali and alkaline earth metals; the lanthanide and actinide metals; the transition metals; and the post-transition metals [21].

The reaction mechanism for oxidative coupling is now fairly generally accepted. Firstly, methyl radicals, $\text{CH}_3\cdot$, are formed by hydrogen abstraction from CH_4 on the catalyst's surface. These radicals then desorb and dimerize in the gas phase producing C_2H_6 .

In addition to dimerization, $\text{CH}_3\cdot$ radicals can undergo a series of chain reactions in the gas phase to form CO_x . Complete oxidation of methane to carbon oxides, CO_x , always occurs simultaneously and selectivity has been the major difficulty facing this technology to date.

Ethylene can also be formed as a secondary product by reaction of ethane either homogeneously or heterogeneously. Of course, unlike CO_x , ethylene is a desirable byproduct.

A large variety of different oxide catalysts have been used and selectivities to ethane and ethylene of about 60 % at 35 % methane conversion have been achieved [1].

Oxidative processes, such as oxidative coupling, which use oxygen or reducible metal oxides all suffer from the loss of methane to CO_x . By contrast if processes are

developed which take place in the absence of oxygen or other reducible species loss of CH₄ due to CO_x formation can be eliminated.

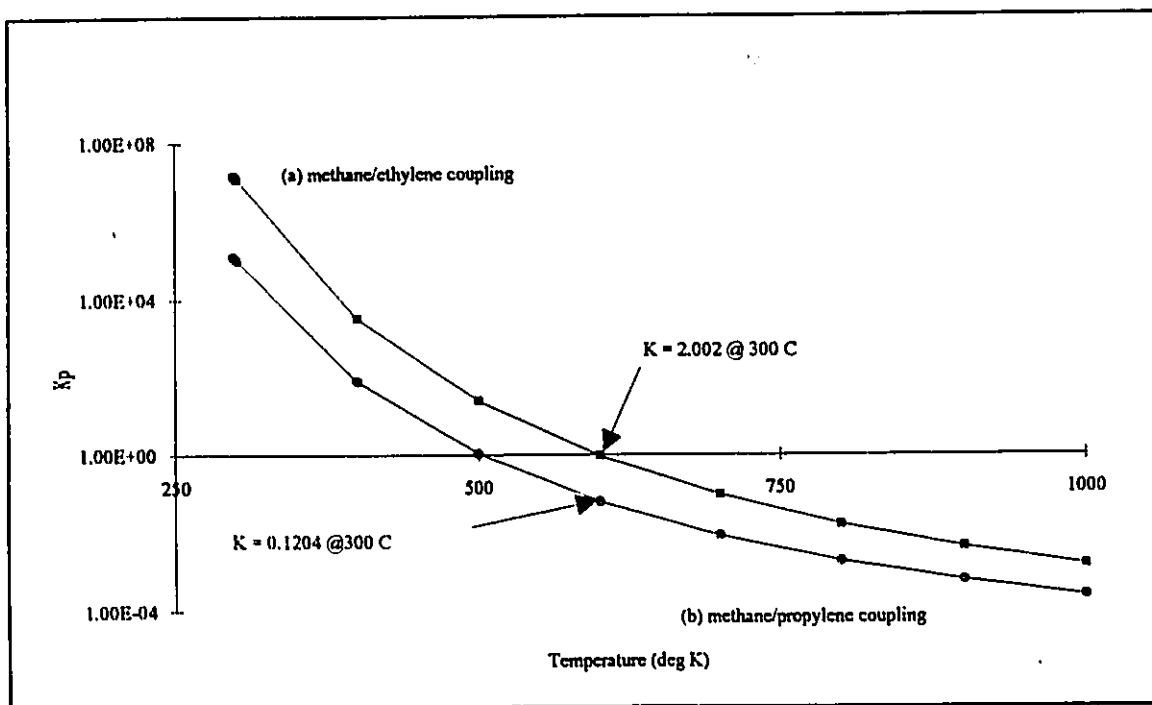
Methane Coupling with Unsaturated Compounds:

An alternate route to higher molecular weight hydrocarbons is the direct coupling of methane with unsaturated hydrocarbons. For example, methane could be reacted with olefins such as ethylene or propylene to produce propane or butane, respectively. These coupling reactions:



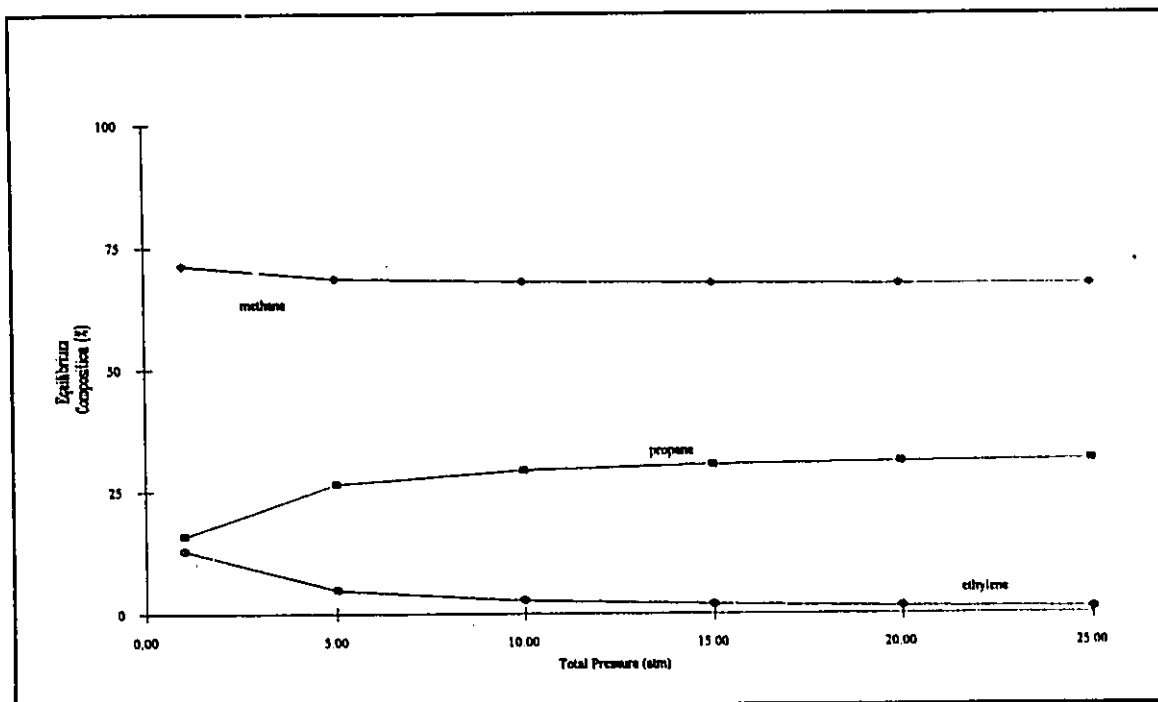
are thermodynamically more favourable at lower temperatures. In Figure 1.2 the equilibrium constant, K_p , for each of the above reactions is plotted as a function of temperature. From the Figure, the upper temperature limit for methane/ethylene or propylene coupling is approximately 300°C. At temperatures above this point the equilibrium amount of propane or butane formed will be quite small. It should also be noted that the equilibrium constant for methane/ethylene coupling is two orders of magnitude larger than that for methane/propylene coupling over the temperature range shown.

Figure 1.2: The equilibrium constant versus temperature for the methane/olefin coupling reactions: (a) $\text{CH}_4 + \text{C}_2\text{H}_4 = \text{C}_3\text{H}_8$ and (b) $\text{CH}_4 + \text{C}_3\text{H}_6 = \text{n-C}_4\text{H}_{10}$



The coupling reaction is also thermodynamically favoured by increased pressure. For example, Figure 1.3 shows the equilibrium composition as a function of initial pressure for a mixture of methane and ethylene (initial mole ratio= 2:1) at 300°C.

Figure 1.3: Equilibrium composition as a function of total pressure for a mixture of methane and ethylene (initial mole ratio 2:1) at 300°C.



As is shown above the equilibrium amount of propane increases from 16 % to 31% as the initial total pressure is increased from 0.1 to 2.5 MPa (1 to 25 atmospheres). The percent conversion of ethylene increases from 55.2 % to 96.3 % over this pressure region.

Previous Research Involving CH₄ Coupling with Unsaturated Compounds:

To date, research into the coupling of methane with unsaturated compounds has been carried out using two distinctly different types of catalysts: oxide-supported transition metals; and "superacid" catalysts. Published literature involving the latter type is by far more extensive.

Coupling via Supported Transition Metal Catalysts:

Very little has been published on the coupling of methane with unsaturated hydrocarbons using supported transition metal catalysts. In a short communication Loffler *et al.* [24] reported that methane-activated supported nickel catalysts could be used to produce modest but definite amounts of higher hydrocarbons when methane was reacted at 300°C with benzene, cyclopentene, methylene-cyclopentane, and simple alkenes such as ethylene, propylene and butenes. The paper gave no details concerning the conditions for methane preactivation. The formation of higher hydrocarbons was postulated to be due to reaction of carbonaceous fragments, formed during CH₄ preactivation, with the unsaturated compounds, possibly by a carbene-like addition to the double bond.

More recently, Ovalles *et al.* [25] have published a surface characterization study of the coupling of propylene with methane over alumina- and silica-supported nickel catalysts to form C₄ hydrocarbons. The catalysts were preactivated with CH₄ or reduced in hydrogen prior

to reaction. The production of C_4 hydrocarbons under some conditions was attributed to methane coupling with propylene. A mechanism was proposed, in agreement with Loffler *et al.*, that methane reacts with metal to generate CH_x species ($x = 0, 1, 2, \text{ or } 3$), which in turn react with propylene to produce C_4 's. Methane present in the feed regenerates the CH_x species, thus completing the cycle.

The study by Ovalles *et al.* reported results using methane preactivation at 600°C only. In addition, the effects of reaction conditions such as: space velocity; reaction temperature; *etc.* were reported in an internal communication [26].

In Chapter 2 of this thesis the results of a detailed study of the reaction of CH_4 and C_3H_6 over Ni/SiO_2 to form higher molecular weight hydrocarbons are presented. Several reaction conditions were systematically varied and the resultant product distributions are examined in order to understand the processes involved.

Coupling of Methane and Unsaturated Compounds using Superacid Catalysts:

The production of higher molecular weight compounds by electrophilic alkylation of methane by olefins has been demonstrated in solutions containing superacids such as HSO_3F-SbF_5 [27] and references therein. The first report of heterogeneous catalysis of this reaction in a pressurized flow system using solid superacids such as: SbF_5 intercalated into graphite; TaF_5 on AlF_3 ; and TaF_5 (all activated by HF) was reported by Olah *et al.* [28]

in 1983. Other solid superacids such as sulphate-promoted ZrO_2 [29] and TaF_5 supported on Y-zeolite [30] have also been used.

Superacids and their use as catalysts will be discussed in greater detail later in this thesis. For the moment, it is only necessary to point out that these acids are strong enough to protonate even extremely weak bases such as olefins. The resultant penta-coordinate carbonium ion intermediates are extremely reactive and are capable of electrophilic attack on the carbon-hydrogen bond of methane, thus resulting in alkylation. Unfortunately, the extreme reactivity of the carbonium ion intermediates formed also enables side-reactions such as oligomerization to occur. These oligomers can cause rapid deactivation of the catalyst. In an effort to minimize these side-reactions, CH_4 /olefin reaction mixtures possessing large excesses of CH_4 are employed [31].

As mentioned above, the coupling of methane and ethylene mixtures has been reported to occur over sulphated-zirconia catalysts at 300°C [29,31]. Thermal pretreatment of these catalysts (approximately 3 wt.% sulphate) at around 500°C was found to be necessary for activity at 300°C ; thermal activation was regarded as generating superacidity in these catalysts. Mixtures of CH_4 and C_2H_4 (with mole ratios between 2:1 and 3:1) were passed through the reactor at 1.93 MPa and a gaseous hourly space velocity (GHSV) of 960 hr^{-1} (m^3 reactant at 0°C and 0.1 MPa per m^3 catalyst bed per hour). The catalyst behaviour was found to vary greatly with increasing time on stream. After one hour the conversion of ethylene was high (80-90 %) and C_6 and C_7 hydrocarbons dominated. However, as the time

on stream increased the products became lighter (propane, C_4 's and C_5 's dominated). Also deactivation of the catalyst occurred. After 23 hours on stream the total conversion of methane and propylene was only 3 %. Ethylene oligimerization was found always to be a competing process, but experiments performed with and without CH_4 revealed that methane did have a marked effect on the product spectrum obtained.

Catalyst deactivation during methane-olefin coupling over solid super acid catalysts has been attributed to coking as a result of olefin oligomerization reactions, which are significant even if a hundred-fold excess of methane is used [27, 29, 31]. Recently, attempts have been made to suppress the formation of high molecular weight compounds by supporting superacids such as TaF_5 on Y-zeolite, using the zeolite's cage structure to limit the size of the compounds formed [30]; however, these catalysts were also found to rapidly deactivate due to coking.

As discussed above, attempts have been made to exploit the superacidic nature of sulphated ZrO_2 in order to catalyze methane/ethylene coupling. Sulphate-promoted ZrO_2/SiO_2 has also been found to possess superacid properties. It is known to catalyze ring-opening of cyclopropane, under recirculation, at $100^\circ C$ [32]. Sulphated ZrO_2/SiO_2 has also been shown to catalyze the dehydration of 2-propanol at $180^\circ C$ and the dealkylation of cumene at $400^\circ C$ [33]. The ability to catalyze reactions such as those mentioned above under such mild conditions is evidence of superacidity [34].

We have considered the possibility that the dispersion of zirconia on an inert support such as silica, at lower loadings of zirconia, approximately 10 wt.% , prior to sulphation might lower its catalytic activity for olefin oligomerization reactions, as compared to sulphated-zirconia. If so, such materials might act as catalysts for CH₄-olefin coupling, but alleviate deactivation due to coking. In Chapter 5, the results of reactions of: methane; ethylene; methane/ethylene and methane/propylene mixtures over sulphate-promoted ZrO₂/SiO₂ catalysts are reported.

In addition to its utility as a catalyst, the nature of the surface properties of sulphate-promoted ZrO₂/SiO₂ are of interest in their own right; indeed, the two subjects are intimately related. However, prior to an understanding of the sulphate-promoted material, one must first understand the nature of the ZrO₂/SiO₂ itself. We have therefore studied the properties of both the sulphated and non-sulphated materials using such techniques as: transmission Fourier Transform Infrared Spectroscopy (FTIR); Temperature-Programmed Desorption (TPD); and X-ray Diffraction (XRD).

Although ZrO₂/SiO₂ does not possess "superacidity", it, as well as a host of other binary oxide mixtures, is known to possess surface acidity which is greater than that of either zirconia or silica alone. This enhanced acidity is of major use in preparing solid acid catalysts for industrial purposes. As a result, considerable research has been undertaken in this area and several theories have been postulated to account for this phenomenon [35,36]. However, although most theories apply to binary systems in which intimate chemical mixing

has taken place (for example, systems prepared by coprecipitation) some binary mixtures which have been prepared by impregnation (where intimate mixing is not certain) also possess enhanced acidity. In Chapter 3 we present the results of characterization of $\text{ZrO}_2/\text{SiO}_2$ catalysts prepared by impregnation of silica. The results obtained are discussed in the context of existing theories, where applicable.

The results of surface characterization studies of sulphate-promoted $\text{ZrO}_2/\text{SiO}_2$ are discussed in Chapter 4.

Chapter 2:

Methane-Propylene Coupling over Ni/SiO₂

and CH₄-Activated Ni/SiO₂

As was briefly discussed in the introduction, very little has been published on the coupling of methane with unsaturated hydrocarbons using supported transition metal catalysts. Löffler *et al.* [24] reported that methane-activated supported nickel catalysts could be used to produce modest but definite amounts of higher hydrocarbons when methane was reacted at 300°C with benzene, cyclopentene, methylene-cyclopentane, and simple alkenes such as ethylene, propylene and butenes. The paper gave no details concerning the conditions for methane preactivation. The reaction of propylene was studied most extensively. When a 6 % mixture of C₃H₆ in CH₄ was passed over a CH₄-preactivated 7.5 % Ni/SiO₂ catalyst at 330°C and 1 MPa the following products were obtained: 53 % C₁ and C₂'s; 26 % C₃H₈; 8.5 % C₄H₁₀; and 13 % C₅'s and C₆'s. When methane in the feed gas was replaced by nitrogen the resultant products were: 40.5 % C₁ and C₂'s; 42 % C₃H₈; 8 % C₄H₁₀; and 9.5 % C₅'s and C₆'s. The formation of butenes was not mentioned. The formation of higher hydrocarbons was postulated to be due to reaction of carbonaceous fragments, formed during CH₄ preactivation, with the unsaturated compounds, possibly by a carbene-like addition to the double bond.

Recently, Ovalles *et al.* [25] have published a surface characterization study of the coupling of propylene with methane over alumina- and silica-supported nickel catalysts to form C₄ hydrocarbons. The catalysts were preactivated with CH₄ or reduced in hydrogen prior to reaction. They reported that Ni/SiO₂ was more active for the coupling reaction at 350°C than Ni/Al₂O₃. This was attributed to higher metal dispersion of nickel on silica, as measured by x-ray photoelectron spectroscopy (XPS). The lower dispersion on alumina was attributed to the formation of NiAl₂O₄. XPS studies showed that high concentrations of carbonaceous species were present on the surface of the silica catalysts and it was suggested that these species were intermediates in the coupling reaction. A mechanism was proposed, in agreement with Löffler *et al.*, that methane reacts with metal to generate CH_x species (x = 0,1,2, or 3), which in turn react with propylene to produce butanes. Methane present in the feed regenerates the CH_x species, thus completing the cycle.

The study by Ovalles *et al.* reported results using methane preactivation at 600°C only. In addition, the effects of reaction conditions (space velocity, reaction temperature, etc.) were reported in an internal communication [26].

We present the results of a detailed study of the reaction of CH₄ and C₃H₆ over Ni/SiO₂ to form higher molecular weight hydrocarbons. We have systematically varied several reaction conditions and examined the resultant product distributions in order to understand the processes involved.

The following reaction conditions were investigated:

(a) Methane preactivation of NiO/SiO₂ : The role of CH₄ preactivation was studied by varying parameters such as: temperature of preactivation and the flow rate of CH₄ during preactivation. These results are compared with those obtained over Ni/SiO₂ previously reduced by hydrogen;

(b) Reaction temperature;

(c) Contact time of reactants with catalyst;

(d) Composition of Feed Gas: C₃H₆/CH₄ and C₃H₆/He mixtures were used over both CH₄-preactivated and H₂-reduced Ni/SiO₂ catalysts.

Reactions of Olefins:

With regards to both (a) and (d) above, in order to establish the role of CH_4 -preactivation and/or in the feed gas, we must also consider the reactions that C_3H_6 itself might conceivably undergo.

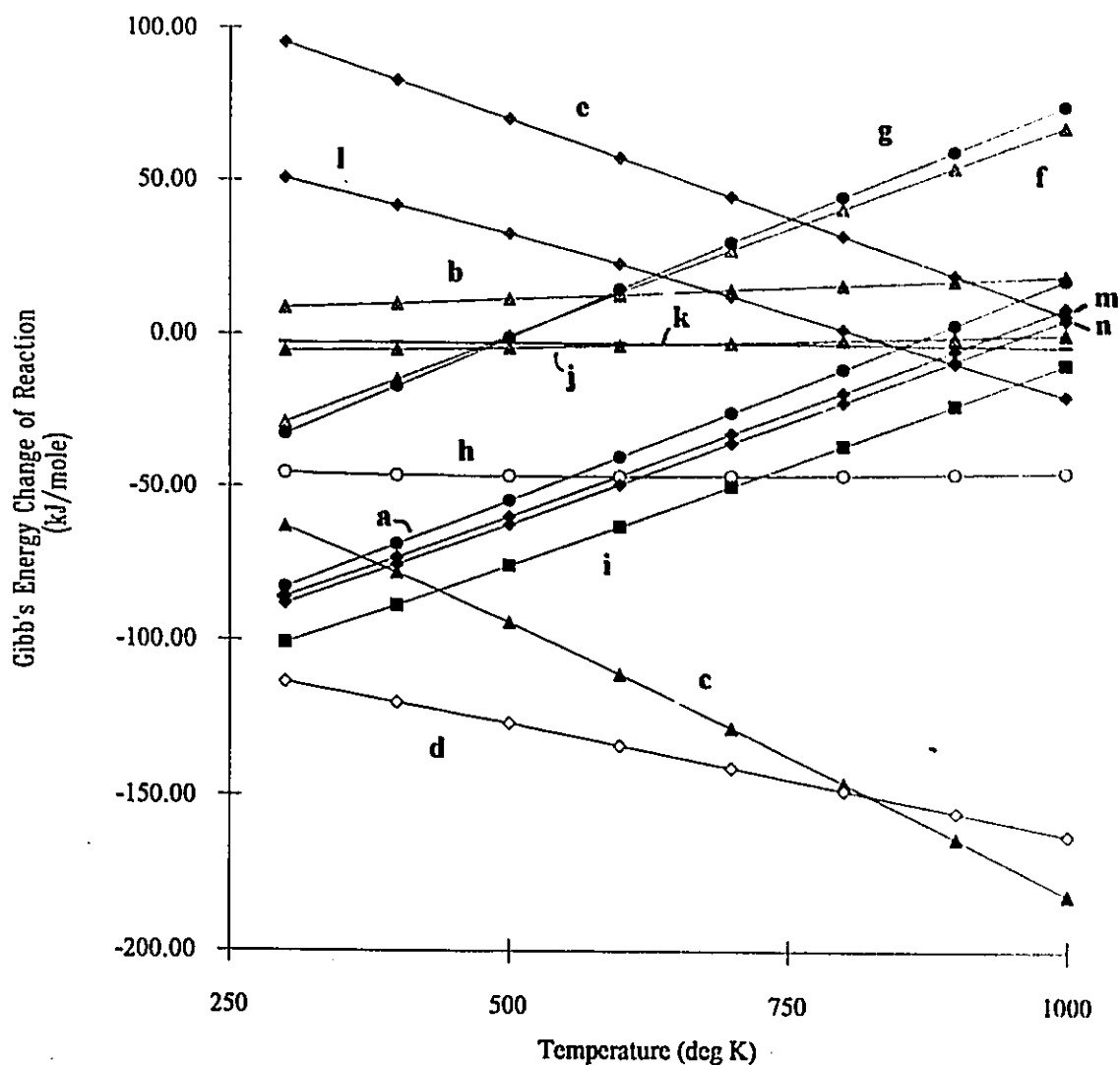
Thermodynamics of Various Reactions Involving C_3H_6

The change in Gibb's energy for several pertinent hydrocarbon reactions, most involving C_3H_6 , are shown in Figure 2.1 as a function of temperature. The reactions are listed below:

	Reaction	Description
a	$\text{C}_3\text{H}_6 + \text{H}_2 = \text{C}_3\text{H}_8$	propylene hydrogenation
b	$2 \text{C}_3\text{H}_6 = \text{C}_2\text{H}_4 + \text{cis-2-C}_4\text{H}_8$	propylene metathesis
c	$\text{C}_3\text{H}_6 = 3 \text{C} + 3 \text{H}_2$	propylene decomposition
d	$\text{C}_3\text{H}_6 = \text{CH}_4 + 2 \text{C} + \text{H}_2$	" "
e	$\text{C}_3\text{H}_6 = \text{CH}_4 + \text{C}_2\text{H}_2$	" "
f	$\text{C}_3\text{H}_6 + \text{CH}_4 = \text{n-C}_4\text{H}_{10}$	methane coupling
g	$\text{C}_3\text{H}_6 + \text{CH}_4 = \text{iso-C}_4\text{H}_{10}$	"
h	$\text{C}_3\text{H}_6 + \text{H}_2 = \text{C}_2\text{H}_4 + \text{CH}_4$	propylene hydrogenolysis
i	$\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_6$	ethylene hydrogenation

	Reaction	Description
j	$\text{cis-2-C}_4\text{H}_8 = \text{trans-2-C}_4\text{H}_8$	cis-trans isomerization
k	$1\text{-C}_4\text{H}_8 = \text{cis-2-C}_4\text{H}_8$	double bond migration
l	$\text{CH}_4 = \text{C} + 2 \text{H}_2$	methane decomposition
m	$4 \text{C}_3\text{H}_6 + \text{H}_2 = 1\text{-C}_4\text{H}_8 + 1\text{-C}_5\text{H}_{10} + \text{C}_2\text{H}_4 + \text{CH}_4$	propylene homologation
n	$1\text{-C}_4\text{H}_8 + \text{H}_2 = \text{n-C}_4\text{H}_{10}$	butene hydrogenation

Figure 2.1: Gibb's Energy of Reaction versus Temperature for a Variety of Reactions.



legend

- | | | |
|---|--------------------------------------|---------------------------------|
| a $C_3H_6 + H_2 = C_3H_8$ | b $2 C_3H_6 = C_2H_4 + cis-2-C_4H_8$ | c $C_3H_6 = 3 C + 3 H_2$ |
| d $C_3H_6 = CH_4 + 2 C + H_2$ | e $C_3H_6 = CH_4 + C_2H_2$ | f $C_3H_6 + CH_4 = n-C_4H_{10}$ |
| g $C_3H_6 + CH_4 = iso-C_4H_{10}$ | h $C_3H_6 + H_2 = C_2H_4 + CH_4$ | i $C_2H_4 + H_2 = C_3H_6$ |
| j $cis-2-C_4H_8 = trans-2-C_4H_8$ | k $1-C_4H_8 = cis-2-C_4H_8$ | l $CH_4 = C + 2 H_2$ |
| m $4 C_3H_6 + H_2 = 1-C_4H_8 + 1-C_3H_{10} + C_2H_4 + CH_4$ | n $1-C_4H_8 + H_2 = n-C_4H_{10}$ | |

From Figure 2.1, we note the following trends:

- (1) C_3H_6 hydrogenation to C_3H_8 , reaction (a), is favourable to 1000 K; the Gibb's energy of reaction becomes more positive with increasing temperature;
- (2) C_3H_6 hydrogenolysis to CH_4 and C_2H_4 , reaction (h), is favourable, and fairly temperature independent over the range;
- (3) C_3H_6 metathesis to C_2H_4 and cis-2- C_4H_8 , reaction (b), represents a small, positive Gibb's energy change thus the equilibrium pressures of C_2H_4 and cis-butene will be low;
- (4) decomposition of C_3H_6 to CH_4 and carbon and hydrogen and to carbon and hydrogen, reactions (c) and (d), is favourable over the entire range and increases with temperature;
- (5) decomposition of C_3H_6 to CH_4 and C_2H_2 , reaction (e), is unfavourable due to the large Gibb's energy of formation of acetylene;
- (6) as mentioned previously, C_3H_6 - CH_4 coupling, reaction (f) or (g), has a negative Gibb's energy change up to about 500 K;
- (7) CH_4 decomposes to its elements, reaction (l), above approximately 800 K.

In summary, the formation of C_4 's from propylene is thermodynamically possible via reactions such as methane coupling and metathesis at some or all of the temperatures between 250 and 1000 K. The product C_4 's may undergo reactions such as: hydrogenation; cis-trans isomerization; and double bond migration. In addition, propylene can be consumed by: hydrogenation; hydrogenolysis and decomposition. Products such as ethylene can undergo further reactions to ethane.

In the previous section we have discussed the thermodynamics of a variety of reactions of propylene and their implications, with the exception of homologation which is discussed below, in greater detail.

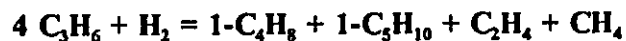
Homologation:

Perhaps the most important reaction in terms of this study is "homologation". Homologation of olefins, a metathesis-related reaction, can be defined by the following equation [37]:



Thus olefins react to form higher (up to approximately $n+2$) olefins and lower olefins and methane. This reaction is known to occur on supported Group VIII metals, especially Fe, Ru, and Os [37-44].

Propylene may homologate to form olefins ranging from ethylene to approximately pentene, in addition to methane. The Gibbs energy of the reaction:



is shown in Figure 2.1 (reaction m); it is negative to approximately 900 K.

Homologation of alkanes has also been observed but it is thought to proceed through an olefin intermediate [45].

The homologation reaction is accompanied by hydrogenation and isomerization of the starting and formed olefins [37]. Studies have revealed that the carbon skeleton is maintained after homologation. This result indicates that the C_{n+1} olefin is formed by addition of a C_1 fragment to the C_n skeleton and not by a kind of random association of C_1 fragments [37,39].

The term "homologation" has been used in a variety of ways in the literature, which may lead to confusion. For example, Ovalles *et al.* [25] suggest that reactions such as: $CH_4 + C_2H_4 \rightarrow C_3H_8$ are "commonly known as homologation reactions mainly because the final product has one more carbon atom than the starting olefin". They use the term "self-homologation" to describe the formation of higher molecular weight compounds that appear to form by reaction of the olefins themselves. In this work, "homologation" will refer to the class of olefin reaction as defined above, and in reference [37]. The term "coupling" will be used to imply involvement of CH_4 , either from CH_4 -preactivation or from the feed gas, with the olefin to form higher hydrocarbons. From the above it is obvious that a plethora of reactions are possible involving C_3H_6 over Ni/SiO_2 and therefore careful study is required to determine if higher molecular weight hydrocarbons, such as butanes and butenes are formed by the reaction of propylene with methane from the feed gas or from previous CH_4 preactivation, ie. methane-propylene coupling, or simply by reactions of propylene itself.

Experimental:

Materials:

Methane (Ultra-high purity, 99.97 % min.) and propylene (CP Grade, 99.0 % min.) were obtained from Matheson Gases Ltd. Hydrogen (Ultra-high purity, 99.995 %) and helium (Ultra-pure carrier grade, < 1 ppm O₂ and H₂O) were obtained from Air Products Ltd. Helium was further deoxygenated by passing it through a Model OT-1 oxygen trap supplied by Chromatographic Specialties Ltd.

Fumed silica (Sigma) was used as a catalyst support. This material was not calcined prior to use. Its stated BET surface area was 400 m²/g. The stated particle size was 0.007 μm.

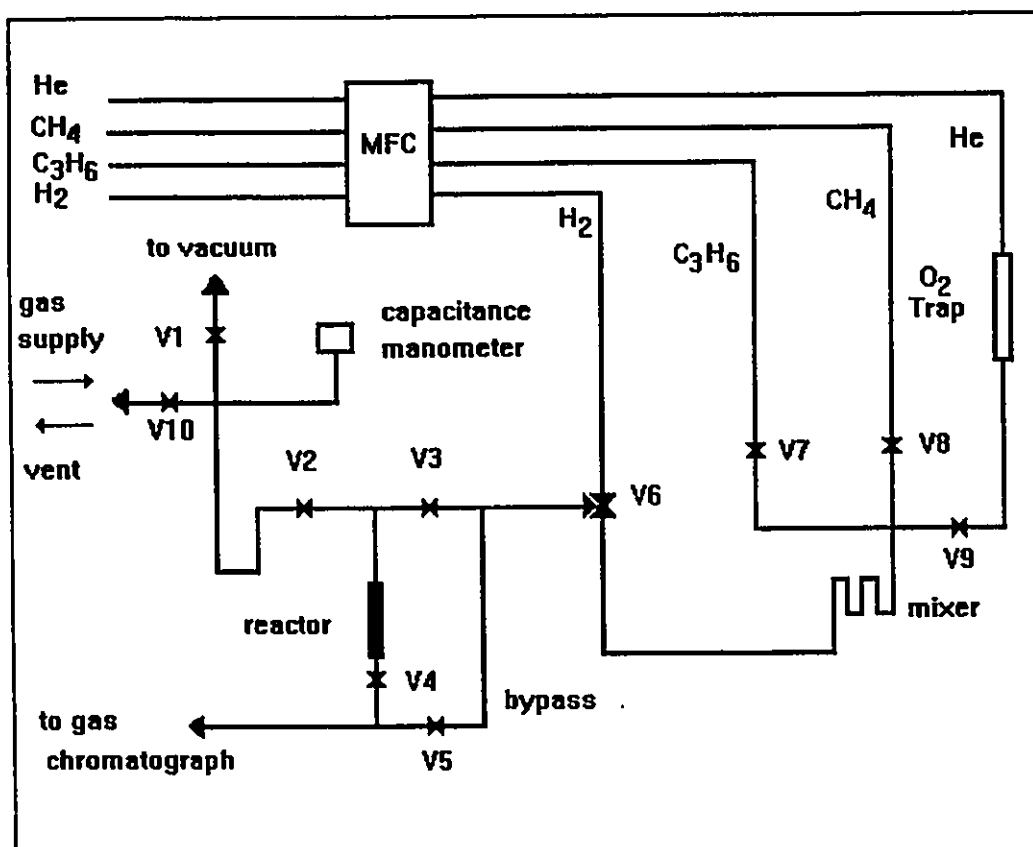
A nominally 9.6 wt.% Ni/SiO₂ catalyst was prepared by impregnation in the following manner. Ni(NO₃)₆H₂O (5.0 g) was dissolved in deionized water (344 mL). Silica (9.5 g) was added to the stirring solution and the slurry was evaporated to dryness. The catalyst was oven-dried at 100°C for two hours. The resultant material was crushed into granules of between 16 and 32 mesh. A fresh sample of catalyst was used for each experiment.

The percentage of Ni exposed (the dispersion factor) of the hydrogen-reduced Ni/SiO₂ catalyst was determined to be 9.2 % by H₂ chemisorption at room temperature [46].

Apparatus:

Experiments were conducted using a single-pass flow system with a fixed-bed microreactor (see Figure 2.2). The system consisted of three segments: a gas delivery segment; a reactor/bypass segment; and a vacuum manifold.

Figure 2.2: Schematic Diagram of Fixed Bed, Single-Pass Flow System.



The gas delivery segment was constructed from 1/4" OD. copper tubing and brass Swagelok fittings. Brass Nupro B-4HK packless bellows sealed valves were used (V7,V8,and V9). Gases were delivered from their cylinders via two-stage regulators. Gas flow rates were controlled using a Matheson Model 8249 multiple mass flow controller (MFC). All experiments were performed at atmospheric pressure.

A three-way valve (V6) allowed the selection of hydrogen for reduction purposes or mixtures of propylene, methane, and helium for reaction.

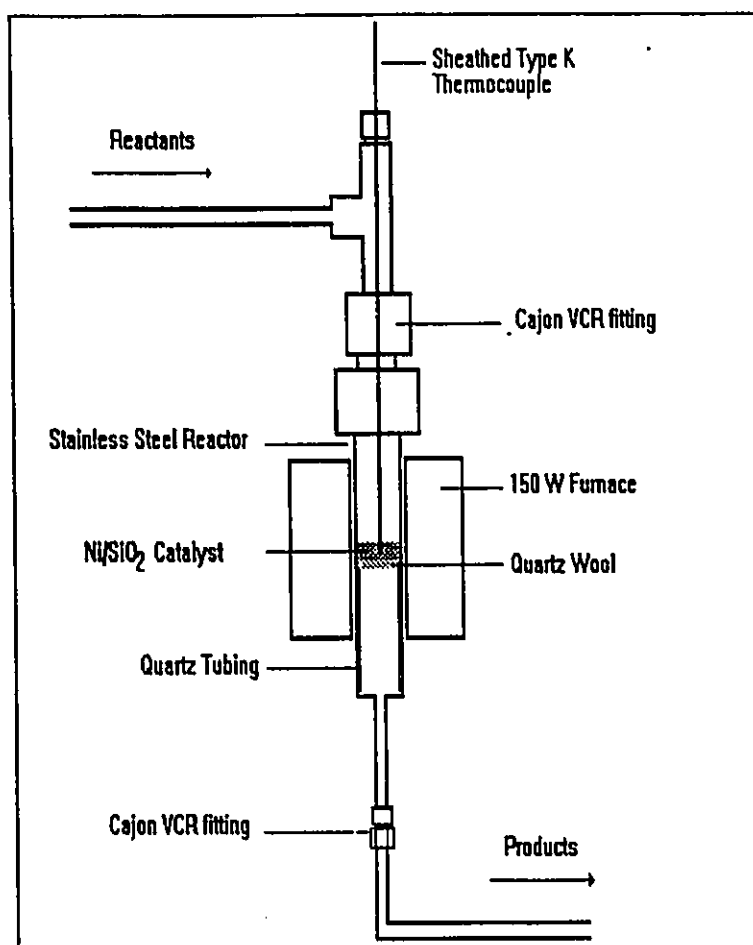
The reactor/bypass segment was constructed from 1/8" stainless steel tubing and stainless steel Swagelok fittings. Stainless steel Hoke packless bellows sealed valves (4251G4Y) were used (V2,V3, and V4). The reactor could be isolated by closing valves V3 and V4 and gas mixtures could be bypassed to the gas chromatograph through V5 (a Nupro bellows sealed valve (SS-2H)). Alternatively, with valves V2 and V5 closed and V3 and V4 open, gases were passed downwards through the reactor and the product effluent was sent to the on-line gas chromatograph.

The section enclosed by valves V1,V2 and V10 was constructed from 1/4" stainless steel tubing and was equipped with an MKS Type 122A 100 torr capacitance manometer. Valves V2 and V10 were Hoke packless bellows sealed valves (4251G4Y).

Valve V1 , a Nupro bellows sealed valve (SS6BK), isolated the system from a vacuum manifold. The pyrex vacuum manifold was fitted with a liquid nitrogen-cooled cold trap and was evacuated using an Edwards Model EO40/55 oil diffusion pump backed by an Edwards Model E2M2 rotary pump. This system was capable of reducing the pressure inside the reactor system to roughly 0.1 Pa (10^{-4} torr). Pressures within the manifold were monitored using a Varian Type 0531 Thermal Conductivity vacuum gauge fitted to a Varian Model 801 controller.

An exploded view of the micro-reactor is shown in Figure 2.3. The reactor was constructed from a 3/8" OD stainless steel tube and was attached to the system via Cajon VCR fittings using copper gaskets. The inner diameter of the reactor was 8 mm. The catalyst bed consisted of 270 mg 9.6 wt. % Ni/SiO₂. The bed depth was 21 mm, hence the reactor bed volume was 1.06 mL. The catalyst bed was supported on glass wool atop a 7 mm OD. quartz tube (80 mm in length). The catalyst temperature was measured by a sheathed, Type K thermocouple immersed in the bed; its output was displayed by an Omega Model 670 digital thermocouple thermometer.

Figure 2.3: Exploded View of Fixed-Bed Microreactor.



The reactor was heated by a home-made, coaxial, resistive-heating furnace constructed from Nichrome windings. The total resistance of the furnace windings was 9.3 ohms.

The temperature was controlled using an Omega Series CN-2010 Programmable Temperature Controller. A Type K thermocouple housed in the block of the furnace served as the temperature probe for the unit. Signals from the temperature controller were output to an Omega SSR240A25 solid state relay. Experiments showed that this power was too great for sensitive temperature control, hence the output was first stepped down through a variable transformer. Optimum control was achieved if the transformer was adjusted to 40 V. At this voltage 100% output from the temperature controller produced a current of 3.8 A through the furnace windings. Therefore the impedance of the furnace windings was 10.7 ohms; the furnace's power was 150 W. Although the experiments described here are isothermal, it was determined that the maximum heating rate that produced a linear increase in temperature with time was 40°C/min between 25°C and 600°C under these conditions.

Gas Chromatographic Analysis:

Reactant mixtures and product effluents were analyzed using an on-line Varian Model 3700 gas chromatograph. Separation was effected at 100°C using a 3.05m long HayeSep Dip (a divinylbenzene polymer ,100/120 mesh) column. The column diameter was 1/8 ". A helium carrier gas (38 mL/min) was employed.

Separation of all C₁ to C₃ hydrocarbons was possible using the above conditions, however overlap existed between n-butane and three of the four butene isomers. Complete separation of C₄ hydrocarbons was felt to be unnecessary. A list of the retention times for each compound is given below.

Table 2.1: GC Retention Times of Various Compounds.

Compound	Retention Time (minutes)
methane	0.98
ethylene + acetylene	1.98
ethane	2.37
propylene	6.00
propane	6.92
isobutane	19.2
1-butene	20.7
trans-2-butene	23.8
n-butane	24.4
cis-2-butene	25.5
isobutene	26.0
hexane	37.1

A thermal conductivity detector and a flame ionization detector were used in series. Their signals were integrated using a Spectra-Physics SP4290 integrator and a Hewlett-Packard 3300A integrator respectively. Known amounts of CH_4 , C_2H_4 , C_3H_6 , and $\text{n-C}_4\text{H}_{10}$ were analyzed under identical conditions and the response curves were used for quantification *ie.* an external standard method was used.

Analysis of the reactant propylene (stated purity 99.0% min.) revealed the following impurities: C_2H_6 ; C_3H_8 ; $\text{iso-C}_4\text{H}_{10}$; and $\text{n-C}_4\text{H}_{10}$. All stabilized reactant mixtures were analyzed prior to the experiment and the subsequent product effluent analyses were corrected for these impurities.

Catalyst Preactivation:

NiO/SiO_2 catalysts were preactivated before reaction either by reducing with hydrogen or by treating with methane.

Hydrogen Reduction:

Hydrogen reduction of NiO/SiO_2 catalysts was performed by flowing hydrogen (80 mL/min) through the catalyst. The temperature was increased to 350°C (unless otherwise stated) over 30 minutes, then the catalyst was maintained at that temperature, typically for 90 minutes. Reductions for as long as 19 hours at 350°C were performed. In some experiments the hydrogen was left in the reactor, while in others, hydrogen was evacuated via a diffusion pump at elevated temperature (see Table 2.2).

Table 2.2: Experimental Conditions for Control Experiments over 9.6 wt.% Ni/SiO₂.

Expt #	H ₂ Reduction Conditions	Reactant Mixture (8.8vol.%)	Reaction Temperature (°C)	W/F (mg min/mL)
6	350°C for 19 hours, evac. at 350°C for 2 hours	C ₃ H ₆ / CH ₄	350	8.1
8	350°C for 4 hours, evac. at 350 °C for 2 hours	C ₃ H ₆ / CH ₄	350	16.2
7	350°C for 4 hours, H ₂ not evacuated	C ₃ H ₆ / CH ₄	350	16.2
10	350°C for 4 hours, H ₂ not evacuated	C ₃ H ₆ / He	350	16.2
11	350°C for 4 hours, evac. at 350°C for 2 hours	C ₃ H ₆ / He	350	16.2
24	400°C for 2 hours, H ₂ not evacuated	C ₃ H ₆ / CH ₄	350	16.2
31	Standard Protocol	C ₃ H ₆ / CH ₄	350	8.1
33	Standard Protocol	C ₃ H ₆ / CH ₄	350	24.3
32	He purge (40 mL/min) for 4 hours at 400°C then Standard Protocol	C ₃ H ₆ / CH ₄	350	16.2
25	Standard Protocol then reacted with H ₂ at 300°C for 75 min., He purge	C ₃ H ₆ / CH ₄	350	16.2
29	Prereduction with H ₂ at 400°C for 2 hours, evac. for 90 min. at 400°C, then Standard Protocol	C ₃ H ₆ / CH ₄	350	16.2

Standard Methane Preactivation Protocol:

Methane preactivation of the NiO/SiO₂ catalyst was typically performed by flowing mixtures of 20 vol. % CH₄ in helium through the bed at atmospheric pressure (50 mL/min.). The temperature was increased to 400°C (unless otherwise stated) over 45 minutes and maintained for 75 minutes at that temperature. Methane flow was stopped. The helium flow (40 mL/min.) was continued through the reactor and the reactor was heated or cooled to the desired reaction temperature, often 350°C. The highest selectivity to C₄ hydrocarbons was obtained at this temperature; the effects of reaction temperature are discussed in detail later in this thesis. The reactor was then isolated in an atmosphere of helium.

Propylene/ (Methane or Helium) Reactions:

Following the hydrogen reduction or the methane preactivation procedure as described above, mixtures of 8.8 vol. % C₃H₆ in He or CH₄ were flown through the bypass (typical total flow rate 16.7 mL/min (W/F= 16.2 mg min/mL)) at atmospheric pressure and room temperature. Once the reactant mixture had stabilized (as determined by GC analysis) the reactants were diverted through the reactor. Product effluents were sampled by GC every 30 minutes until the reaction had reached a steady-state (typically within two hours) or until catalyst deactivation occurred. Table 2.3 lists the experimental conditions used over CH₄-preactivated 9.6 wt.% Ni/SiO₂.

Table 2.3: Experimental Conditions over CH₄-Preactivated 9.6 wt.% Ni/SiO₂.

Expt. #	CH ₄ Preactivation Conditions	Reactant Mixture (8.8 vol.%)	Reaction Temperature (°C)	W/F (mg min/mL)
9	CH ₄ (40mL/min) at 600°C for 3 hours	C ₃ H ₆ / CH ₄	350	16.2
13	CH ₄ (10mL/min) at 450°C for 3 hours	C ₃ H ₆ / CH ₄	350	16.2
19	No Pretreatment	C ₃ H ₆ / CH ₄	350	16.2
18	Standard Protocol ie. 20 vol.% CH ₄ /He (50 mL/min) at 400°C for 2 hours	C ₃ H ₆ / CH ₄	350	16.2
20	as in #18 but at 350°C	C ₃ H ₆ / CH ₄	350	16.2
21	as in #18 but at 450°C	C ₃ H ₆ / CH ₄	350	16.2
16	as in #18 but at 500°C	C ₃ H ₆ / CH ₄	350	16.2
17	as in #18 but at 500°C	C ₃ H ₆ / He	350	16.2
22	as in #18 but at 550°C	C ₃ H ₆ / CH ₄	350	16.2
23	as in #18 but at 600°C	C ₃ H ₆ / CH ₄	350	16.2
26	Standard Protocol	C ₃ H ₆ / CH ₄	300	16.2
27	Standard Protocol	C ₃ H ₆ / CH ₄	400	16.2
28	Standard Protocol	C ₃ H ₆ / CH ₄	325	16.2

Results and Discussion:

As was described in the experimental section, product distributions were obtained as a function of time on stream under a variety of reaction conditions, in order to better understand the processes involved. In most cases the distribution of products reached fairly constant values after one to two hours on stream. In the discussion that follows, the propylene conversions and the yields and selectivities to various hydrocarbons that are reported are the values measured at this plateau, so-called "steady-state values". We only will discuss the time course of a reaction when it deviated significantly from other experiments.

Control Experiments over H₂ Reduced Ni/SiO₂

Effects of Methane in C₃H₆/CH₄ Feed Gas:

Reactions were carried out at 350°C over H₂-reduced Ni/SiO₂ catalysts using feed gas mixtures of either C₃H₆ in CH₄ (Expt.#7) or in He (Expt.#10) to investigate the role of methane in the feed gas. The results are shown in Table 2.4. Details of all experimental conditions are listed in Table 2.2 in the experimental section.

Table 2.4: Effects of Methane in Feed Gas on Propylene Conversion and on Various Hydrocarbon Yields at 350°C.

Expt.#	Feed Gas	C ₃ H ₆ Conversion (%)	Yields (%)		
			C ₄ 's	C ₃ H ₈	C ₂ 's
7	C ₃ H ₆ /CH ₄	33.6	1.28	6.96	3.94
10	C ₃ H ₆ /He	46.4	2.60	20.2	6.57
Ratio Y _{Cx} (He)/Y _{Cx} (CH ₄)			2.03	2.90	1.67

The results above show increased C₃H₆ conversion and an increase in the yields of all hydrocarbons when helium was used as a carrier gas rather than methane. The effect was most pronounced for propylene hydrogenation to propane, which approximately tripled. This suggests that CH_x species, formed by the dissociative adsorption of CH₄, act to block active metal sites for such reactions. Most importantly, the yields of C₄'s and C₂'s were both increased in the presence of helium. This is the opposite to the trend that would be observed if methane were necessary in the feed gas for direct methane-propylene coupling. In addition, since propylene was the sole source of carbon for C₃H₆/He mixtures reacted over H₂-reduced catalysts, C₄ appears to have been formed by C₃H₆ homologation or metathesis, rather than by direct coupling of CH_x and C₃H₆.

The lower C₃H₆ conversions and yields of C₄'s and C₂'s in the presence of a methane carrier gas can again be explained by blocking of active metal sites by CH_x species.

Effects of Contact Time:

Propylene/ methane mixtures were flown through H₂-reduced Ni/SiO₂ catalysts at 350°C. The effects of contact time were examined by changing the flow rate from 8.1 mg min/ mL (Expt.#6) to 16.2 mg min/ mL (Expt.#8); the contact time in Expt.#8 is twice that of Expt.#6. The results are shown in Table 2.5.

Table 2.5: Effects of Contact Time on Propylene Conversion and Various Hydrocarbon Yields at 350°C.

Expt.#	W/F (mg min/ mL)	C ₃ H ₆ Conversion (%)	Yield (%)		
			C ₄ 's	C ₃ H ₈	C ₂ 's
6	8.1	18.0	0.57	2.76	2.53
8	16.2	29.5	1.09	5.44	3.59
Yield C _x (#8/#6)			1.91	1.97	1.42

The steady-state C₃H₆ conversion increased by 64 % as the contact time was doubled. The steady-state yields of C₃H₈ and C₄'s approximately doubled. These observations suggest that the reactions responsible are under kinetic control under the experimental conditions used, *ie.* equilibrium was not established under the conditions in Expt.#6.

Effects of Residual Hydrogen on the C_3H_6/CH_4 Reaction:

Experiments were performed to examine the effects of residual hydrogen (following H_2 reduction of the catalyst at $350^\circ C$) on the subsequent C_3H_6/CH_4 reactions. In the first case the catalyst was evacuated at $350^\circ C$ for 90 minutes prior to feeding the C_3H_6/CH_4 mixture at $350^\circ C$ (Expt.#8). In the second case, the reactor was not evacuated following reduction; the residual hydrogen was left in the reactor prior to the reaction of the C_3H_6/CH_4 mixture at $350^\circ C$ (Expt.#7).

During the initial stages of the reaction (30 minutes on stream) propylene conversion was increased from 40% to 60% by the presence of residual hydrogen. The increased conversion was mainly due to increased hydrogenation to propane; a 20% initial yield was calculated compared to an 11% yield in the absence of H_2 . The initial yields of C_4 's and C_2 's were also increased but to a lesser extent. C_4 yields increased from 1.6% to 2.5% . However, within 90 minutes on stream both reactions had reached similar yields and conversions. The steady-state C_3H_6 conversion was 30%. The effects on the steady-state yields are shown in Table 2.6. The presence or absence of H_2 (or H-species) had little effect on the steady-state yields. Hydrogenation of propylene was increased slightly (28%) if H_2 remained, as would be expected.

Table 2.6: Effects of Residual Hydrogen on Steady-state Yields of Various Hydrocarbons
at 350°C.

	Steady-state Yields (%)		H_2 Left/ H_2 Evacuated
	H_2 Evacuated	H_2 Left	
C_4 's	1.09	1.28	1.17
C_3H_8	5.44	6.96	1.28
C_2 's	3.59	3.94	1.10

8.8% C_3H_6/CH_4 , W/F= 16.2 mg min/ mL

Effects of Residual Hydrogen on the C_3H_6/He Reaction:

As in the previous section the effects of the presence or absence of H_2 on the subsequent reaction were investigated. However, in these experiments (#10 and #11) the feed gas was an 8.8% C_3H_6/He mixture rather than a mixture of C_3H_6 and CH_4 . The reaction temperature was again $350^\circ C$. All other parameters were as before.

Initial propylene conversions were large (88% with residual hydrogen, 74% without). Within 120 minutes on stream no difference in the steady-state C_3H_6 conversion was observed (both 45%).

The yield of propane was approximately twice as large in the presence of residual hydrogen as in its absence over the entire course of the reaction (6 hours).

The steady-state yields to various hydrocarbons are shown in Table 2.7.

It was stated above that the steady-state conversion of propylene remained constant. However, the yield of propane increased when hydrogen was left in the reactor prior to reaction. Therefore, the selectivity to propane was increased. In addition, it would appear that residual hydrogen caused hydrogenation of carbonaceous material in the case of C_3H_6/He .

Table 2.7: Effects of Residual Hydrogen on Steady-state Yields of Various Hydrocarbons
During C₃H₆/He Reaction at 350°C.

	Steady-state Yields (%)		H ₂ Left/ H ₂ Evacuated
	H ₂ Evacuated	H ₂ Left	
C ₄ 's	1.75	2.60	1.50
C ₃ H ₈	10.13	20.2	2.00
C ₂ 's	4.37	6.57	1.50

8.8% C₃H₆/He, W/F= 16.2 mg min/ mL.

The steady-state yield to propane increased two-fold when hydrogen was left in the reactor rather than evacuating prior to exposure to propylene in helium mixtures.

Hydrogenation was thus greatly enhanced by residual hydrogen. This should be compared with the slight enhancement in hydrogenation (28%) that was observed in the presence of methane (see previous section).

The effects of residual hydrogen on the yields of C₄'s and C₂'s were much less than on propane formation. An increase of 50% was observed in both yields when hydrogen was left in the reactor prior to reaction.

In addition, comparison of the results obtained using either helium or methane as a co-reactant show that the yield of propane approximately doubled (an increase of 86%) from 5.44% when hydrogen was pre-evacuated and methane was used as a carrier gas to 10.13% when helium was used as a carrier following evacuation. Residual hydrogen had a much greater effect when helium was used as a carrier gas rather than methane. The propane yield nearly tripled from 6.96% in methane to 20.2% in helium.

In summary, residual hydrogen or H-species remaining on the Ni/SiO₂ surface prior to reaction of propylene in methane caused no change in the propylene conversion and only a slight (28%) increase in propane formation. By contrast, residual hydrogen greatly enhanced propylene hydrogenation (doubled) when propylene was reacted in the presence of helium. The yield of propane was tripled when propylene was reacted, in the presence of residual hydrogen, in a helium carrier gas rather than in methane. All of the above observations are further evidence that methane in the feed gas dissociatively adsorbs on the nickel sites blocking propylene hydrogenation. Although to a lesser degree, the yields of C₄'s and C₂'s were also reduced by methane in the presence of residual hydrogen, hence hydrogenation sites are not selectively blocked by methane adsorption but rather all sites are affected.

Experiments over Methane-Preactivated NiO/SiO₂

Preactivation of NiO/SiO₂ with pure Methane:

All attempts to preactivate the catalysts using pure methane led to total inactivity in subsequent C₃H₆/CH₄ reactions at 350°C. For example, a catalyst that had been pretreated with methane (40 mL/min; GHSV=2400 hr⁻¹) at 600°C for 3 hours (Expt.#9) showed no activity for C₄ production or even for propylene hydrogenation (see Table 2.3 for details). Visual examination of the catalyst after only one hour on stream revealed extensive carbon deposition. Similar results were obtained following methane pretreatment (10 mL/min; GHSV=600 hr⁻¹) at 450°C for 3 hours (Expt.#13). Methane was therefore diluted to 20 vol.% with helium during preactivation and a standard preactivation protocol (discussed previously) was established which avoided deactivation by excessive carbon deposition.

These results are in conflict with those reported by Ovalles *et al.*[25]. In their study 620 mg 7.5 wt.% Ni/SiO₂ was preactivated in flowing CH₄ (10 mL/min; GHSV= 600 hr⁻¹) at 600°C for 8 hours. The resultant catalysts still showed activity for formation of C₄ hydrocarbons as well as C₂'s and C₃H₈. The reason for this difference is not apparent. Greater detail will be given later.

Carbon Deposition During C_3H_6/He and C_3H_6/CH_4 Reactions:

Carbon deposition also played an important role during reactions under all experimental conditions studied. Although a steady-state was typically achieved within two hours, continued reaction eventually led to deactivation; catalysts were totally deactivated within eight hours on stream. Similar behaviour was observed over hydrogen-reduced catalysts. Carbon deposition will be discussed in greater detail later.

Effects of CH_4 Preactivation Temperature:

NiO/SiO_2 catalysts were preactivated in 20 vol.% CH_4/He for two hours as described previously. The preactivation temperature was varied from 350°C to 600°C. The catalysts were then used in the reaction of 8.8 vol.% C_3H_6/CH_4 (16.2 mg min mL⁻¹) at 350°C. The results are shown in Table 2.8.

Table 2.8: Effects of Temperature of CH₄ Preactivation of 9.6 % Ni/SiO₂ on Steady-state Yields of Various Hydrocarbons.

Expt. #	Preact. Temp (°C)	CH ₄ Conversion during Preactivation. (%)	C ₃ H ₆ Conversion (%)	Yield (%)		
				C ₄ 's	C ₃ H ₈	C ₂ 's
19	no preact.	0	0	0	0	0
20	350	1.4	3.8	0	0	0
18	400	6.3	55.8	1.26	12.3	2.65
29**	400	4.3	33.8	1.79	12.3	4.01
25 [†]	400	-	52	1.62	15.8	3.35
21	450	14.8	55.4	1.18	9.7	3.67
16	500	-	50.3	1.05	9.11	2.77
22	550	46	34.4	0.49	3.54	1.72
23	600	60	6.4	0.46	3.16	1.63

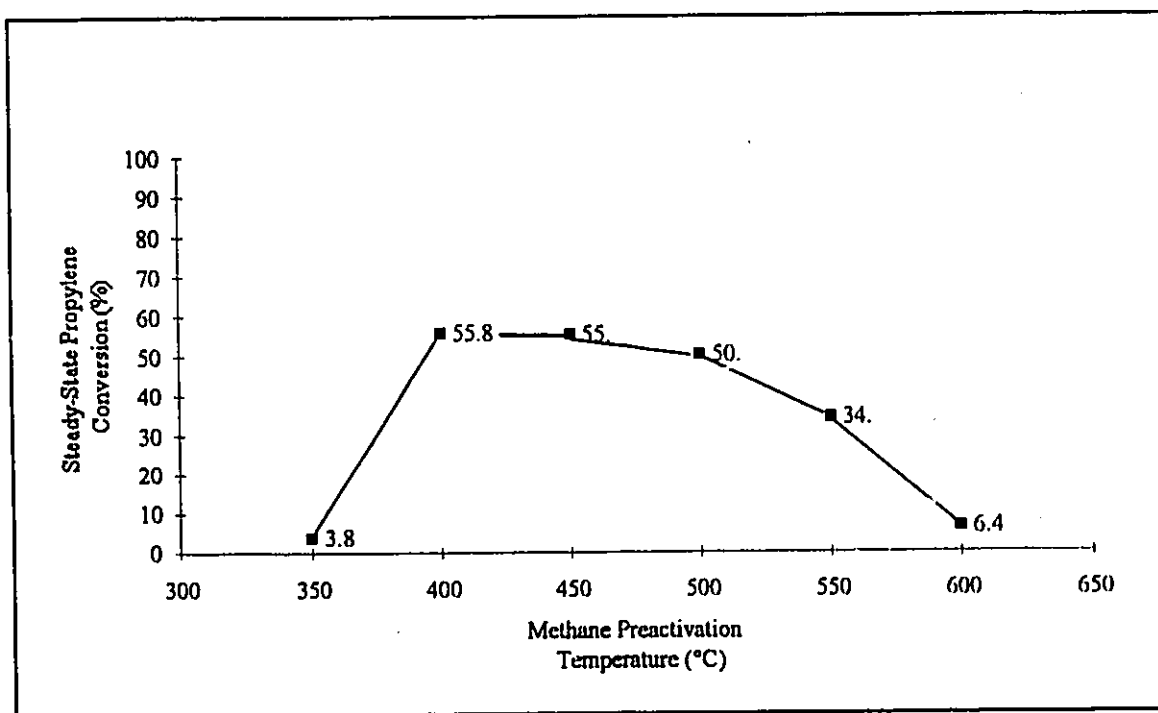
* Reaction Conditions: 8.8% C₃H₆/CH₄ at 350°C;
W/F= 16.2 mg min/mL

** catalyst reduced by hydrogen prior to CH₄ activation

[†] catalyst reacted with hydrogen after CH₄ activation

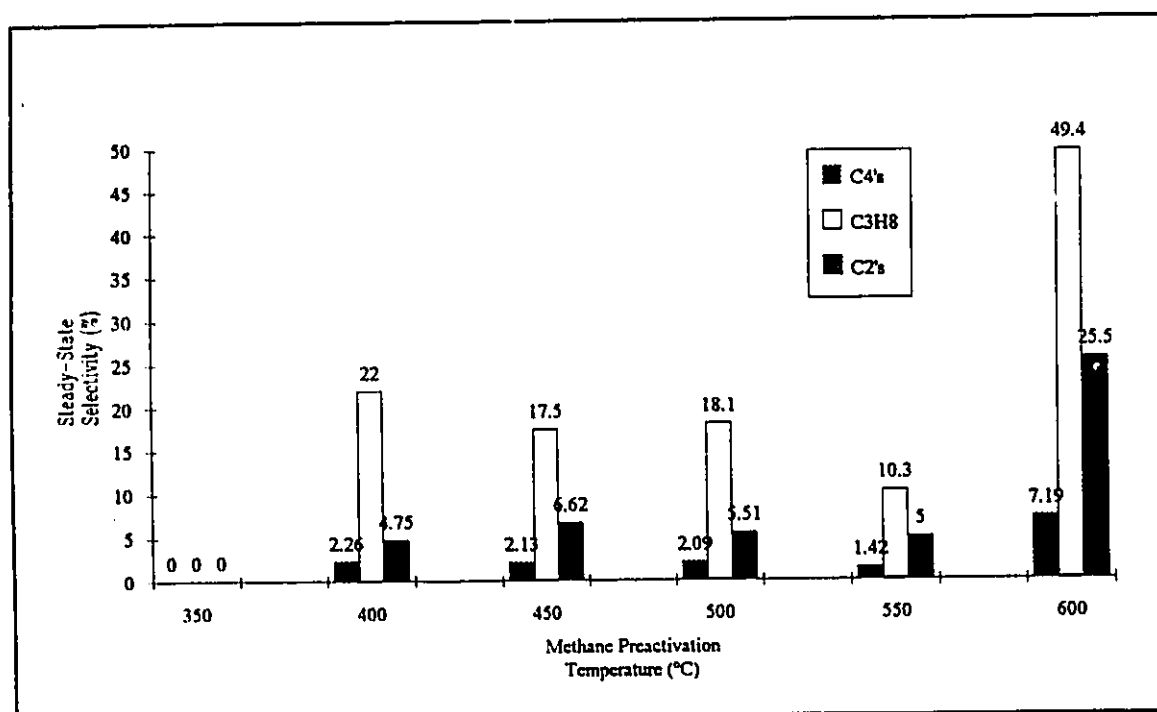
The steady-state C_3H_6 conversions achieved over these catalysts are plotted in Figure 2.4. As the Figure shows C_3H_6 conversion over a catalyst preactivated at $350^\circ C$ was very low (3.8%). For preactivation temperatures between $400^\circ C$ and $450^\circ C$ a maximum was observed at about 55%. Above $500^\circ C$ propylene conversion dropped off rapidly; by $600^\circ C$ it was only 6.4%.

Figure 2.4: Effects of CH_4 Preactivation Temperature on C_3H_6 Conversion During Reaction of 8.8 % C_3H_6/CH_4 at $350^\circ C$.



Steady-state selectivities to various hydrocarbons as a function of CH₄ preactivation temperature are shown in Figure 2.5.

Figure 2.5: Effects of CH₄ Preactivation Temperature on the Selectivity to Various Hydrocarbons During Reaction of 8.8 % C₃H₆/CH₄ at 350°C.



As can be seen in Figure 2.5, for all catalysts that showed activity, *i.e.* those preactivated with methane at 400°C or above, the selectivity for hydrogenation of propylene to propane exceeded the selectivity to C₄'s. In most cases hydrogenation was favoured by an order of magnitude. For preactivation temperatures between 400°C and 550°C the selectivities to C₄'s and C₂'s remained fairly constant at approximately 2 % and 5 % respectively.

For the catalyst that had been preactivated at 600°C all selectivities were larger than those over catalysts preactivated at lower temperatures. It should be recalled however that propylene conversion was quite low (6.4 %). As a result the steady-state yields of the various hydrocarbons were very similar to those observed at the lower preactivation temperature of 550°C where the C₃H₆ conversion was 5 times larger (see Table 2.8). It should be recalled that yield is the product of conversion and selectivity.

As was previously mentioned Ovalles *et al.* [25] reported that Ni/SiO₂ was active in the production of C₄ hydrocarbons after activation with CH₄ at 600°C (GHSV= 600 hr⁻¹) for 8 hours. After one hour on stream, reaction at 350°C of 9 % C₃H₆/CH₄ (GHSV= 968 hr⁻¹) resulted in a C₃H₆ conversion of 4.7%. The selectivities to C₄'s, C₃H₈ and C₂'s were: 81.4%; 16.4%; and 2.2% respectively. Reaction of 9% C₃H₆/N₂ under similar conditions resulted in a 4.3% C₃H₆ conversion and selectivities of: 2.2% C₄'s; 96.1% C₃H₈; and 1.7% C₂'s.

It is important to note that these authors have defined selectivity as the number of moles of C_x formed divided by the total moles of products (C_4 's, C_3H_8 , and C_2 's) detected. With this definition the yield of C_x is **not** equal to the product of conversion and selectivity; the yield cannot be calculated. Care must therefore be taken when comparing their data with the results presented here.

Although yields cannot be calculated from the data in [25] it is apparent that very different selectivities were observed when CH_4 was co-fed with C_3H_6 rather than nitrogen. In the former case the selectivity to C_4 's was much larger than the selectivity to C_3H_8 (81.4% versus 16.4%). Cofeeding C_3H_6 and N_2 produced a very high selectivity to C_3H_8 (96.1%). Hydrogenation of propylene was therefore suppressed when CH_4 was co-fed. Olefin hydrogenation is known to compete with homologation [43].

As was shown previously in Figure 2.5, CH_4 preactivation at 600°C led to larger selectivities for C_4 's, C_3H_8 , and C_2 's than preactivation at lower temperatures. However, propylene hydrogenation was still favoured over C_4 production. Again this behaviour differs from that previously observed [25].

The Role of CH₄ During Preactivation:

In order to evaluate the role that methane was playing during the preactivation of the NiO/SiO₂ catalysts, the reactor effluent during preactivation was monitored by GC analysis at 15 minute intervals. Methane conversion was monitored using both the flame ionization detector (FID; sensitivity 10⁻¹⁰ A/mV) and the thermal conductivity detector (TCD; sensitivity 0.5 mV/mV). Carbon dioxide and water were detected via the TC detector.

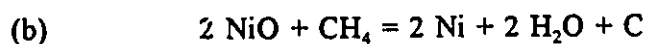
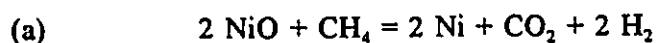
In all cases methane conversion was observed to increase as the catalyst temperature was increased from room temperature to its final value until a plateau was reached during the constant temperature period. The percentage methane conversions observed (measured at the plateau) are shown in Table 2.8. The plateau values increased greatly with temperature (from approximately 1 % at 350°C to 60 % at 600°C).

Carbon dioxide was detected during preactivation. CO₂ first appeared at approximately 240°C, passed through a maximum, and then disappeared by 400°C.

In experiments in which no water was removed from the catalyst by evacuation prior to methane pretreatment H₂O was detected after 100°C. Evolution of H₂O remained constant over an extended period of time. In one experiment (Expt.#32) the catalyst was first purged in flowing helium (40 mL/min) at 400°C for 4 hours until no water was detectable by GC-TCD. No H₂O was detected during the subsequent CH₄ activation procedure to 400°C.

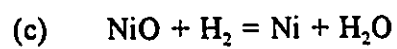
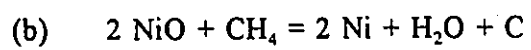
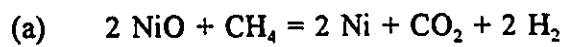
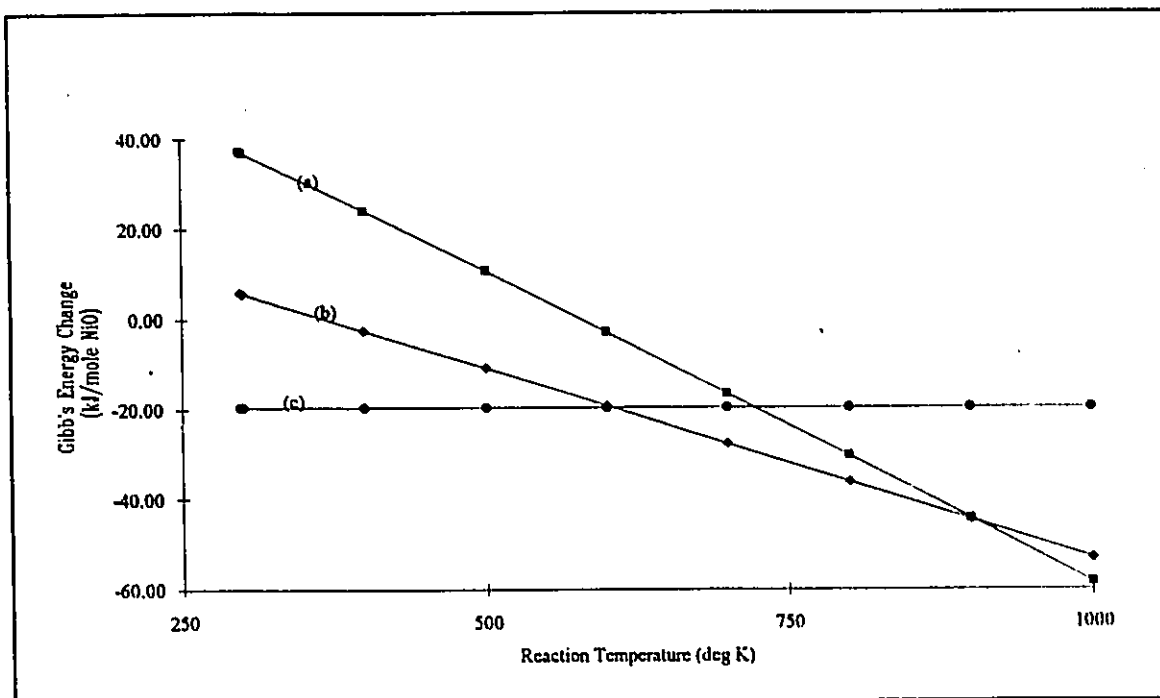
In summary, the following results were observed during monitoring of the CH₄/He preactivation of NiO/SiO₂ catalysts at temperatures between 350°C and 600°C. Methane conversion was found to increase from approximately 1% at 350°C to 60% at 600°C. Carbon dioxide was detected during preactivation between 240°C and 400°C. No water was detected during preactivation to 400°C if the catalyst bed was first purged with helium to 400°C.

Figure 2.6 shows the Gibb's energy of reaction versus temperature for the reactions:



For comparison the reduction of NiO by hydrogen is also included. From the Figure, Reaction (a) has a negative Gibb's energy change for temperatures above 580 K (300°C). Reaction (b) has a negative Gibb's energy change for temperatures above 315 K (40°C). Thus both reactions are thermodynamically feasible during preactivation at 600°C.

Figure 2.6: Gibb's Energy Change for CH₄ Reduction of NiO versus Temperature.



From the observations it appears that NiO is reduced by CH₄ mainly via Reaction (a) in the present instance, since CO₂ was detected but no water was detected after purging. Reaction (b) may however also have occurred to a lesser extent; this would result in the formation of some surface carbon.

Once reduced nickel is produced, dissociative adsorption of CH₄ can occur. The dissociative chemisorption of CH₄ on supported transition metal catalysts is well-known. At temperatures between 200°C and 500°C methane is decomposed by Group VIII metal catalysts into hydrogen and different carbide and graphite species [47]. Three different kinds of carbonaceous surface species have been identified [47]. These species can be distinguished by their differing reactivities towards hydrogen [48]. Carbodic (C_α) surface carbon, which is formed at low carbon surface coverages, is a highly dispersed species which can be hydrogenated below 100°C. This form produces the greatest amount of C₂ to C₄ hydrocarbons upon hydrogenation. An amorphous carbonaceous layer (C_β) is hydrogenated around 200°C. This form is less reactive than C_α, producing only trace amounts of C₂ to C₄ hydrocarbons. Above 375°C a fairly unreactive graphitic carbon is formed; upon hydrogenation this graphite produces only methane [47,48].

The adsorption of CH₄ on pre-reduced Ni/SiO₂ catalysts at sub-monolayer coverages has been studied by Kuijpers *et al.* [49,50] between 300 K and 575 K. Over the entire temperature range chemisorption was found to occur according to:



The activity of the carbon deposit towards hydrogen showed that at all temperatures studied (between 25°C and 450°C) the only product observed was methane. Reactivity passed through a maximum at 200°C and strongly decreased above 400°C. This latter decrease in activity is consistent with that observed earlier by McCarty and Wise [48].

Studies by Kuijpers *et al.* [51] of methane adsorption on Ni/SiO₂ at higher surface coverages showed that CH_x species (0 < x < 4) are present. The presence of these species inhibited the formation of Ni₃C. This phenomenon was explained by surmising that carbon atoms that were still bonded to hydrogen atoms could not penetrate into the nickel surface.

In the present study very little reduction occurred with 350°C preactivation as indicated by the low CH₄ conversion (1%) and by the absence of activity in subsequent C₃H₆/CH₄ reactions. At activation temperatures of 400°C and 450°C methane conversions were 6.3% and 14.8% respectively. These catalysts showed very similar activities; the same C₃H₆ conversions and virtually identical steady-state yields were observed. At temperatures of 550°C and 600°C methane conversions were quite large (45-60%). The resultant coked catalysts demonstrated lower C₃H₆ conversions and C_x yields.

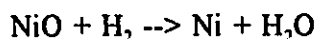
Other experimental evidence supports the reduction of NiO by methane:

(1) in a blank experiment (Expt.#19), no prior evacuation or methane-preactivation was carried out on a NiO/SiO₂ catalyst. No activity was observed when a C₃H₆/CH₄ mixture

was flown through the catalyst at 350°C;

(2) the results of an experiment (Expt.#29) in which the NiO/SiO₂ catalyst was first reduced by hydrogen prior to methane treatment. The experiment was conducted as follows: reduction in flowing hydrogen (80 mL/min) at 400°C for two hours; evacuation at 400°C for 90 minutes, followed by cooling to room temperature in flowing helium. Methane preactivation was then carried out on this Ni/SiO₂ catalyst to 400°C (as in Expt.#18). A slightly lower methane conversion was observed (4.3% versus 6.3%, see Table 8). No CO₂ or H₂O was detected. The yields to various hydrocarbons were very similar in either case.

An attempt was made to hydrogenate the carbonaceous deposit that formed during CH₄-preactivation before the C₃H₆/CH₄ reaction was carried out (Expt.#25). Hydrogen was flown through the bed at a rate of 10 mL/min at 350°C. GC analysis of the effluent during hydrogenation revealed small quantities of CH₄. No higher hydrocarbons were detected. This result is consistent with the observations of van Santen *et al.* [47] and of McCarthy *et al.* [48] that fairly unreactive, graphitic carbon exists under these conditions. We note this with caution since C₂+ hydrocarbons may have been present at concentrations below the GC detection limit. Trace amounts of water were also detected. It is uncertain whether the moisture was residual moisture desorbing from the catalyst (since no previous evacuation was performed) or whether reduction of NiO was occurring via



The low flow rate of hydrogen was meant to minimize the possibility of the latter.

As can be seen in Table 2.8 no change in C_3H_6 conversion or in C_x yields was observed by prior hydrogenation (compare Expts.#25 and #18). This indicates that no appreciable change to the catalyst surface resulted from the attempted hydrogenation of the carbonaceous layer, again indicating that the carbonaceous species present were fairly unreactive.

Effects of Reaction Temperature on the C_3H_6/CH_4 Reaction:

From the previous study of the effects of CH_4 -preactivation temperature on the C_3H_6/CH_4 reaction, a preactivation temperature of 400°C was chosen. This temperature gave the highest C_3H_6 conversion and the maximum yield of C_4 hydrocarbons.

NiO/SiO_2 catalysts were preactivated in 20 vol.% CH_4/He as before. Propylene/methane mixtures were then flown through these catalysts at temperatures ranging from 300°C to 400°C . The results are shown in Table 2.9.

Table 2.9: Effects of Reaction Temperature of C_3H_6/CH_4 Reaction on Steady-state Yields over CH_4 -Preactivated (400°C) 9.6% Ni/SiO_2 .

Expt.#	Reaction Temperature ($^\circ\text{C}$)	Yield(%)		
		C_4 's	C_3H_8	C_2 's
26	300	0.09	0.73	0.24
28	325	0.50	3.07	1.13
18	350	1.26	12.3	2.65
27	400	0.65	14.3	4.43

The steady-state C_3H_6 conversion increased dramatically, in an almost linear manner, with increasing temperature as is shown in Figure 2.7. The conversion varied from 6 % at 300°C to near completion (97 %) at 400°C .

Figure 2.7: C_3H_6 Conversion versus Reaction Temperature over CH_4 -Preactivated (400°C) 9.6% Ni/SiO_2 during Reaction of 8.8 % $\text{C}_3\text{H}_6/\text{CH}_4$.

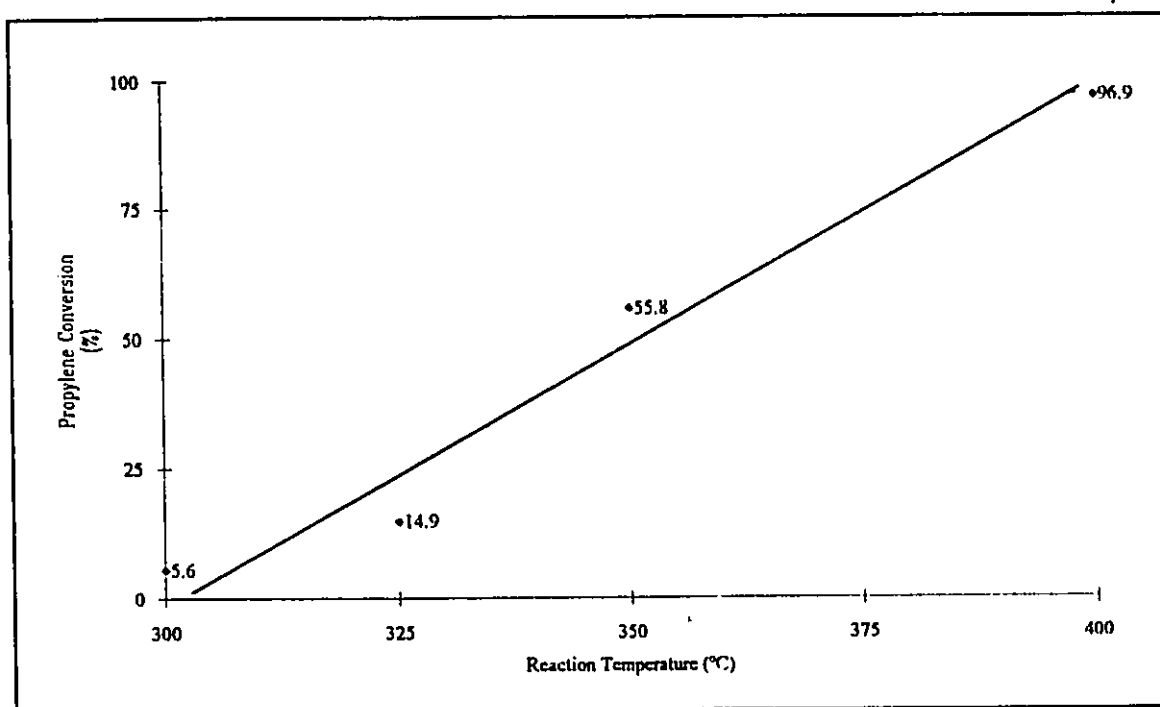
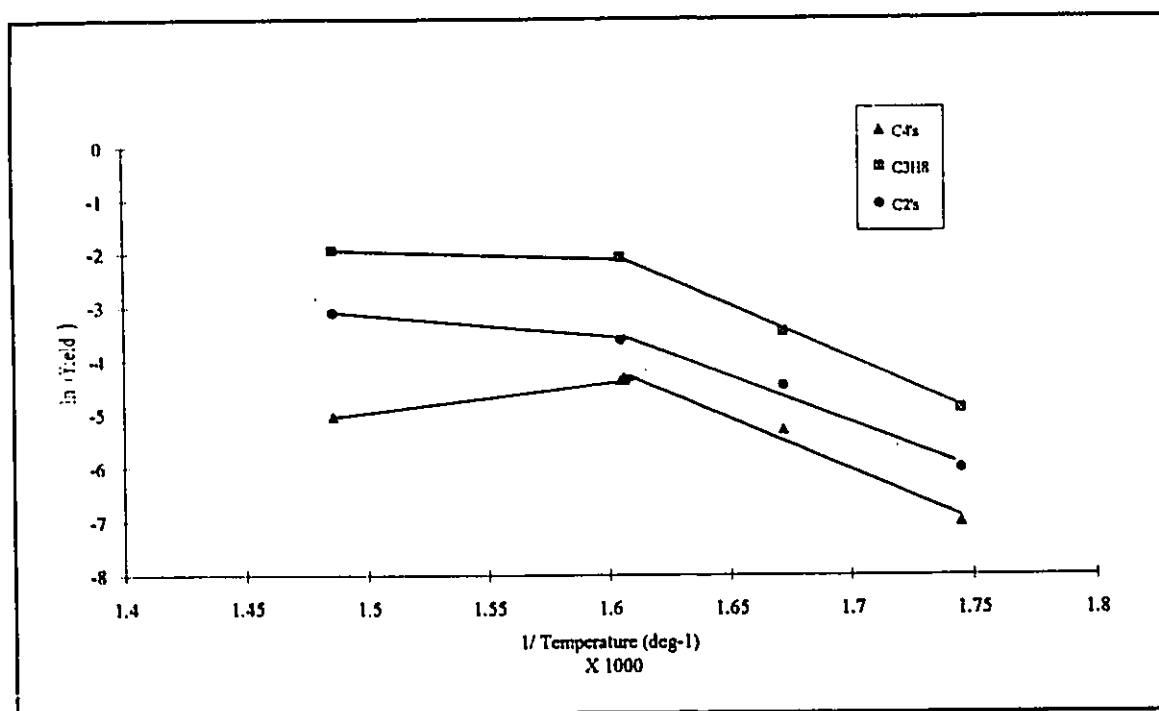


Figure 2.8 shows an Arrhenius-type plot of the natural logarithms of the yields of the various hydrocarbons versus reciprocal temperature. The data for the various hydrocarbons show linearity at the three lower temperatures with each line bending downwards at the highest temperature. The linearity indicates that the various reactions are under kinetic control over this temperature region. The deviation from linearity at high temperature can be expected because the conversion of propylene is near total.

Figure 2.8: Arrhenius-type plot for C_3H_6/CH_4 Reaction over CH_4 -Preactivated Ni/SiO_2 .



From the slopes of the linear portions of the curves shown in Figure 2.8, the apparent energy of activation of the overall reactions can be calculated; the slope is related to the apparent energy of activation by the expression:

$$\text{slope} = -E_{\text{apparent}} / R$$

where R is the ideal gas constant, 8.314 J/mole/deg.

The measured apparent activation energies are:

Reaction	Measured Apparent Energy of Activation for Overall Reaction (kJ/mole)
C ₄ 's	156.8
C ₃ H ₈	167.5
C ₂ 's	142.5

Each overall reaction has a similar apparent energy of activation, approximately 2.4 kJ/mol. This is also seen by the similarities in the slopes of the linear portions of the curves in Figure 2.8. This similarity may suggest that all reactions may take place through a common rate-determining step. This would imply that the formation of C₄ hydrocarbons is not due to direct methane-olefin coupling.

Effects of Methane in the C_3H_6/CH_4 Feed Gas at 350°C:

The effects of methane in the propylene/ methane feed mixture were investigated over a NiO/SiO_2 catalyst that had been previously preactivated with methane at 500°C using the standard protocol. In one case (Expt.#16) an 8.8 vol.% C_3H_6 in CH_4 was reacted at 350°C as previously described. For comparison, a mixture of 8.8 vol.% C_3H_6 in He was reacted over a similarly-preactivated catalyst. The results are shown in Table 2.10.

Table 2.10: Effects of CH_4 in Feed Gas on C_3H_6 Conversion and on Various Hydrocarbon Yields at 350°C .

Expt.#	C_3H_6 Conversion (%)	Yields (%)		
		C_4 's	C_3H_8	C_2 's
16 ($\text{C}_3\text{H}_6/\text{CH}_4$)	50.3	1.05	9.11	2.77
17 ($\text{C}_3\text{H}_6/\text{He}$)	59.2	1.76	18.7	3.31

From the above table propylene conversion was higher when helium was co-fed rather than methane. The yield of propane was doubled in the presence of helium. An increase in the yields of C_4 's (68 %) and C_2 's (19 %) was observed with helium as a carrier gas rather than methane. These results are identical to those observed over hydrogen-reduced Ni/SiO_2 catalysts. As before, they can be interpreted by a blocking effect of sites by CH_x species. A decrease in the yields of C_4 's and C_2 's suggests that CH_4 in the feed hinders rather than aids their production. Again, propylene homologation and/or metathesis is proposed to be responsible for C_4 production rather than direct coupling of CH_x and C_3H_6 .

Effects of Contact Time on the C_3H_6/CH_4 Reaction:

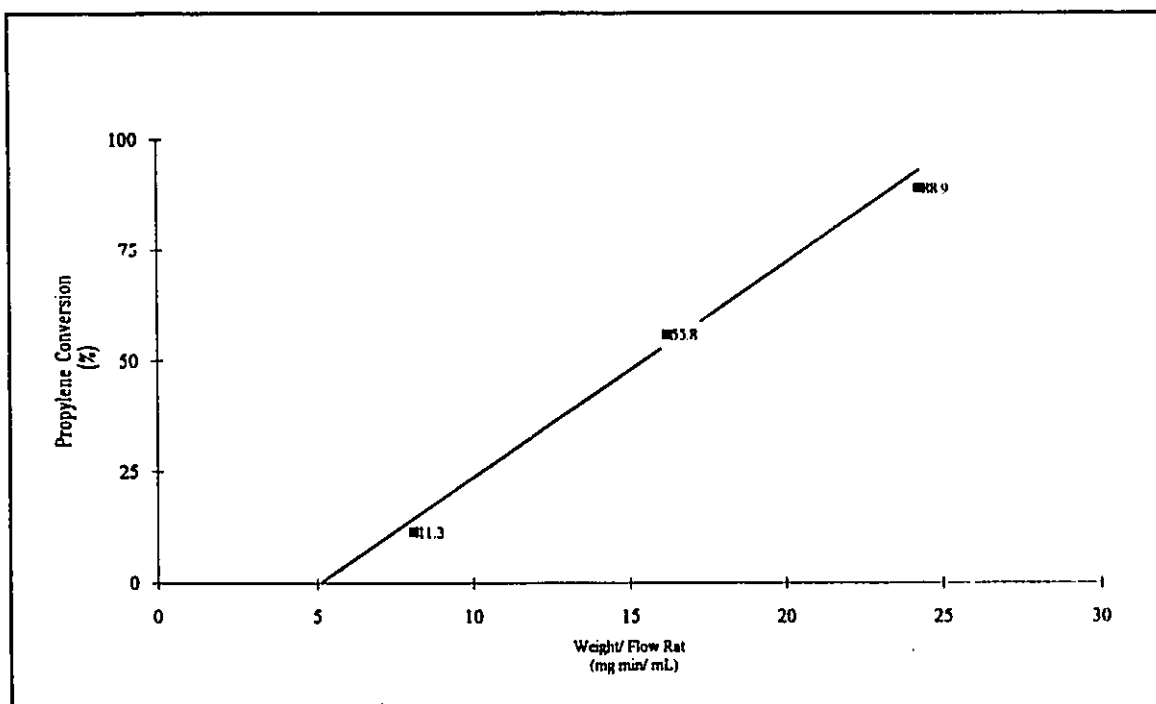
The effects of contact time on propylene conversions and on the yields of various hydrocarbons during the reaction of 8.8 vol.% C_3H_6/CH_4 mixtures over CH_4 -preactivated NiO/SiO_2 at $350^\circ C$ were examined. The results are tabulated in Table 2.11. Contact time is directly proportional to the parameter (W/F), catalyst weight/ flow rate of reactant gas mixture, which is used in the Table.

Table 2.11: Effects of Contact Time on C_3H_6 Conversion and on the Yields of Various Hydrocarbons at $350^\circ C$.

Expt.#	W/F (mg min/mL)	C_3H_6 Conversion (%)	Yields (%)		
			C_4 's	C_3H_8	C_2 's
33	24.3	88.9	6.33	20.1	5.14
18	16.2	55.8	1.26	12.3	2.65
31	8.1	11.3	0.26	1.75	1.02

From the data above, as the contact time was increased (*ie.* as W/F became larger) the propylene conversion increased. This trend is plotted in Figure 2.9. The linear dependence of the conversion with (W/F), and therefore with contact time, indicates kinetic control under the reaction conditions used.

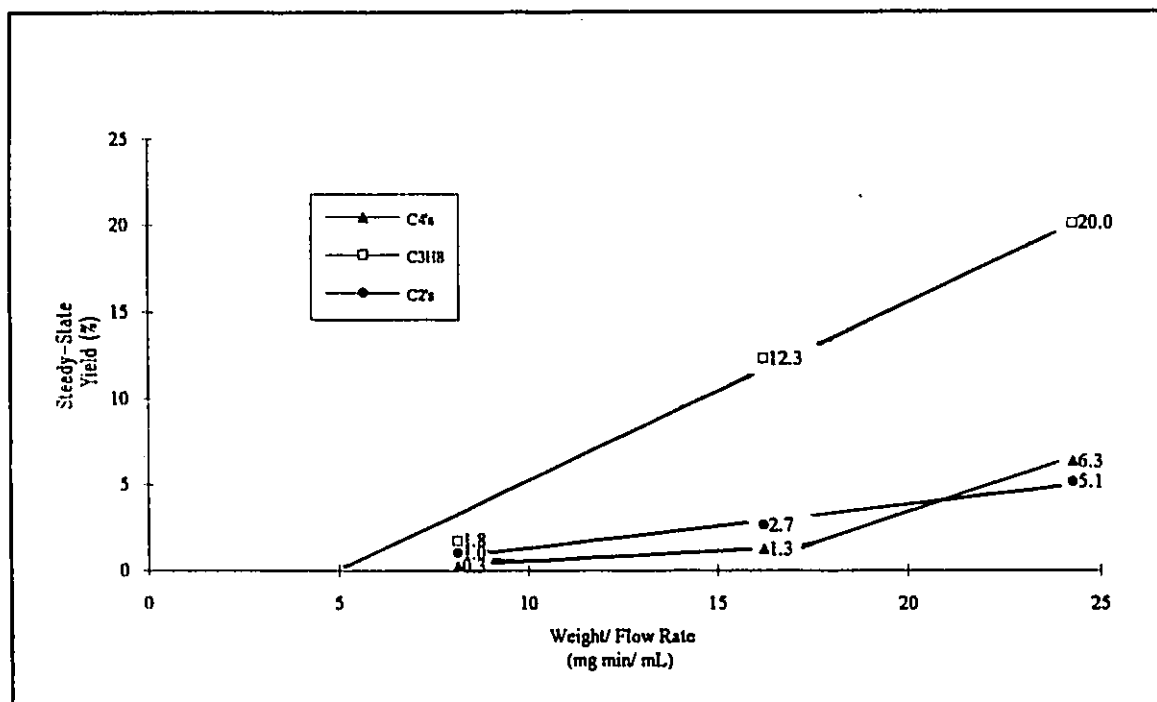
Figure 2.9: C_3H_6 Conversion versus Weight/Flow Rate.



The steady-state yields of the various hydrocarbons also increased with increased contact time. The data is plotted in Figure 2.10. Here again linearity implies kinetic control.

The deviation from linearity in the curve for C_4 's in Figure 2.10 is possibly due to the fact that the small quantities produced made errors in measurement relatively more significant.

Figure 2.10: Yields of Various Hydrocarbons versus Weight/Flow Rate (W/F).



All of the curves in both Figure 2.9 and Figure 2.10 appear to have similar intercepts; each curve crosses the x-axis at a W/F value of approximately 5 mg min/mL. In theory all curves pass through the origin. Deviation is likely due to factors such as: the differences in the actual flow rate and the set value of the flow rate and non-ideal plug flow.

**A Comparison of CH₄-preactivation versus H₂-reduction of NiO/SiO₂
Catalysts on C₃H₆/CH₄ Reactions at 350°C:**

The results of the reaction of an 8.8 vol.% C₃H₆/CH₄ mixture over a CH₄-preactivated (400°C) catalyst (Expt.#18) are compared with the results obtained in a control experiment in which the catalyst was activated by reduction in H₂ (400°C) for the same length of time (Expt.#24). The data are shown in Table 2.12.

Table 2.12: A Comparison of CH₄-Preactivation versus H₂ Reduction of NiO/SiO₂
Catalysts on Subsequent C₃H₆/CH₄ Reactions.

Expt.#	Pretreatment	C ₃ H ₆ Conversion (%)	Yields (%)		
			C ₄ 's	C ₃ H ₈	C ₂ 's
18	CH ₄ /He at 400°C for 2 hours	55.8	1.26	12.3	2.65
24	H ₂ reduction at 400°C for 2 hours	51.2	1.76	14.7	3.67

From the data listed above it can be seen that both methods of catalyst pretreatment at 400°C led to almost identical activities for the subsequent reaction of C_3H_6/CH_4 mixtures at 350°C. The propylene conversions and the yields to various hydrocarbons were virtually identical. These results further confirm that both methods of pretreatment led to reduction of NiO to elemental Ni and that carbon deposition was not extensive under these CH_4 -preactivation conditions. It should be recalled that the steady-state conversion of methane was found to be only 6.4% at 400°C.

As was shown in the Table 2.1, the retention times for C_1 to C_4 compounds were less than 26 minutes and the retention time for hexane was 37.1 minutes. Although GC sampling of the product effluent was routinely carried out at 30 minute intervals, many GC runs of over 60 minutes were performed. No products higher than C_4 hydrocarbons were detected.

If propylene homologation was occurring, and homologation of C_n olefins produces up to about C_{n+2} as discussed previously, this raises the question of why no C_5 's were detected.

Several explanations are explored below:

- (1) The concentration of C_5 hydrocarbons was below the detection limit;
- (2) C_5 's condensed in the effluent line between the reactor exit and the GC inlet, which was at room temperature. This should be disregarded since the normal boiling point of

n-pentane is 36°C. Only C₆ compounds and higher would condense. The normal boiling point of n-hexane is 69°C at room temperature;

(3) Products such as C₃'s and higher were "cracked" to lower molecular weight compounds.

Of the reasons discussed only the first seems plausible.

Conclusions

Control experiments over hydrogen-reduced Ni/SiO₂ in which propylene was co-fed with helium rather than with methane resulted in increased C₃H₆ conversions and an increase in the yields of all of the following hydrocarbons: propane; C₄'s; and C₂'s. The increase in the yield of C₄'s when propylene was the only carbon source suggests that C₄'s are produced by homologation or metathesis, rather than by coupling of CH_x and C₃H₆. It was concluded that CH_x species, formed by the dissociative adsorption of CH₄ from the feed gas, only block active metal sites thus leading to lower catalyst activities.

GC analysis during the preactivation of NiO/SiO₂ catalysts with methane/ helium mixtures showed that methane served first to reduce NiO to elemental nickel, forming mainly CO₂. Some reduction to form H₂O and surface carbon may also have occurred but to a lesser degree. Methane was then dissociatively adsorbed on the surface of the nickel catalyst.

Variation of the temperature of the methane preactivation treatment from 350°C to 600°C revealed an increased CH₄ conversion from approximately 1% at 350°C to 60% at 600°C. Subsequent reaction of C₃H₆/CH₄ mixtures over these catalysts at 350°C revealed that there was virtually no activity over the former catalyst and very little over the latter. However, catalysts activated between 400°C and 500°C showed very similar activities. These results suggest that insufficient reduction of NiO occurred at 350°C (no activity was observed

over a NiO/SiO₂ catalyst that had not been preactivated) and that preactivation at 600°C led to excessive carbon deposition. At intermediate temperatures sufficient reduction occurred without excessive carbon deposition.

At all preactivation temperatures the selectivity for propylene hydrogenation exceeded that of C₄ formation by an order of magnitude.

Attempts to hydrogenate the carbonaceous deposit that was formed during CH₄-preactivation at 400°C produced only small amounts of methane with no detectable, higher hydrocarbons being formed. This result is consistent with previous studies which concluded that a particularly unreactive form of graphitic carbon existed on the surface under these conditions.

An increase in propylene conversion from 6% at 350°C to 97% at 400°C was observed as the reaction temperature of the C₃H₆/CH₄ mixtures was raised. In addition, an Arrhenius-type dependence of the yields of C₃H₈, C₄'s, and C₂'s was found. Deviations from Arrhenius behaviour were observed at 400°C where near complete C₃H₆ conversion occurred. The above results suggest that the reactions were under kinetic control under the conditions used. Calculations of the apparent activation energies of the overall reactions from the linear portions of the curves for C₄'s, propane, and C₂'s resulted in very similar values, ranging from 142.5 to 167.5 kJ/mole. It is suggested that this similarity may indicate that all reactions proceed through a common rate-determining step.

Kinetic control was also indicated by a near-linear dependence of propylene conversion and of the yields of propane, C_4 's, and C_2 's with increased contact time.

The effects of CH_4 in the feed gas over CH_4 -preactivated catalysts were found to be similar to those observed over H_2 -reduced catalysts, i.e. all yields were increased in the presence of a helium carrier gas rather than in CH_4 .

A direct comparison of the results obtained over a CH_4 -preactivated ($400^\circ C$) catalyst and a catalyst that had been reduced in hydrogen at the same temperature for the same length of time revealed virtually identical activities in subsequent reactions of propylene and methane at $350^\circ C$.

The above evidence suggests that the same processes are responsible for C_4 production over CH_4 -reduced NiO/SiO_2 and hydrogen-reduced NiO/SiO_2 i.e. propylene homologation and/or metathesis. There was no evidence to support a mechanism by which CH_x species, formed by the dissociative adsorption of methane either during activation or during reaction, coupled with propylene to produce C_4 's. Rather, dissociatively adsorbed methane only served to block metal sites at which reactions could otherwise occur.

Chapter 3:

Characterization of $\text{ZrO}_2/\text{SiO}_2$

Introduction:

The catalytic properties of solids are intimately related to the surface properties of these materials. Hence, before we can obtain a detailed understanding of a catalytic mechanism on a molecular scale, we must first have an understanding of the nature of the surface. In these chapters, sulphate-promoted zirconia-silica is of interest. However, this is a complex, multicomponent system and it is necessary to understand the individual parts of the system in order to understand the whole. In this chapter, we describe the surface characterization of the substrate material, $\text{ZrO}_2/\text{SiO}_2$. The characterization of sulphate-promoted $\text{ZrO}_2/\text{SiO}_2$ is discussed in Chapter 4.

Acidity and Basicity in Solids:

Coordinative Unsaturation:

In order to form a new surface in a metal oxide crystal, metal oxygen bonds must be broken. As a result, the atoms on this new surface have fewer nearest neighbours than they do in the bulk crystal. These resultant ions are said to be "coordinatively unsaturated". The

degree of coordinative unsaturation (c.u.s.) of a particular ion, either cation or anion, is a measure of the number of bonds that must be broken to form the new surface [35].

Coordinatively unsaturated metal cation sites, M^{n+} , are electron-deficient and thus often act as Lewis acid sites for adsorption, *ie.* as electron-pair acceptors from an adsorbate. Coordinatively unsaturated oxide ions, O^{2-} , being electron-rich compared to bulk oxide ions, often act as Lewis bases.

If water is dissociatively adsorbed on a metal oxide surface, surface hydroxyl groups may be generated. Due to inductive effects from the electron-deficient metal cation, the oxygen-hydrogen bond of the surface hydroxyl groups is weakened. As a result the hydrogen atom may be abstracted as a proton by a suitable Bronsted base. Therefore, surface hydroxyl groups may act as Bronsted acid sites towards basic adsorbates.

In summary, the phenomenon of coordinative unsaturation gives rise to surface acidity and basicity, of both Lewis and Bronsted types. This acidity and basicity is the source of catalytic activity in many solid materials. Solid acid and base catalysts have tremendous importance in industrial petroleum chemistry. For example, solid acid catalysts are used in processes such as: hydrocarbon cracking; the synthesis of methyl tertiary butyl ether (MTBE); disproportionation of aromatics; and alkylation [52].

Enhancement of Surface Acidity in Binary Oxide Mixtures:

Many binary oxide mixtures show acidity greater than the sum of the acidities of their component oxides. That is to say, they possess greater numbers of acid sites and some of these sites may have greater acid strength than those found in either of the parent oxides. The most common example is silica-alumina. A great deal of research has been done on the nature of this enhanced acidity and several theories have been proposed to explain this phenomenon. In spite of this, the nature of the acidic properties of these mixtures remains strongly dependent upon their method of preparation and pretreatment and, therefore, *a priori* prediction of their properties remains difficult. Thus, this area remains to a considerable degree empirical and further work is necessary in order to achieve a more complete understanding of this phenomenon.

The first model proposed to explain the enhanced acidity of binary oxide mixtures was reported by Thomas in 1949 [53]. His model was meant to explain the acidity of silica-alumina mixtures, as well as their catalytic activity for hydrocarbon cracking reactions. He made three assumptions: (1) Al atoms in silica-alumina that contribute to the catalytic activity are tetrahedrally coordinated to oxygen atoms; (2) a positively charged hydrogen ion is associated with the tetrahedral aluminum in the catalyst; (3) the catalytic activity of these materials is due to the acidity of these hydrogen ions. Since Al has a valence of +3, each Al-O bond in a tetrahedral unit has $3/4$ of a valence unit (v.u.). Therefore, each oxygen atom is unsatisfied by $1/4$ v.u. and since each Al atom has four oxygens associated with it, the

valency of the Al is unsatisfied by -1 v.u. This negative charge is compensated by the presence of a positively charged hydrogen ion, therefore Bronsted acidity results. Thomas' model can only predict Bronsted acidity, not Lewis acidity.

In 1974, Tanabe [54] proposed a new hypothesis that acid sites on binary oxides are formed by an excess of a negative or a positive charge in the mixed oxides and that whether the charge is positive or negative is determined by the coordination numbers and valences of the positive and negative elements in the model structure according to two postulates. The postulates are: (1) the coordination number of a positive element of a metal oxide, C_1 , and that of a second metal oxide, C_2 , are maintained upon mixing; (2) the coordination number of a negative element, oxygen, of a major component oxide is retained for all oxygens in the binary oxide.

Thus, the model is capable of predicting the generation of both Lewis acid sites (assumed to appear upon the presence of an excess positive charge) as well as Bronsted sites (appearance of an excess negative charge). This hypothesis was applied to 31 kinds of binary oxide mixtures and the predictions were compared with available literature data. Agreement was found between theory and experiment for 28 of 31 systems (90 %). Predictions were also made based on Thomas' model, but agreement was only 48 %. Tanabe's model predicts the generation of Lewis acid sites when zirconia and silica are mixed.

The theories above attempt only to predict the generation of acidity. They cannot predict the acid strength of the resultant acid site. However, a correlation has been found between the acid strength and the average electronegativities of the metal ions in the oxides [55].

The models discussed so far are limited to cases in which intimate chemical mixing of the two oxide components takes place. Such mixtures are normally prepared by coprecipitation. However, it has been observed that binary oxides prepared by impregnation can exhibit enhanced acidity although "intimate chemical mixing" may not have occurred.

Seiyama [56] has developed a model for cases in which chemical mixing may not be adequate. In this model it is assumed that acidity appears at the boundary where two oxides contact. The appearance of excess charge at this boundary leads to acidity as in Tanabe's model.

More recently, Kung proposed a predictive model for the formation of new acid sites in dilute solid solutions of binary oxides based on the electrostatic potential at the substituting cation site and the change in the matrix necessary to balance the stoichiometry [57]. The model also predicts Lewis acidity for zirconia/silica mixtures.

The important difference between the models of Tanabe and of Kung is that Tanabe uses a localized approach such that any new acid site formed will be formed at the

substituting cation site. Kung however emphasizes the effects on the entire matrix. The new acid site may be formed on the matrix surface far away from the substituting site as well as at the site.

Again, no theory presently exists that can reliably predict the acid strength of a generated acid site. Recently, Hattori *et al.*[58 and references therein] have attempted to apply methods of artificial intelligence to this problem with some success. They have used a technique known as neural networking to aid in their predictions. Essentially, one assumes that acid strength, H_0 , can be represented by a function. The function, which is arbitrarily chosen, contains such variables as: valence; coordination number; ionic radius; electronegativity; and electrostatic potential for metal ions and the partial charge of the oxygen ion for the oxides. One then gives the above data, as well as the measured acid strength for known systems, and using a technique known as back-propagation, an attempt is made to train the equation so that it may calculate the acid strengths for unknown binary oxide mixtures. Good agreement was obtained between estimated values and experimentally measured values.

Zirconium Dioxide:

Zirconium dioxide (ZrO_2), exists in three polymorphic, crystalline forms: monoclinic; tetragonal; and cubic. The monoclinic form is stable below 1170°C and consists of a seven-fold coordinate zirconium ion. The Zr-O distances range from 0.205 nm to 0.228 nm. At 1170°C , a phase transition from monoclinic to tetragonal occurs. In the tetragonal phase, which is stable to 2370°C , an eight-coordinate zirconium ion is surrounded by four oxygens at a distance of 0.2455 nm, and four more at a distance of 0.2065 nm. [59].

Zirconium oxide is an important material for heterogeneous catalysis because of its special surface characteristics. It has been claimed to possess four chemical surface properties: acidic; basic; oxidizing; and reducing [60]. Therefore, ZrO_2 exhibits catalytic activity for many reactions such as: methanol synthesis [61-3]; hydrogenation [64,65]; H_2 - D_2 exchange [66,67]; isomerization [68]; and dehydration [69-71].

Zirconia/Silica:

Binary mixtures of ZrO_2 and SiO_2 are of interest because they combine the chemical properties of zirconia with the stable mechanical and thermal properties of silica, in addition to showing enhanced acidity. $\text{ZrO}_2/\text{SiO}_2$ has been prepared using several different techniques; the surface properties have been found to vary greatly with the method of preparation. In one

of the earliest studies, Dzisko [72] produced $\text{ZrO}_2/\text{SiO}_2$ catalysts by impregnation of silica gels and by coprecipitation of ortho-silicic acid ethyl ester and zirconium nitrate. The purpose of this study was to examine the acidity of these materials; however, several points are not clear. The acidity (*ie.* the number of acid sites) was determined by n-butylamine adsorption and the acid strength was determined using indicators. The author found that for impregnated materials, the number of acid centres increased linearly with ZrO_2 content from 0.1 % to 1 %. Between 1% and 10% the rate of increase in acidity slowed and between 10% and 20% the number of acid sites was constant, being approximately 280 $\mu\text{equivalents/g}$. It is not clear however whether percentages are expressed in wt. % or in mole %. In addition, the number of acid sites/ m^2 is given but no surface area data are reported. It is unclear from the discussion which data applies to materials prepared by coprecipitation. However, the fact remains that the acidity of the impregnated catalysts remained constant after 10 % , as will be discussed later. The acid strength of the catalysts, examined by using Hammett indicators, showed $\text{H}_0 \leq -8.2$ which is comparable to that of the well-known acidic catalyst $\text{Al}_2\text{O}_3\text{-SiO}_2$.

More recently, Niemantsverdriet *et al.* [73] have studied the preparation of $\text{ZrO}_2/\text{SiO}_2$ systems by incipient wetness impregnation of a silica whose original surface area was $250 \text{ m}^2/\text{g}$, using aqueous zirconium nitrate solutions. These authors have also prepared materials by "a controlled surface reaction between zirconium ethoxide ligands and the protons from the surface hydroxyl groups on the silica support." These materials were investigated by XPS, SIMS, temperature programmed oxidation (TPO), and IR spectroscopy. By measuring the zirconia-to-silica ratios obtained from XPS analysis, these authors found

that the dispersion of zirconia on silica ranged from 12 % for 8 and 16 wt. % $\text{ZrO}_2/\text{SiO}_2$ to 7 % for 24 wt. % $\text{ZrO}_2/\text{SiO}_2$ for impregnated materials, previously calcined at 600°C. The materials prepared by reaction using zirconium ethoxide were found to have a much higher dispersion (about 75 %) following calcination at the same temperature. The acidity of these materials was not studied. Niemantsverdriet *et al.* have obtained similar results using a model system in which zirconia was deposited onto thin SiO_2 layers formed on the surface of Si (100) and studied using XPS and Auger spectroscopy [74].

Navio *et al.* have recently prepared $\text{ZrO}_2/\text{SiO}_2$ mixtures by a sol-gel method [75]. Gels with compositions $x \text{ ZrO}_2 \cdot (100-x)\text{SiO}_2$, $x = 3 - 100$ mole % were prepared using zirconyl chloride and commercial silica gels. It was found that bulk zirconium dioxide exhibited both basic and acidic hydroxyl groups, but that only acidic hydroxyl groups remained once zirconia was deposited on silica. No attempt was made to measure the acidity of these materials as a function of composition.

From the above, it is apparent that the surface properties depend on the method of preparation and that further study is required. We have prepared $\text{ZrO}_2/\text{SiO}_2$ by impregnation of silica with zirconyl nitrate solutions. The acidic properties of these catalysts, and those of silica and zirconia, were investigated using TPD of adsorbed NH_3 and pyridine. In addition, these materials were studied by: transmission Fourier Transform Infrared (FTIR) spectroscopy using ammonia and pyridine as probe molecules; and by X-ray Diffraction (XRD).

Temperature Programmed Desorption (TPD):

Temperature Programmed Desorption (TPD) was developed in 1963 by Amenomiya and Cvetanovic [76] in order to adapt the flash-filament desorption method, a technique widely used to study adsorption on metals, to powders or particles, *ie.* materials of great interest in catalysis that tend to be electrical insulators with poor thermal conductivities. TPD has become one of the most widely used methods for the study of adsorption in catalysis; an overview of this technique has been published by Amenomiya [77].

By heating the sample of interest in a programmed manner with time, desorption of adsorbed material will occur. Analysis of the desorbed products can lead to: identification of various adsorption sites; the strength of adsorption; and their populations. However, although it may be useful TPD cannot distinguish the molecular nature of the adsorption site. Therefore, other techniques must be used in conjunction with TPD. For example, FTIR spectroscopy of adsorbed, basic molecules can be used to probe the nature of acidic adsorption sites.

Ammonia is a relatively strong basic molecule because it possesses a lone pair of electrons at the nitrogen atom which is available for donation to the coordinately unsaturated sites or for accepting a proton from proton donating sites of an oxide surface. Thus, it has been used as a probe for the presence and the nature of surface acid sites on oxides. It may non-dissociatively interact with the surface in one of three different ways. The first involves

the transfer of proton from Bronsted acid sites of the oxide to yield ammonium ions. The second involves the coordination of ammonia through the lone pair of electrons to coordinately unsaturated sites, *i.e.* to Lewis acid sites. The third mode is via hydrogen bonding, which may involve the interaction of the nitrogen with the hydroxyl groups on the surface or of the hydrogen with surface oxygen or the surface oxygen atom of hydroxyl groups. Finally, dissociative adsorption of ammonia is known to occur on some M_xO_y oxide surfaces [78]; yielding surface $M-NH_2$ plus $M-OH$ species.

It is possible to distinguish between the different modes of interaction of ammonia with acid sites using infrared spectroscopy because each type has characteristic vibrations and vibrational frequencies. Coordinated ammonia adsorbed on Lewis acid sites gives rise to: an asymmetric stretching vibration, ν_3 , at $3330-3380\text{ cm}^{-1}$; a symmetric stretching vibration, ν_1 , at $3260-3280\text{ cm}^{-1}$; and an asymmetric bending mode, ν_4 , at $1600-1620\text{ cm}^{-1}$. Ammonium ions adsorbed on Bronsted acid sites show an asymmetric stretching vibration, ν_3 , near 3200 cm^{-1} and an asymmetric bending vibration, ν_4 , near $1400-1470\text{ cm}^{-1}$. Ammonia adsorbed via hydrogen-bonding appears at 3400 and 3320 cm^{-1} due to N-H stretching vibrations [78]. Dissociatively adsorbed MNH_2 species exhibit a very characteristic HNH angle deformation mode in the narrow frequency region from $1560 - 1540\text{ cm}^{-1}$.

Although pyridine is less basic than ammonia, it is also widely used as a probe molecule in infrared studies. Pyridine can interact with Lewis acid sites through the lone pair of its nitrogen atom to form an adsorbed Lewis acid-base adduct. It may also interact with

Bronsted acid sites yielding an adsorbed pyridinium ion. The infrared spectra of these two species are easily distinguishable [79,80]. The ring vibration modes 19b and 8a, according to the original assignments of Kline and Turkevich [81], are the most sensitive vibrations with regard to the nature of intermolecular interactions via the nitrogen lone pair electrons. These two modes are observed at 1447 to 1464 cm^{-1} and at 1600 to 1634 cm^{-1} for Lewis coordinated pyridine and at 1535 cm^{-1} to 1550 cm^{-1} and at around 1640 cm^{-1} for pyridinium ions [79]. Hydrogen bonding is also possible; the same modes are found at 1440 to 1447 cm^{-1} and at 1580 to 1600 cm^{-1} .

Experimental:

Catalyst Preparation:

Silica: Cabosil M-5 fumed silica was used as received. Its stated BET surface area was 200 m²/g.

Zirconia: Degussa zirconia (an experimental product said to be monoclinic) was used as received. Its stated BET surface area was 42±2 m²/g.

Precipitated zirconia was prepared by precipitating zirconium hydroxide from an aqueous solution of zirconyl nitrate [Fisher]. The hydroxide was then filtered and oven-dried overnight at 110°C. The oxide was formed by dehydration of Zr(OH)₄ by heating at 600°C for ten hours in an ashing furnace.

Zirconia/ Silica: Mixtures of 5, 10, and 20 wt.% ZrO₂/SiO₂ were prepared by impregnation of Cabosil M-5 silica with aqueous solutions of zirconyl nitrate [Fisher] by vigorously stirring 2 g of silica into 6 mL of solution of the appropriate concentration until a relatively non-viscous slurry was obtained. The slurry was then oven-dried at 110°C for 24 hours.

Temperature Programmed Desorption (TPD) Experiments:

Samples of $\text{ZrO}_2/\text{SiO}_2$ or precipitated ZrO_2 were ground to a fine powder using a mortar and pestle. All powders were pressed into disks under 27.2 MPa (4000 psig) pressure in a similar fashion to those used as infrared samples (see later). The disks were then broken up and sieved. Granules ranging from 16 to 32 mesh (0.5- 1.0 mm diameter) were used.

A 3/8" diameter stainless steel, fixed-bed reactor was used to house samples for TPD experiments. The oxide samples (100 mg, 16-32 mesh) were placed in the reactor atop a glass wool support. The resulting bed was 1 cm deep. A type K thermocouple was immersed in the bed to monitor the sample temperature.

The system was evacuated to approximately 10^{-2} Pa (10^{-4} torr) via an Edwards Model E0/40 diffusion pump. The samples were activated by heating under vacuum using a resistive-heating furnace. Heating was controlled using an Omega Model CN2011 digital proportional temperature controller. Activation was typically performed at 450°C for one hour. The sample was then cooled to 25°C under dynamic vacuum.

Pyridine and ammonia were purified by repeated freeze-pump-thaw cycles using liquid nitrogen prior to adsorption. Adsorption of pyridine or NH_3 was typically carried out by expanding a known quantity of base into the reactor at room temperature. After the desired contact time, typically between 5 and 60 minutes, the base was recondensed using liquid

nitrogen. After isolation of the reactor, helium was flowed through the catalyst bed (30 mL/min.) at room temperature for at least 30 minutes.

Temperature programmed desorption experiments were conducted by increasing the sample temperature linearly with time at a rate of 15°C/min. A helium gas flow-rate of 30 mL/min was maintained throughout.

Desorbing products were detected in the helium carrier gas using a thermal conductivity detector. In some instances the products were trapped by condensation in a liquid nitrogen cold trap placed after the TCD detector. Analog voltage signals from the TCD and from an Omega Model 670 thermocouple thermometer were recorded on a strip chart recorder.

The amounts of products desorbed during TPD experiments were measured by both direct and indirect means. Direct measurement was performed by condensing the desorbing products with liquid nitrogen into a U-tube sampler that was placed in the effluent line after the thermal conductivity detector. Following an experiment the sampler was isolated, removed from the system, and connected to a vacuum manifold of known volume. After evacuation of helium gas the liquid nitrogen-condensable products were expanded and their pressures were measured.

Integration of the areas under the peaks of the TPD spectra was used as an indirect method for measuring the amounts of desorbed products. Integration was performed by weighing the chart paper encompassed by the spectra. Graph weights were converted into amounts by use of a "standard" experiment. The amount of products desorbed from silica were measured manometrically during an NH_3 experiment, to be 13.23 μmoles . The weight of its corresponding TPD peak was measured to be 0.5939g. Hence a conversion factor of 22.27 $\mu\text{moles/g}$ chart paper was obtained.

In many experiments both methods were used to determine the amounts of products desorbed. Direct comparison of the results showed that the two methods agreed within $\pm 10\%$. Since both methods were ultimately based on manometric measurement they both have comparable accuracies, estimated to be $\pm 10\%$.

Infrared Spectroscopy:

For the IR study, 30 mg of powdered sample was compacted into a self-supporting disk of 25 mm in diameter under 27.2 MPa (4000 psig) pressure. The samples were then placed in quartz sample holders inside a specially designed quartz cell, as described previously [82].

The 300 mL quartz IR cell was connected via an Apiezon N greased ball joint to a Pyrex vacuum line (about 300 ml volume) capable of attaining a base pressure of about

5×10^{-4} Pa (5×10^{-6} torr). All reactant gases were transferred from the main manifold to the IR cell and the pressures were measured with a capacitance manometer.

Fourier transform infrared (FTIR) spectra were recorded by using a Bomem Michelson MB 100 spectrometer equipped with a DTGS detector. Typically, spectra were recorded over the region 1000 cm^{-1} to 3500 cm^{-1} at a resolution of 4 cm^{-1} , coadding 25 scans. All spectra were recorded at room temperature.

Powder X-ray Diffraction Analysis:

X-ray diffraction analysis was performed using a Philips Analytical Model PW3710 powder x-ray diffractometer. The samples were irradiated with Cu K alpha radiation excited by a 50 keV electron beam impinging on a copper target. The current was 35 mA. A monochromator was used to acquire diffraction peaks between $2\theta = 20^\circ$ and 65° .

Results and Discussion:

Infrared Spectra of the hydroxyl stretching region:

It is well known that the hydroxyl groups on the surface of silica exhibit characteristic OH stretching vibrations in the spectral region from 3800 to 3200 cm^{-1} . The infrared spectrum of silica exhibits a sharp peak at 3747 cm^{-1} , due to the isolated, noninteracting surface silanol groups, and a broad band at lower frequency, which is more complicated, generally due to hydrogen bonding of silanol groups and internal silanols which are perturbed due to interparticle contact [83-85].

Infrared spectra of ZrO_2 in the hydroxyl region have been previously reported [86-88]. In general, the ZrO_2 which is prepared by precipitation from solutions of zirconium salts can exist in either the monoclinic or the tetragonal phase, depending on the thermal treatment. The two zirconia polymorphs have different surface chemical properties and therefore their surface hydroxyl groups exhibit different vibrational frequencies [89,90]. In general, there are two bands in the 3775 to 3650 cm^{-1} region which can be observed for both phases of ZrO_2 . The higher frequency near 3770 cm^{-1} is assigned to stretching vibration of Zr-O-H groups while the lower frequency is assigned to stretching vibration of hydroxyl groups bonded to multiple zirconium atoms [88]. The hydroxyl groups bonded to one zirconium atom are more reactive than the ones bonded to multiple zirconium atoms [86].

The infrared spectra of $\text{ZrO}_2/\text{SiO}_2$ were quite similar to that of pure silica in the 3000 - 400 cm^{-1} region except in the hydroxyl stretching region. The spectra observed in the hydroxyl stretching region for $\text{ZrO}_2/\text{SiO}_2$ samples with different loadings of ZrO_2 , after vacuum activation at 450°C, are shown in Figure 3.1. All of the spectra of $\text{ZrO}_2/\text{SiO}_2$ showed, in addition to the strong band due to isolated SiOH groups at 3747 cm^{-1} [83-85], a shoulder at 3788 cm^{-1} , and a broad band near 3678 cm^{-1} due to ZrOH. The ZrOH bands are shifted to higher frequency relative to those observed for the hydroxyl groups on pure ZrO_2 [86,87]. This shift may result from a strong interaction between zirconia and silica, and this will be discussed later.

Thermal stability of hydroxyl groups:

Figure 3.2 shows the infrared spectra of 10 wt. % $\text{ZrO}_2/\text{SiO}_2$ previously evacuated at different temperatures. It was observed that the intensities of the bands at 3788 and 3678 cm^{-1} decrease with increasing evacuation temperature and that the intensity of band at 3678 cm^{-1} decreased more quickly than that of the band at 3788 cm^{-1} . It appears that the species responsible for the band at 3788 cm^{-1} is more thermally stable than that giving the band at 3678 cm^{-1} .

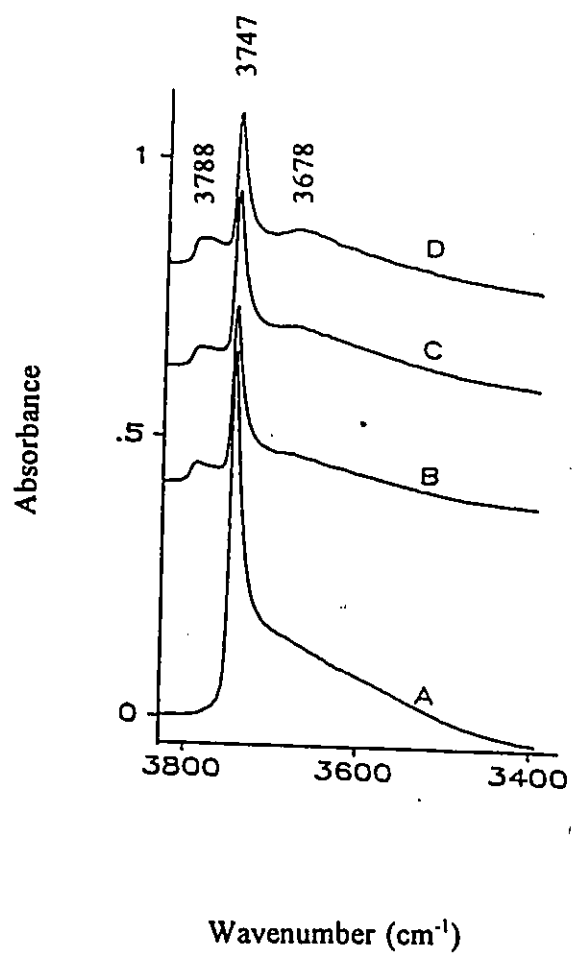


Figure 3.1: Infrared spectra of the hydroxyl stretching region for $\text{ZrO}_2/\text{SiO}_2$ with varying amounts of zirconia. Activated at 450°C .

- (A) Silica
- (B) 5 wt. % ZrO_2
- (C) 10 wt. % ZrO_2
- (D) 20 wt. % ZrO_2

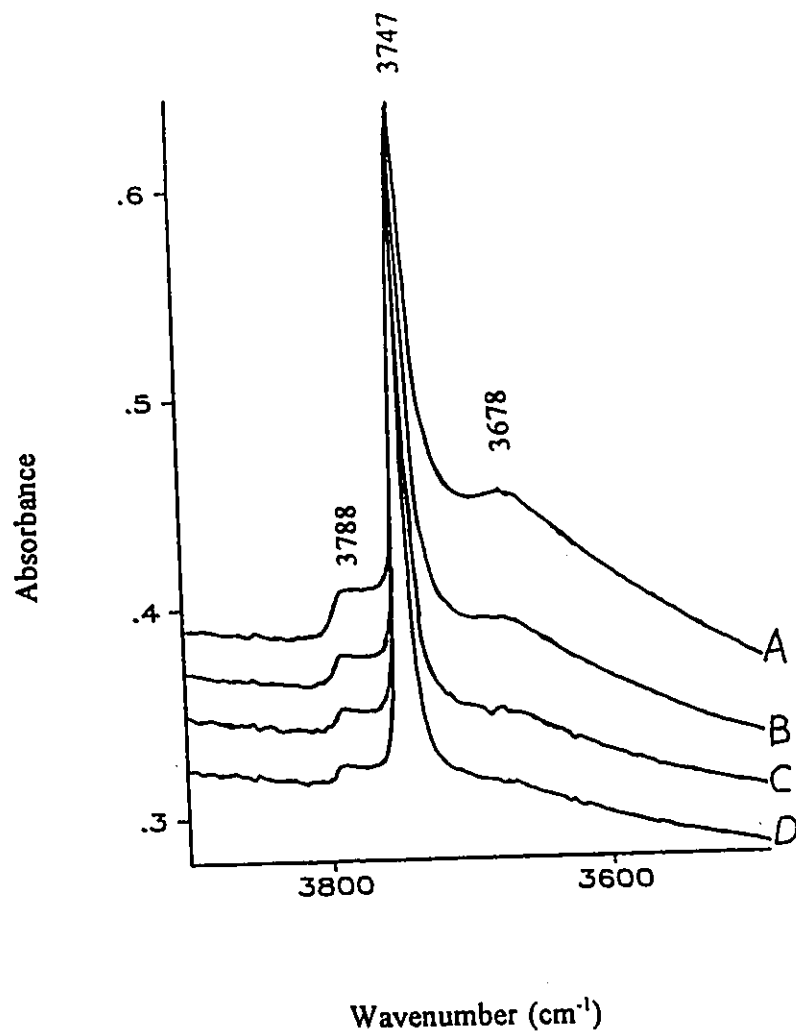


Figure 3.2: Infrared spectra of 10 wt. % $\text{ZrO}_2/\text{SiO}_2$ in hydroxyl stretching region.

Samples activated by evacuation at various temperatures.

- (A) 450°C
- (B) 550°C
- (C) 650°C
- (D) 750°C

Effect of water on hydroxyl groups:

Figure 3.3 illustrates the effects of adsorbed water on the surface hydroxyl groups of $\text{ZrO}_2/\text{SiO}_2$. In this experiment a 10 wt. % $\text{ZrO}_2/\text{SiO}_2$ sample was first evacuated at 450°C , 8 torr of water vapour was added, followed by evacuation at room temperature. The sample was evacuated again at 450°C . It was observed that both bands at 3788 and 3678 cm^{-1} disappeared after water vapour was added and that a new broad band at 3590 cm^{-1} was formed, which is evidently attributed to hydrogen bonding between adsorbed water and the surface hydroxyl groups. Both bands at 3788 and 3678 cm^{-1} were restored by evacuation again at 450°C .

D_2O exchange of surface hydroxyl groups:

Figure 3.4 shows the spectra obtained following D_2O isotopic exchange reactions of the surface hydroxyl groups of 10 wt. % $\text{ZrO}_2/\text{SiO}_2$. The sample was evacuated at 450°C and then the exchange reaction was carried out by adding 5 torr of D_2O , waiting for 30 minutes and then evacuating for 30 minutes at 450°C . The exchange process was performed three times. After the exchange reaction the new bands at 2785 , 2758 and 2712 cm^{-1} appeared and the band at 3788 cm^{-1} disappeared. The intensities of bands at 3747 and 3678 cm^{-1} were also decreased. The strong band at 2758 cm^{-1} is due to the stretching vibration of OD groups on silica [83-85]. The bands at 2785 and 2712 are close to the frequencies of the stretching vibrations of OD groups on pure ZrO_2 which appear at 2780 and 2705 cm^{-1} [86,87].

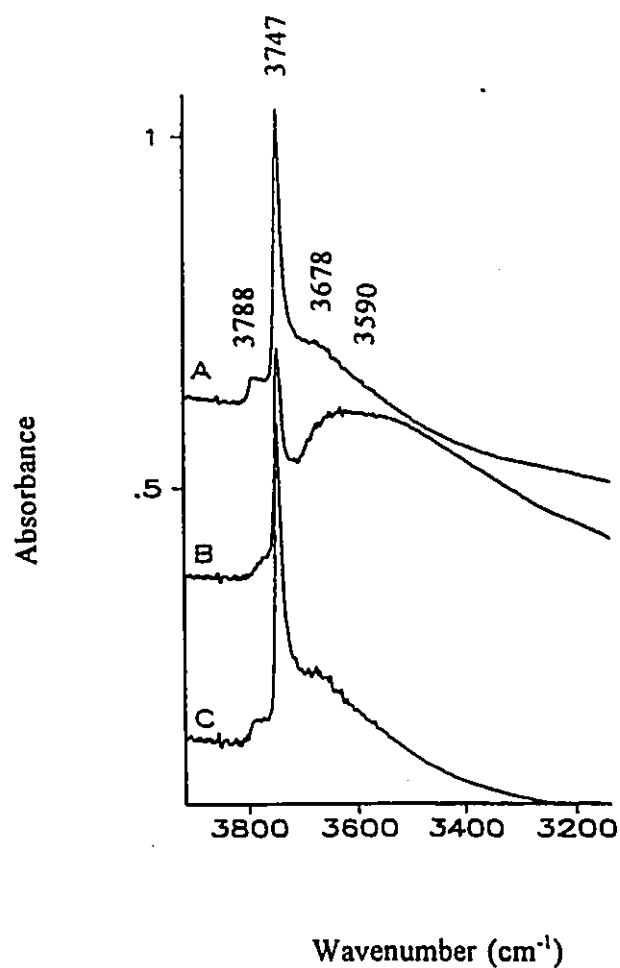


Figure 3.3: Effect of adsorbed water, at 22°C, on the infrared spectra

of 10 wt. % $\text{ZrO}_2/\text{SiO}_2$ in the hydroxyl stretching region.

(A) evacuated at 450°C

(B) following adsorption of water vapour (8 torr) followed by evacuation at room temperature.

(C) following reactivation at 450°C

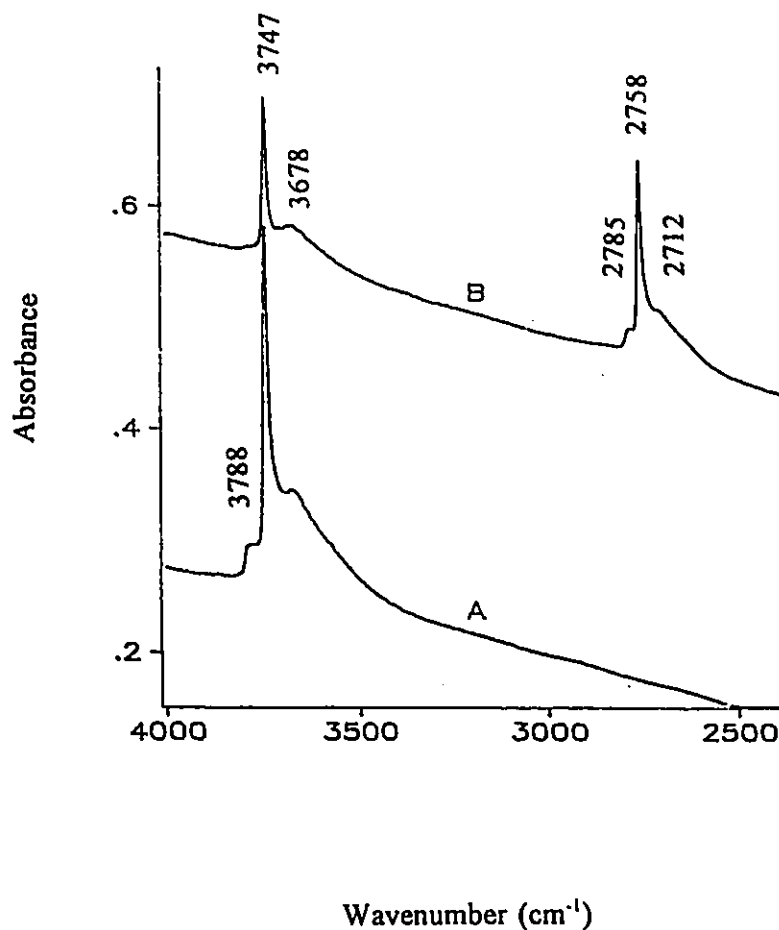


Figure 3.4: Infrared spectra of 10 wt. % $\text{ZrO}_2/\text{SiO}_2$ in hydroxyl stretching region before and after D_2O isotopic exchange reaction.

(A) evacuated at 450°C

(B) after D_2O exchange reaction (5 torr D_2O added and sample heated at 450°C for 30 minutes, process repeated three times to ensure complete exchange.)

NH₃ Adsorption on SiO₂:

Room temperature adsorption of NH₃ (contact time 60 minutes) on silica, activated at 450°C for 1 hour, followed by a 30 minute room-temperature helium purge produced an intense, symmetrical peak at 86°C in the TPD spectrum between 25°C and 450°C. The amount of NH₃ desorbed was 112 μmoles/g SiO₂ (determined by manometric measurement of condensed products). This peak could be totally eliminated if the reactor was first evacuated at room temperature for 21 hours prior to running the TPD experiment. It is therefore attributed to ammonia that was physisorbed or hydrogen-bonded to surface hydroxyl groups on silica. No other peaks were observed.

Infrared Spectrum of NH₃ on SiO₂:

Infrared spectra of ammonia adsorbed on the pure silica have been reported previously [83-85], and the current spectra are consistent with the results published. In this experiment, the silica was first activated under evacuation at 450°C for 2 hours and then exposed to 8 torr of ammonia at room temperature. After adsorption for 40 minutes the spectra were obtained during stepwise reduction of the ammonia pressure; the silica was finally evacuated at room temperature for 40 minutes. In the region 3800-2800cm⁻¹, the spectra exhibit: two absorption bands at 3400 cm⁻¹ and 3320 cm⁻¹; a shoulder at 3260 cm⁻¹ and a broad band with maximum at 3000 cm⁻¹. A decrease in the intensity of the band at 3747 cm⁻¹, which is assigned to the stretching vibration of isolated hydroxyl groups on silica, was also observed. The spectra in

the 1800-1300 cm^{-1} region show an absorption band at 1636 cm^{-1} and a weak band at 1555 cm^{-1} . The intensity of all the bands, except the band at 1555 cm^{-1} , decrease rapidly upon desorption. After evacuation at room temperature, there was a new broad band at 3524 cm^{-1} and a shoulder at 3445 cm^{-1} . Like the band at 1555 cm^{-1} , these were resistant to evacuation.

It has been established that ammonia is adsorbed on surface hydroxyl groups of silica by hydrogen bonding of the nitrogen atom to the hydrogen of the surface hydroxyl groups. The band for the perturbed hydroxyl groups is present at about 3000 cm^{-1} , while the bands of the stretching vibrational modes, ν_3 and ν_1 , of N-H bonds occur at 3400 cm^{-1} and 3320 cm^{-1} ; the asymmetrical bending mode, ν_4 , of the bonds occurs at 1636 cm^{-1} . The symmetric bending mode, ν_2 , cannot be directly observed due to strong absorption by the silica background. However, according to the conclusion drawn in reference [83], the band should be near 1050 cm^{-1} . The bands at 3524, 3445 and 1555 cm^{-1} , which cannot be removed by evacuation at room temperature, are known to be due to the stretching vibrations of surface SiNH_2 groups arising from the dissociation of ammonia molecules on the surface of silica [78].

The above results indicate that most of the ammonia is adsorbed on the surface hydroxyl groups of silica via hydrogen bonding. A small amount of the ammonia underwent dissociative adsorption on the surface of silica, known to be a result of the preactivation of silica under vacuum at 450°C. No Lewis or Bronsted acid sites were detected by infrared studies of the adsorption of ammonia on silica. This supports the previous assignment of the

intense, symmetrical peak at 86°C in the TPD spectrum to physisorbed or hydrogen-bonded ammonia.

NH₃ Adsorbed on Zirconia:

(1) Adsorption on Precipitated ZrO₂:

The TPD spectrum showed a sharp rise to 110°C where a plateau more or less extended to 450°C (see Figure 3.5b). The intensity of this broad, flat peak was quite low compared to the peak observed on silica. The amount of NH₃ desorbed was 143 μmoles/ g ZrO₂ (measured by graphical integration). It is apparent that many different types of adsorption sites exist on the zirconia surface and/or that there is a wide range of energies for these sites. These sites probably include: hydrogen-bonding sites similar to those on silica; and Lewis acid sites. The presence of Bronsted acid sites, ZrO⁺(NH₄⁺), cannot be ruled out by TPD alone. However, it is doubtful that zirconia is acidic enough to protonate NH₃. The IR spectra indicated that no Bronsted acidity exists; only Lewis acidity was observed.

(2) Adsorption of NH₃ on Degussa ZrO₂:

The TPD spectrum was virtually identical in shape to that observed for precipitated zirconia (see Figure 3.5a). However, the total amount of NH₃ desorbed (255 μmoles/ g ZrO₂) was 78 % greater than that desorbed from the precipitated ZrO₂ under similar experimental conditions. The IR spectra were similar to those obtained on precipitated zirconia.

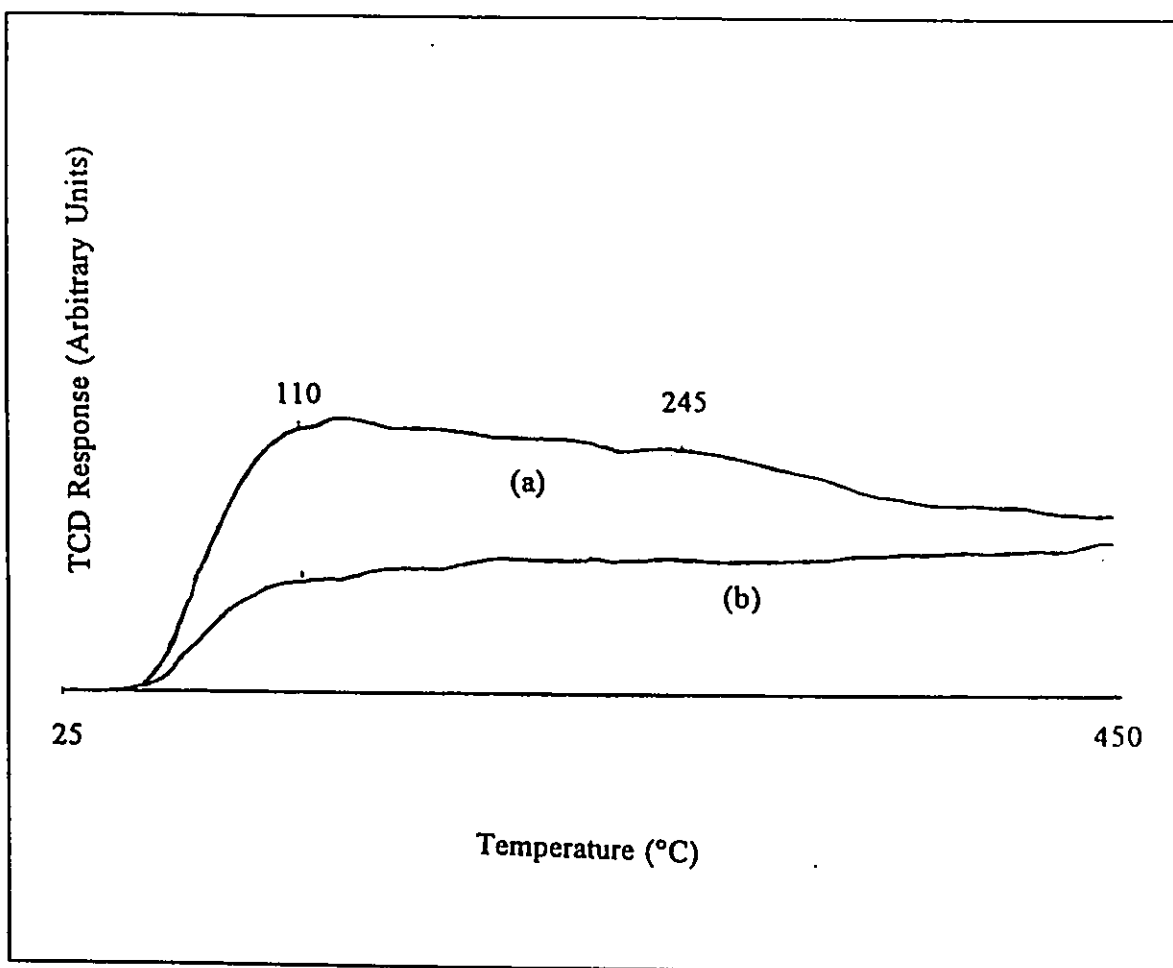


Figure 3.5: TPD spectrum of ammonia on activated zirconia 450°C.

(a) Degussa ZrO₂ (b) precipitated ZrO₂.

Ammonia adsorption on $\text{ZrO}_2/\text{SiO}_2$:

All experiments in which ammonia was adsorbed at room temperature on activated $\text{ZrO}_2/\text{SiO}_2$ catalysts gave characteristically similar TPD spectra. Figure 3.6 shows the TPD spectrum obtained during NH_3 desorption from a 10 wt.% sample that had been previously activated at 450°C . The spectrum shows two peaks. The first peak rises sharply to a maximum at 92°C . It resembles the peak observed for NH_3 on pure silica obtained under similar conditions (maximum at 86°C) but is more intense and it is skewed to the high temperature side (see Figure 3.7, a comparison of SiO_2 to 5,10,20 wt.% $\text{ZrO}_2/\text{SiO}_2$). The second peak is unresolved from the first but appears somewhat symmetrical about a maximum temperature of 240°C .

Figure 3.7 shows the TPD spectra obtained during NH_3 desorption from 5,10, and 20 wt.% $\text{ZrO}_2/\text{SiO}_2$ samples which had been previously activated at 450°C . The spectrum obtained for pure silica is included for comparison. From the figure it is apparent that all three samples adsorb similar amounts of ammonia.

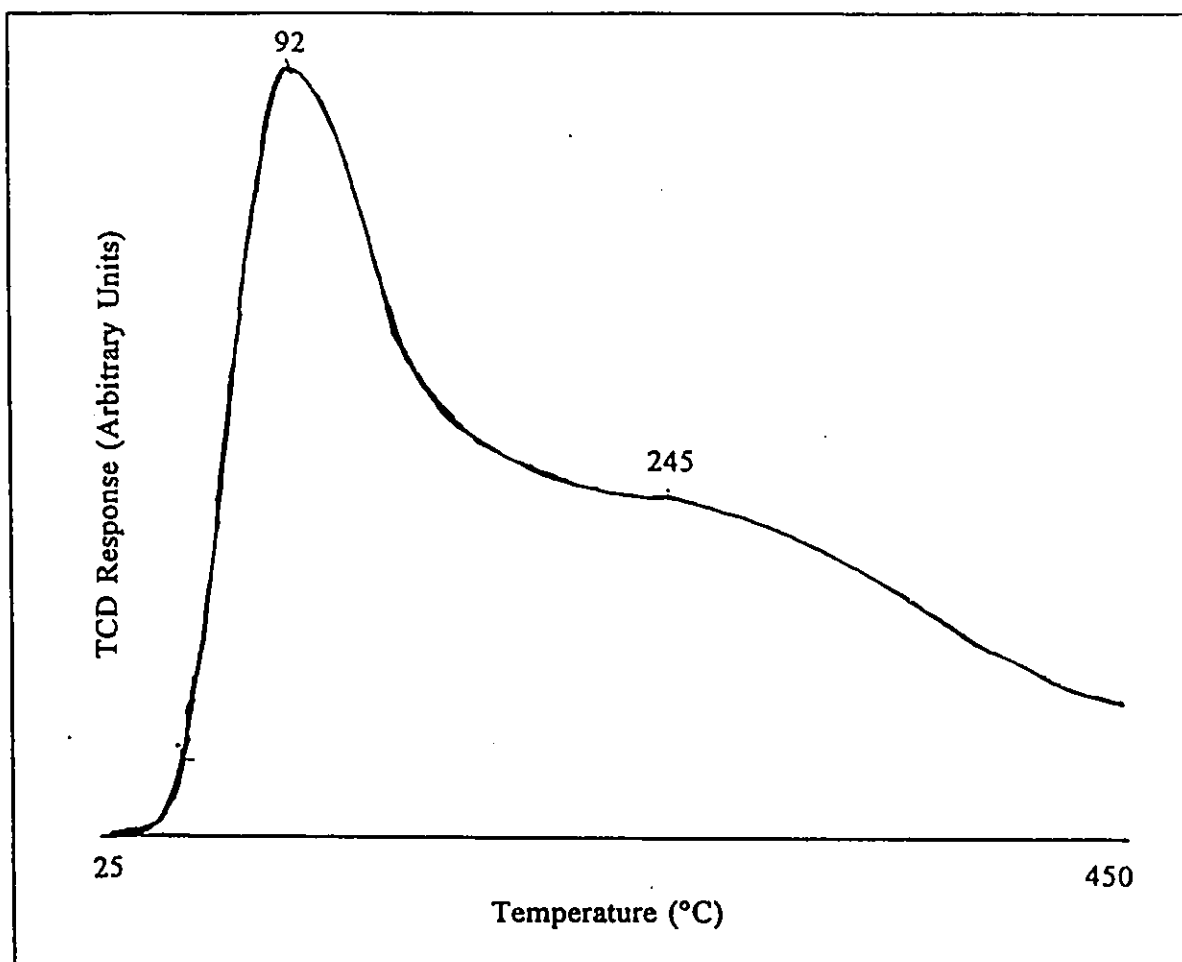


Figure 3.6: TPD spectrum of ammonia on 10 wt.% $\text{ZrO}_2/\text{SiO}_2$ previously activated at 450°C

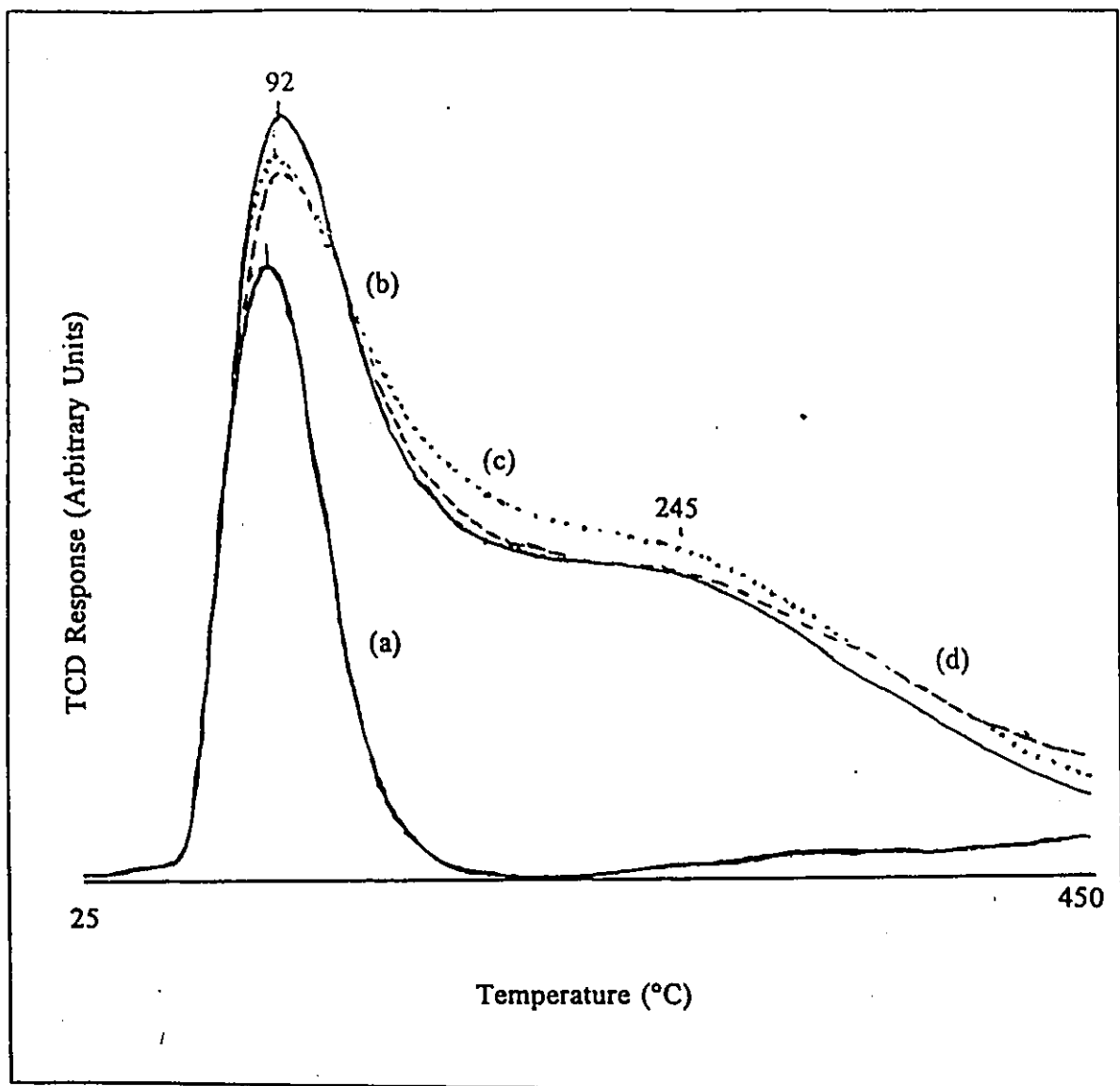


Figure 3.7: Ammonia TPD spectra as a function of loading of zirconia on silica, activated at 450°C. (a) silica (b) 5 wt.% (c) 10wt.% (d) 20 wt.% $\text{ZrO}_2/\text{SiO}_2$

Table 3.1 shows the amounts of products desorbed during TPD from SiO_2 and $\text{ZrO}_2/\text{SiO}_2$ mixtures following NH_3 adsorption at 25°C for one hour. The samples had been previously activated by evacuation at 450°C for 60 minutes.

As shown in the table the amount desorbed increased by more than 350% from silica to 5 wt.% $\text{ZrO}_2/\text{SiO}_2$. The amount was then constant, within experimental error, with varying composition over the range measured.

Table 3.1: Amount of products desorbed from $\text{ZrO}_2/\text{SiO}_2$ during an NH_3 TPD experiment from 25°C to 450°C . NH_3 adsorption was carried out at 25°C for 60 minutes.

Experiment #	Composition (wt.% ZrO_2)	Amount Desorbed ($\mu\text{moles/ g sample}$)
13	0	112
26	5	398
33	10	405
29	20	449

An attempt was made to measure the amounts of products desorbed from the higher temperature peak at various compositions. The adsorbed species responsible for the first peak were first removed by heating the catalyst to 80°C in flowing helium following room

temperature adsorption of NH_3 . Although considerable overlap existed between the two peaks, Figure 3.8 shows that these conditions successfully eliminated the first peak with minimal disturbance to the second. Table 3.2 shows the measured amounts of products that were collected during TPD from 25°C to 450°C after first purging the catalyst in helium at 80°C for 30 minutes.

Table 3.2: Amount of NH_3 desorbed from $\text{ZrO}_2/\text{SiO}_2$ during TPD from 25°C to 450°C after purging at 80°C with helium for 30 minutes.

Experiment #	Composition (wt.% ZrO_2)	Amount Desorbed ($\mu\text{moles/g}$ sample)
27	5	241
30	10	260
28	20	270

Again the amounts measured were constant, within experimental error, with varying composition over the range measured. These values are very close to those determined by Dzisko [72] for 10 and 20 % $\text{ZrO}_2/\text{SiO}_2$ (280 $\mu\text{moles/g}$) by n-butylamine adsorption as mentioned in the introduction.

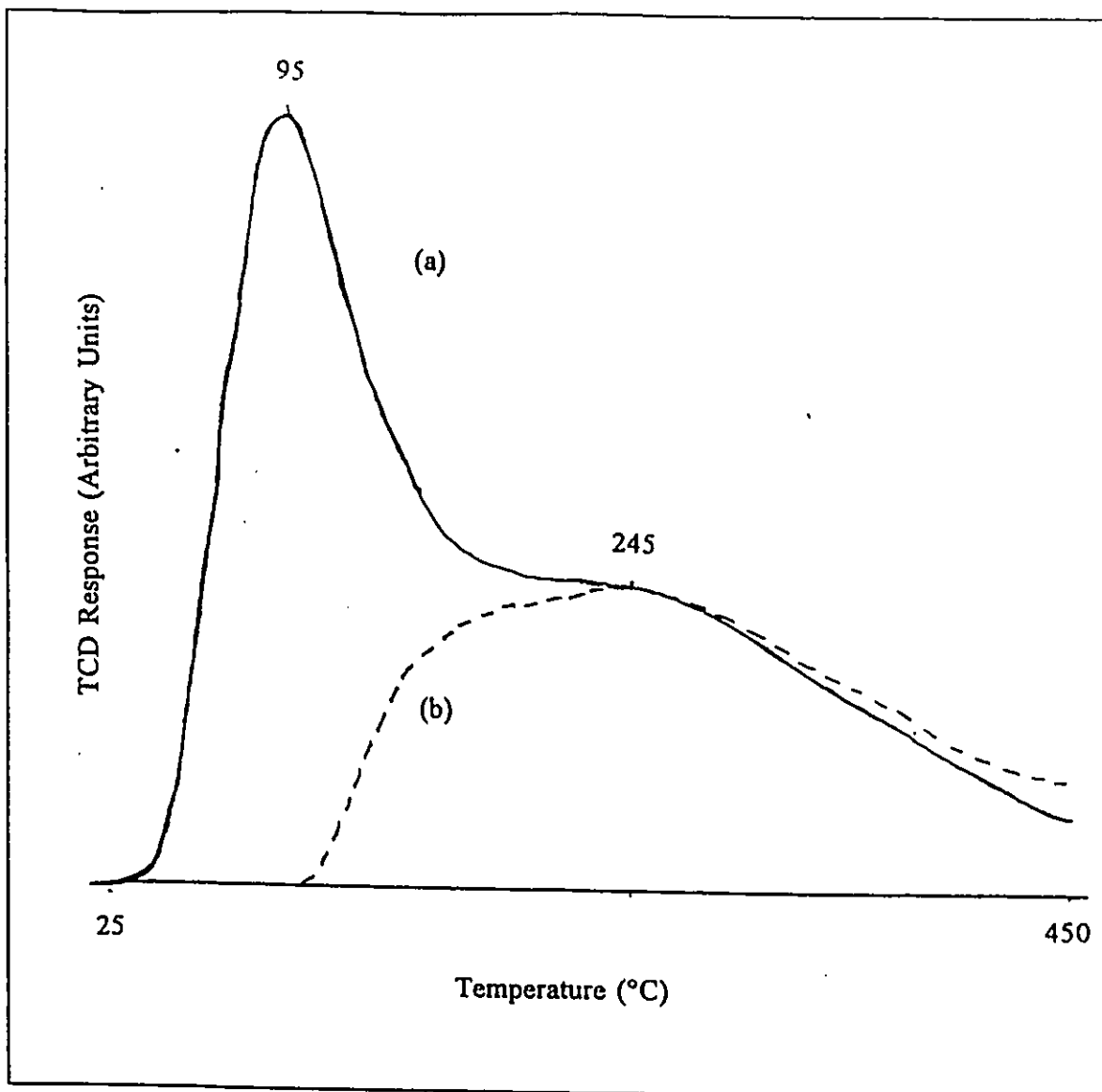


Figure 3.8: TPD spectra following room temperature adsorption of ammonia on 5 wt.% $\text{ZrO}_2/\text{SiO}_2$ (activated 450°C).
(a) Helium purge at room temperature prior to TPD experiment
(b) Helium purge at 80°C for 30 minutes prior to TPD experiment.

As stated above, the first peak observed in the NH_3 TPD spectra (at 92°C) resembled that observed on pure silica, except that it was slightly more intense and was skewed to the high-temperature side. Since this peak was attributed to physisorbed or hydrogen-bonded NH_3 on silica it is likely that on $\text{ZrO}_2/\text{SiO}_2$ the peak also has a large component from these species. In addition there is an unresolved component that is due to analogous hydrogen-bonded NH_3 species on the surface hydroxyl groups of zirconia. It should be recalled that the NH_3 TPD spectra on pure ZrO_2 rose sharply to a plateau at about 110°C . Thus, these species do in fact appear at slightly higher temperatures on zirconia than on silica. This also explains why the peak maxima are slightly shifted to higher temperature and why the peaks are skewed to higher temperatures. As with silica this low temperature peak could be completely removed by evacuation at 25°C for 21 hours.

The second peak in the NH_3 TPD spectrum of $\text{ZrO}_2/\text{SiO}_2$ (at 240°C) could be separated from the first with minimal disturbance by flushing with helium at 80°C (see Figure 3.8). By analogy with the spectra obtained on pure zirconia this broad peak is attributed to Lewis-acid coordinated NH_3 . Again a large range of energies must be present. As with pure zirconia, the presence of Bronsted-acid coordinated NH_3 cannot be excluded on the basis of TPD alone. The assignment of this peak to Lewis-acid coordinated ammonia is supported by infrared studies as will be discussed later in this chapter.

FTIR Results of NH₃ on ZrO₂/SiO₂ :

The infrared spectra of ammonia adsorbed on ZrO₂/SiO₂ with different loading amounts of zirconia were recorded. The experimental procedure was the same as that described previously for ammonia adsorption on silica.

When a lower amount of zirconia (5 wt.%) was supported on silica, the features of the infrared spectra of adsorbed ammonia were quite similar to those of ammonia on pure silica, showing absorption bands at 3400, 3321 and 1632 cm⁻¹; these have been assigned to the N-H stretching and deformation vibrations of hydrogen-bonded ammonia. However, a new weak band appeared at 1607 cm⁻¹ and a weak, broad band appeared with maximum at 1465 cm⁻¹. Following evacuation at room temperature, there were bands remaining at 3385, 3285 and 1607 cm⁻¹ (see Figure 3.9). As the intensity of the bands at 3400, 3321 and 1632 cm⁻¹ decreased, there was an increase in the intensity of the band at 3747 cm⁻¹. Unlike the absorption bands of hydrogen bonded ammonia, the bands at 3380, 3288 and 1607 cm⁻¹ were resistant to evacuation at room temperature. These bands are assigned to Lewis acid-coordinated NH₃ on the surface of ZrO₂/SiO₂.

When the loading amount of zirconia on silica was increased to 10 wt.% and 20 wt.%, there was an obvious decrease in intensity of absorption bands at 3400, 3321 and 1632 cm⁻¹ due to hydrogen-bonded ammonia. However, as is shown in Figure 3.9, there was an increase in the intensity of the absorption bands of coordinately adsorbed ammonia

(at 3385, 3288 and 1607 cm^{-1}) following evacuation at room temperature. It is apparent that an increase in the zirconia loading results in an increase in the quantity of coordinatively adsorbed ammonia. We conclude that the number of coordinately unsaturated sites increases with zirconia loading.

In addition to the aforementioned bands, for adsorbed ammonia on $\text{ZrO}_2/\text{SiO}_2$, a weak, broad band appeared at 1460-1440 cm^{-1} that was resistant to evacuation at room temperature but was easily removed upon evacuation at 100°C. A band in this region is often attributed to the asymmetric deformation mode, ν_4 , of the ammonium ion. This indicates that there are some proton donating sites, *i.e.* Bronsted acid sites, on the surface of $\text{ZrO}_2/\text{SiO}_2$. However, the infrared spectra of pyridine adsorbed on $\text{ZrO}_2/\text{SiO}_2$ indicated that only coordinately adsorbed pyridine was formed under similar experimental conditions. Since ammonia is a stronger base than pyridine, it is possible that the strength of the surface acid sites was sufficient to protonate ammonia but not pyridine. The possibility also exists that the sterically larger pyridine molecule was hindered from contact with surface acid sites. There are however two factors which suggest that ammonium ions were not formed, *i.e.* Bronsted acid sites were not present. The first is the width of the peak at about 1455 cm^{-1} ; its full width at half maximum was about 40 cm^{-1} . Bands at this frequency which are normally observed for an adsorbed ammonium ion with T_d symmetry are sharper. The increased width suggests a lowering of the symmetry; the degeneracy of these modes is removed causing peak broadening. We suggest therefore, that this weak, broad band is attributed to hydrogen-bonded, adsorbed ammonia molecules, which are expected to result from the strong interaction of ammonia molecules

surface hydroxyl groups. The ability to remove this broad band by evacuation at 100°C is further evidence that this broad band is due to a weaker hydrogen-bonding interaction rather than to Bronsted acidity.

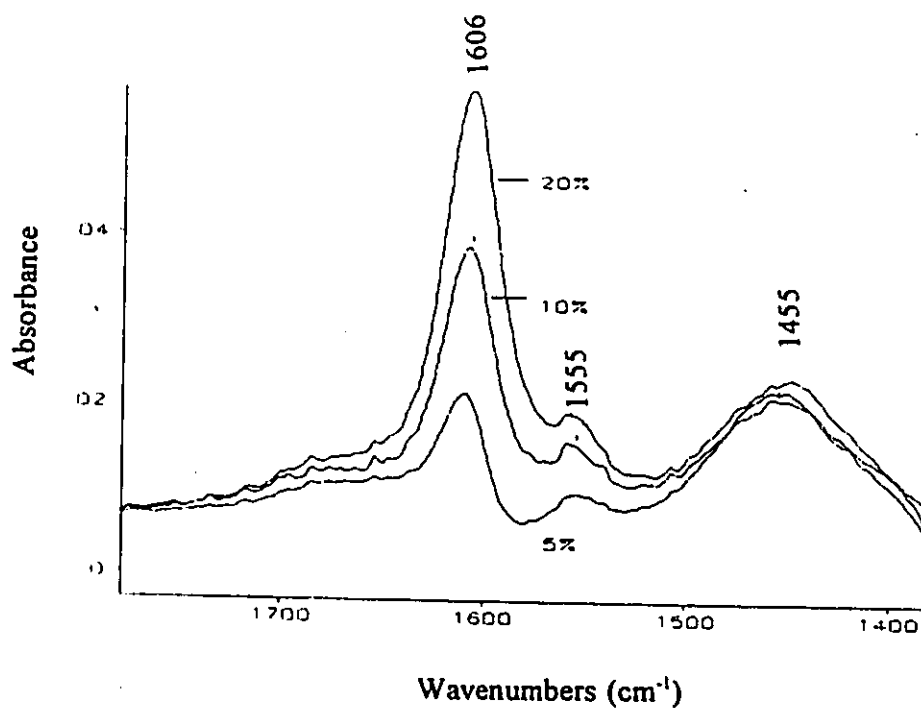


Figure 3.9: Infrared spectra showing ammonia adsorption as a function of zirconia loading on silica (as weight percent). Ammonia (8 torr) was adsorbed at room temperature. The sample was then evacuated at room temperature for 30 minutes.

Effects of NH₃ Contact Time on TPD Spectra:

Very little change was observed in the TPD spectra when the contact time for room temperature NH₃ adsorption was increased from 5 minutes to 60 minutes on 10 wt.% ZrO₂/SiO₂ and on 20 wt.% ZrO₂/SiO₂ samples that had previously been activated at 450°C. In both cases the same two peaks were observed. An 11% increase in the amount of products desorbed (as measured by graphical integration) was observed in both cases. Given that the experimental error for these measurements was estimated to be ±10%, these increases are almost indistinguishable. Nevertheless, most TPD experiments were performed following a 60 minute contact time in order that more direct comparison could be made with infrared experiments.

An experiment was performed in which 10 wt.% ZrO₂/SiO₂ (450°C activation) was exposed to NH₃ gas at 300°C while cooling. Once the sample had reached room temperature (after 60 minutes contact with NH₃) helium purging and TPD was carried out as usual. The resultant TPD spectrum was identical to that obtained following room temperature NH₃ adsorption as described above. This result indicates that the activation energy for adsorption on the stronger adsorption sites is not appreciably larger than the activation energy for adsorption on the weaker sites. The reasoning for this conclusion is as follows. If these sites possess a high activation energy for adsorption the rate of uptake by these sites will be slow at lower temperatures. If the adsorption temperature is increased the rate of adsorption on these sites will increase. Thus by increasing the adsorption temperature the amount of

adsorption would increase (yielding a larger TPD peak) relative to that observed at lower temperature and similar contact time. The constancy of the TPD spectra indicate that this is not the case.

Effects of Activation Temperature on NH₃ TPD Spectra:

Room temperature NH₃ adsorption on 10 wt.% ZrO₂/SiO₂ activated at 450°C and at 600°C for 1 hour produced similar TPD spectra. The lower temperature peak in the spectrum of the 600°C activated sample was reduced in intensity by a small amount relative to that obtained on the 450°C activated sample. Such a reduction can be explained by a decrease in the number of surface hydroxyl groups available for hydrogen-bonding with NH₃ on the sample that had been activated at higher temperature due to a greater degree of surface dehydration. In spite of this, the total amount of product desorbed differed by less than 10%.

Blank Experiments:

In order to ensure the accuracy of the NH_3 TPD experiments several blank experiments were performed. Firstly, a typical NH_3 TPD experiment was performed in a reactor that contained no catalyst. No peaks were observed in the TPD spectrum following room temperature NH_3 exposure of the reactor for 60 minutes. This ensures that no peaks were artifacts due to desorption of NH_3 from the reactor system. Secondly, a 10 wt.% $\text{ZrO}_2/\text{SiO}_2$ sample was activated at 450°C , cooled to room temperature, and held under static vacuum for 60 minutes. Again the TPD spectrum showed no peaks, which excludes the possibility of any artifacts due to contamination via any leakage into the system.

Other NH_3 TPD Experiments:

In order to ensure that room temperature purging of the reactor with helium (30 mL/min) following NH_3 adsorption was sufficient to remove all weakly-bound species, evacuation at room temperature was carried out for 30 minutes via a diffusion pump before helium purging. No differences were observed in the TPD spectra obtained under the two different conditions. However, continued evacuation for 21 hours resulted in the complete removal of the lower temperature peak, as discussed above. This result has significance when comparing the results obtained by TPD with those obtained by infrared. In the latter experiments NH_3 was removed strictly by evacuation.

It should be noted that infrared spectroscopy revealed that no hydrogen-bonded NH_3 remained on the surface of $\text{ZrO}_2/\text{SiO}_2$ samples following room temperature evacuation for 30 minutes. This result is in apparent conflict with the results of TPD, which showed that the intense peak at 92°C , which has been attributed to these species, remains following 30 minutes of purging or evacuation. This discrepancy is due to differences in the two experimental systems used. The IR experiments were performed on thin self-supporting disks (30 mg) which were housed in a large volume pyrex cell on a vacuum manifold which had a minimum constriction of 5 mm ID. and was about 10 cm in length. The TPD experiments were carried out on a packed-bed column (1.0 cm long) of 16-32 mesh particles contained within a reaction system with 1/8" ID. stainless steel tubing. Therefore the conductance of the two vacuum systems was considerably different, the former being much higher than the latter. As a result, care must be taken when comparing results obtained with the two systems.

Kumbhar *et al.*[91] observed similar low temperature desorption peaks (77°C for ZrO_2 ; 97°C for boric acid-treated ZrO_2 ; 100°C for phosphoric acid-treated ZrO_2) during NH_3 TPD experiments conducted in a packed-bed reactor similar to that used in this study. These authors stated that all physisorbed NH_3 was removed by room-temperature purging with dry N_2 prior to performing a TPD experiment and therefore attributed these peaks to "weak acid sites". By comparison, in a study of zeolites having a high silica to alumina ratio ($\text{Si}/\text{Al} > 10$) Lok *et al.*[92] attributed NH_3 TPD peaks below 100°C to "mainly physically adsorbed NH_3 molecules" on the basis of complimentary infrared spectroscopic data. As discussed by Tanabe [93] measurement of acidity by adsorption and desorption of gaseous

bases has the advantage that it can be carried out at temperatures of several hundred degrees centigrade or under actual operating conditions of the catalyst. It suffers from the disadvantage that it is difficult to distinguish between physical and chemical adsorption.

In another experiment NH_3 was adsorbed at room temperature on 10 wt.% $\text{ZrO}_2/\text{SiO}_2$ (450°C activation). The sample was then evacuated at 200°C for 40 minutes prior to TPD from 25°C to 450°C. The resulting spectrum showed a flat baseline to 280°C whereupon a peak rose to a maximum at 370°C. Although the intensity of this peak was not large it clearly showed that some species still remain on the surface following 200°C evacuation. It should be recalled that these high temperature species have been assigned to Lewis-acid coordinated NH_3 . By comparison, infrared experiments performed under similar evacuation conditions showed that all bands due to Lewis-acid coordinated NH_3 were removed. In fact infrared experiments could not detect any remaining adsorbed species. Again the discrepancy was caused by a difference in experimental conditions as discussed previously. Evacuation at 200°C for 6 hours removed the TPD peak.

Following a typical NH_3 TPD experiment a 5 wt.% $\text{ZrO}_2/\text{SiO}_2$ was cooled to room temperature in flowing helium and the TPD spectrum was rerun. No peaks were observed to 450°C. Although this result indicates that all adsorbed NH_3 species were desorbed during the initial TPD experiment to 450°C, the possibility that some very strongly adsorbed species (which would desorb at temperatures greater than 450°C) might remain cannot be excluded. However, the amount remaining cannot be large since the calculated amount of NH_3

remaining on the surface prior to the TPD experiment was typically within 20% of the calculated amount desorbed. However, the vast majority of experiments were performed on new samples.

TPD of Pyridine on $\text{ZrO}_2/\text{SiO}_2$:

$\text{ZrO}_2/\text{SiO}_2$ (10 wt.%) was activated at 450°C for one hour and cooled to room temperature under dynamic vacuum. Pyridine was adsorbed at 25°C for 7 minutes (0.34 torr). Following helium purging at 25°C for 30 minutes the TPD spectrum was run from 25°C to 450°C at 15°C/min. The resultant spectrum is shown in Figure 3.10a. Only a small inflection beginning at 325°C was observed for this small amount of pyridine. Attempts to remove the peak by evacuation at room temperature for 24 hours prior to TPD were unsuccessful. Thus, this peak is attributed to Lewis acid coordinated pyridine. This assignment is supported by infrared studies as will be discussed later.

It should be noted that all physisorbed and weakly-chemisorbed (i.e. hydrogen-bonded) pyridine was removed by room temperature purging with helium. This result agrees with infrared experiments which showed that mainly Lewis acid-coordinated pyridine remained on 10 wt.% $\text{ZrO}_2/\text{SiO}_2$ following evacuation at room temperature for 40 minutes; only a shoulder remains at 1595 cm^{-1} due to hydrogen-bonded pyridine. However, in the case of NH_3 adsorption on SiO_2 , ZrO_2 , and on $\text{ZrO}_2/\text{SiO}_2$, hydrogen-bonded NH_3 was not removed by room temperature helium purging prior to TPD. The difference in behaviour between pyridine and

NH_3 can be explained by their relative basicities in aqueous solution. As suggested by Kung, hydrogen-bonding interactions are similar in nature to the interactions present in solution and hence similar trends would be observed. Since ammonia is a stronger base in solution than pyridine, it would be expected to form a more tenacious hydrogen bond with surface hydroxyls than pyridine would. As a result, hydrogen-bonded pyridine should be more easily removed than hydrogen-bonded NH_3 [94 and references therein]. The data obtained are consistent with this hypothesis.

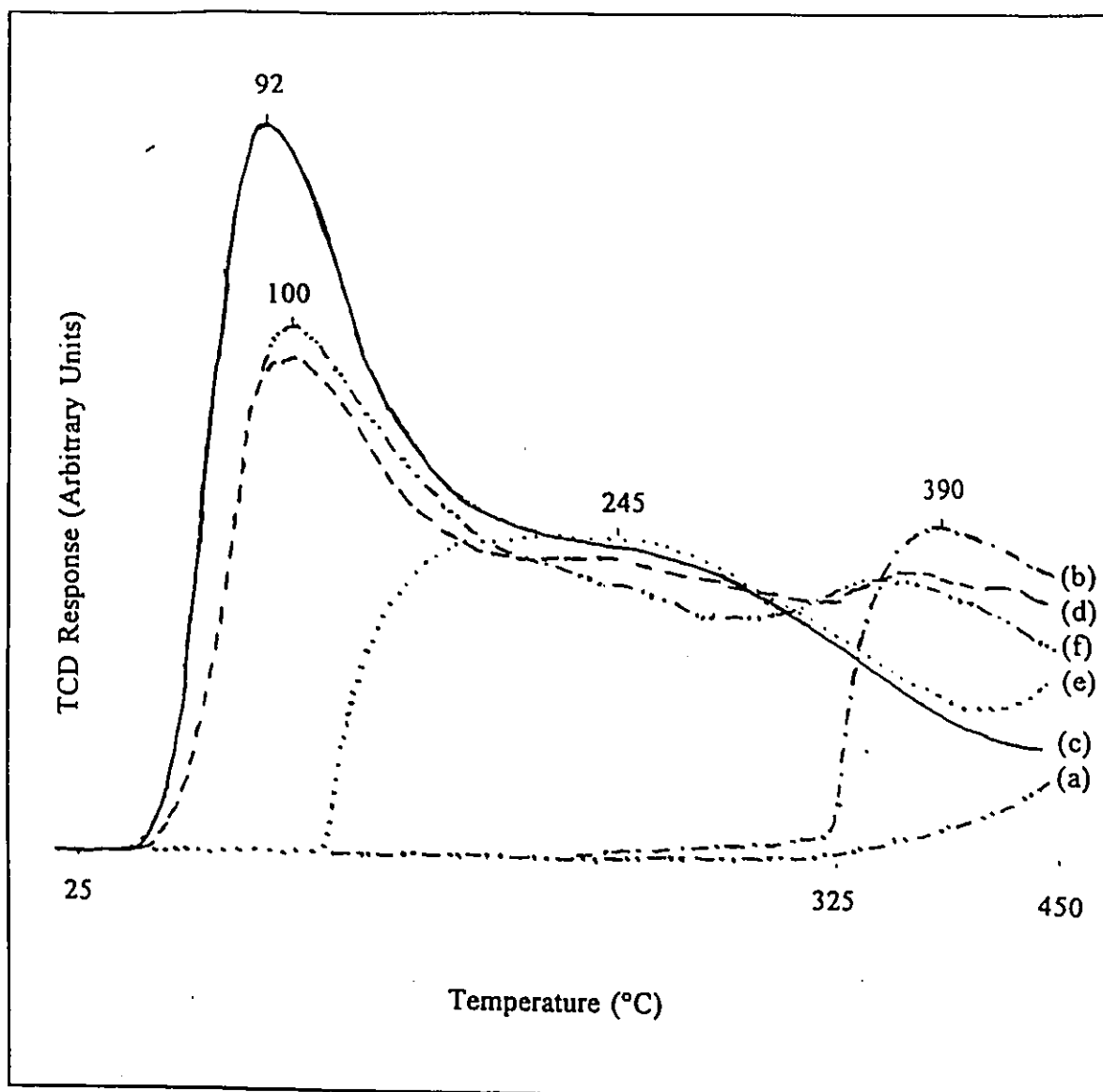


Figure 3.10: TPD spectra following room temperature adsorption of pyridine and/or ammonia on 10 wt. % $\text{ZrO}_2/\text{SiO}_2$ (450°C activation).

- (a) - - - - 0.34 torr pyridine, 7 min., purge 30 min. at RT
- (b) - - - - 3.5 torr pyridine, 5 min., purge 30 min. at RT
- (c) ——— 1.32 torr NH_3 , 60 min., purge 30 min. at RT
- (d) - - - - 0.46 torr pyridine, 5 min., brief evacuation at RT, then 2.70 torr NH_3 , 60 min., purge 30 min. at RT
- (e) ····· 7.18 torr pyridine, 5 min., brief evacuation at RT, then 3.46 torr NH_3 , 60 min., purge 30 min. at RT
- (f) - ··· - 3.84 torr pyridine, 5 min., 90 min. evacuation at RT, then 4.45 torr NH_3 , 60 min., purge 30 min. at RT

When the adsorption pressure of pyridine on 10 wt.% ZrO₂/SiO₂ was increased the peak developed further at 325°C with a maximum at 390°C (see Figure 3.10b). Again these are Lewis acid sites. It remains to be determined if these are the same sites as those revealed by NH₃ chemisorption and subsequent TPD.

Lewis acid-base coordination of a basic gas or vapour with a transition metal oxide surface arises from an interaction of the gas phase molecule and a coordinatively-unsaturated metal cation. In order to compare the relative strengths of adducts formed with different bases, it is more appropriate to compare the gas phase basicities of the two molecules than their solution basicities. In the gas phase pyridine is more basic than NH₃. The proton affinities for pyridine and NH₃ have been measured to be 54±1 kJ and 50±1 kJ [94 and references therein]. As a result of its greater basicity pyridine would form stronger bonds with Lewis acid surface sites and hence the corresponding peaks in the TPD spectra should appear at higher temperatures than those of the NH₃ adduct. Comparison of the spectra show this to be the case; a peak with a maximum of 240°C was attributed to Lewis acid-coordinated NH₃ while the lowest temperature peak in the pyridine TPD spectra occurred at 370°C. Although we have shown that the correct trend is observed with respect to peak position, we have not determined unequivocally that these peaks belong to the same Lewis acid sites. To establish this we performed pyridine poisoning experiments.

Pyridine Poisoning Experiments:

If pyridine and NH_3 occupy the same Lewis acid sites on the surface of $\text{ZrO}_2/\text{SiO}_2$, preadsorption of pyridine should block the sites thus rendering them unavailable for NH_3 adsorption, i.e. the sites would be "poisoned" by pyridine.

Figure 3.10c shows the TPD spectrum obtained following room temperature adsorption of NH_3 on 10 wt.% $\text{ZrO}_2/\text{SiO}_2$ previously activated at 450°C . By comparison, when pyridine was preadsorbed on the sample (0.46 torr) and briefly evacuated at room temperature prior to NH_3 adsorption, the spectrum shown in Figure 3.10d was obtained. Lewis acid coordinated pyridine desorbed above 325°C as before. However, the peak at 100°C was decreased in intensity relative to that obtained for NH_3 alone (see 3.10c). Thus it appears that pyridine partially blocks the physisorption of NH_3 . When the amount of preadsorbed pyridine was increased (7.18 torr), the peak due to physisorption of NH_3 disappeared completely (Figure 3.10e). When pyridine was preadsorbed (3.84 torr) and then evacuated at room temperature for 90 minutes prior to NH_3 adsorption, physisorption of NH_3 again appeared (Figure 3.10f). In fact the spectrum was very similar to that obtained following a smaller amount of pyridine adsorption (i.e. Figure 3.10d). Hence it would appear that some of the preadsorbed pyridine was removed by evacuation at room temperature.

In every case where pyridine was preadsorbed, the peak at 240°C , which has been attributed to Lewis acid coordinated NH_3 , was totally unaffected (compare 3.10d,e,f with

3.10c). This suggests that there is more than one type of Lewis acid site. Given that pyridine is a stronger base in the gas phase than NH_3 (as discussed earlier) NH_3 should not be able to displace pyridine since the latter forms stronger bonds with Lewis acid sites. Thus relative basicities cannot explain this observation. However, pyridine and NH_3 also differ on the basis of molecular size. Pyridine has a molecular cross-sectional area of 0.313 nm^2 while that of NH_3 is 0.127 nm^2 [94]. Thus the smaller NH_3 molecule can access sterically-hindered acid sites which are inaccessible to pyridine. Given that the catalyst contained a large amount of ZrO_2 (10 wt.%) and was prepared by impregnation it is quite conceivable that the dispersion is quite low. Morshige *et al.* [95] found similar behaviour when using NH_3 and pyridine to probe the Lewis acid sites on chromia.

The preadsorption of pyridine also had an effect on the physisorption of ammonia. As is shown in Figure 3.10, the peak at 100°C was decreased by preadsorption of a small amount of pyridine (compare curves c and d). When a larger amount of pyridine was preadsorbed the peak was removed altogether (see curve e). It would appear that physisorption of ammonia is hindered by the presence of bulky pyridine molecules.

Infrared experiments in which pyridine was adsorbed followed by ammonia were inconclusive due to the severe overlap of the region of interest.

Infrared spectroscopy of pyridine adsorbed on $\text{ZrO}_2/\text{SiO}_2$:

$\text{ZrO}_2/\text{SiO}_2$ samples were activated at 450°C under evacuation for 2 hours, and then cooled to room temperature. Pyridine (2.2 torr) was introduced into the cell. The infrared spectrum of pyridine adsorption was recorded after 30 minutes contact. In order to observe the desorption of physically adsorbed pyridine, the cell was evacuated for 1 minute and then the spectrum was recorded. After evacuation for 40 minutes the spectrum was recorded again. Finally, in order to observe the acid strength, pyridine was desorbed by evacuating the sample at 200°C for 40 minutes. The cell was cooled to room temperature and the infrared spectrum was again recorded.

In the IR spectra of pyridine adsorbed on the surface of silica there were only two strong bands at 1445 and 1595 cm^{-1} ; both bands decreased in intensity upon room temperature evacuation. All adsorption bands disappeared upon evacuation at 200°C . These two bands have been previously assigned to the 19b and 8a modes of hydrogen-bonded pyridine [79]. In agreement with earlier work, pure silica does not possess Lewis or Bronsted acid sites.

The infrared spectra of pyridine adsorbed on $\text{ZrO}_2/\text{SiO}_2$ are shown in Figure 3.11A. In addition to the absorption bands which have been assigned to hydrogen-bonded pyridine on silica, new adsorption bands appeared at 1607 , 1576 , 1489 , and 1447 cm^{-1} . All of these new bands increased in intensity with increased loadings of zirconia. This was accompanied by a decrease in the intensity of the band at 1595 cm^{-1} due to hydrogen-bonded pyridine on silica.

Upon evacuation at room temperature, as seen in Figure 3.11B, the intensity of the 1595 cm^{-1} band decreased greatly compared with Figure 3.11A. Its intensity varied inversely with the amount of zirconia. The infrared spectra following evacuation at 200°C are shown in Figure 3.11C. All bands due to hydrogen-bonded pyridine were removed leaving new bands due to adsorbed pyridine at 1611 , 1576 , 1491 , and 1449 cm^{-1} whose intensity increased with the loading of zirconia. These bands can be attributed to coordinatively adsorbed pyridine on Lewis acid sites; the number of these sites increased with the zirconia loading. Further, the decrease in the intensity of the 1595 cm^{-1} band due to hydrogen-bonded pyridine as the zirconia loading increased can be correlated with the generation of an increasing number of Lewis acid sites.

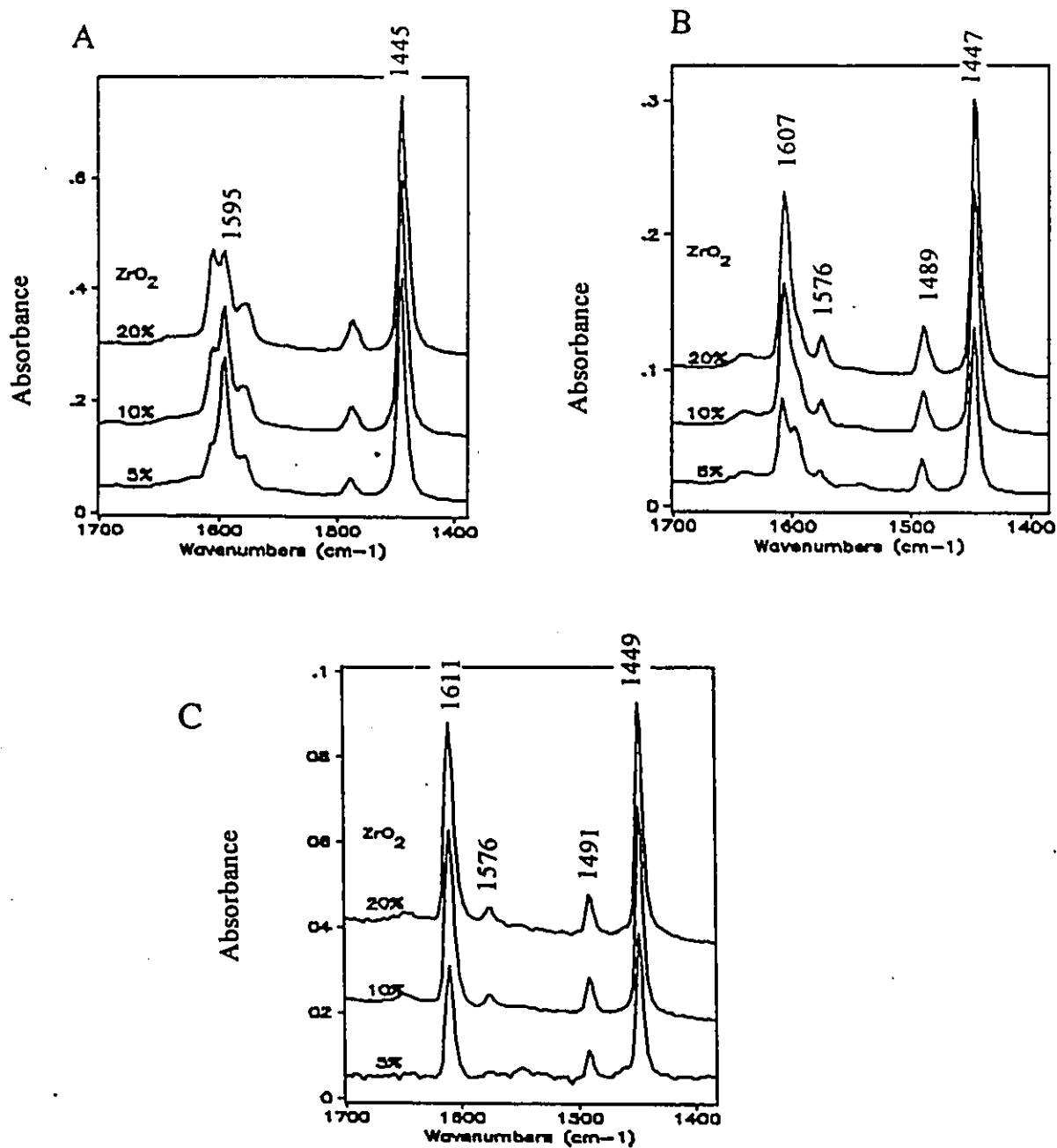


Figure 3.11: Infrared spectra of pyridine on $\text{ZrO}_2/\text{SiO}_2$ as a function of zirconia loading; previously activated at 450°C .

- (A) following adsorption of 2.2 torr pyridine at room temperature for 30 minutes.
- (B) after evacuation at room temperature
- (C) after evacuation at 200°C .

Results of X-ray Diffraction Analysis:

Degussa Zirconia (as received):

Although this material was said to be monoclinic, XRD analysis of the as received material revealed that it was actually a mixture of both monoclinic and tetragonal phases; the tetragonal phase appeared to be slightly more abundant.

XRD analysis of Degussa zirconia that had been previously calcined in air at 500°C for 3 hours showed that the amount of the tetragonal phase decreased by approximately 50 %, with a corresponding increase in the amount of monoclinic phase. As discussed earlier, the monoclinic phase is the more stable phase below 1170°C.

Precipitated Zirconia:

Zirconia prepared by precipitation of zirconyl nitrate using aqueous ammonia followed by calcination at 500°C for 3 hours was also a mixture of both monoclinic and tetragonal phases in approximately equal proportions.

Zirconia/Silica Mixtures:

Samples of 5, 10 and 20 wt. % $\text{ZrO}_2/\text{SiO}_2$, prepared by impregnation as described above, showed no detectable reflections due to crystalline zirconia or compounds such as zirconium silicate. In fact, the XRD spectra of all samples, previously calcined at 500°C for 3 hours, showed only a very broad, low intensity peak between 20° and 40° . No other peaks were observed between 20° and 65° . The broad peak is characteristic of the amorphous silica support. The absence of any other peaks suggests that these samples were amorphous.

The suggestion that these materials are amorphous is interesting given the large amount of zirconia present, up to 20 wt. %. Generally, there are three different means by which a material may be dispersed in another: (1) it may retain its chemical identity as a separate crystalline or amorphous phase; (2) it may form a new stoichiometric compound with the support; or (3) it may dissolve in the support to give a solid solution. Since there were no detectable XRD peaks observed, no new chemical compounds were formed. The question of whether zirconia retained its crystalline identity once dispersed on the surface of silica is not certain, however, if some crystallinity was preserved, the size of these particles must have been small (on the order of a few nanometers) in order to escape detection by XRD.

Most frequently, the absence of an XRD pattern is caused by the fact that the active component is too dilute to be detected. This behaviour is common for catalysts with low loadings, for example less than 1 wt. %. However, the $\text{ZrO}_2/\text{SiO}_2$ samples used had zirconia

loadings of up to 20 wt. % , yet only the pattern of the amorphous support was detected. As discussed by Xie and Tang [96], for materials in which the surface area of the support material is high (greater than about 100 m²/g) and the active components are large amounts of heavy metals (approximately 20 wt. %), it is common that these materials do not produce an XRD pattern.

As was seen in the hydroxyl stretching region of the infrared spectra, even at zirconia loadings of 20 wt. %, the intensity of the bands due to SiOH species was far greater than the intensity of the bands due to ZrOH species. Assuming that the extinction coefficients are of comparable magnitude, this would suggest that the dispersion of zirconia on silica remained low. As discussed previously, recent XPS analysis of zirconia impregnated silica catalysts found dispersion values in the range of 7 to 12 % [73]. However, the increase in the frequency of the bands due to ZrOH measured for ZrO₂/SiO₂ relative to those measured for zirconia suggests that there exists strong interaction between zirconia and silica in spite of the low dispersion. The dramatic enhancement of the acidity of these materials relative to that of silica is also evidence of strong interaction.

Conclusions:

The impregnation of silica by zirconia results in enhanced acidity. Using TPD of ammonia, the number of acid sites was measured and was found to be essentially constant at 260 $\mu\text{moles/g}$ sample for zirconia loadings above 5 wt.%. XRD analysis of zirconia/silica catalysts containing between 5 and 20 wt. % zirconia showed no peaks due to the presence of crystalline phases. It is uncertain whether some very small crystallites of zirconia existed on the surface which could elude detection by XRD.

In the hydroxyl stretching region of the infrared spectra, the bands due to SiOH species were much more intense than those due to ZrOH species, even at loadings of 20 wt. % zirconia. This suggested that the dispersion of zirconia on silica remained low. For $\text{ZrO}_2/\text{SiO}_2$, the band due to ZrOH species was shifted to higher frequency relative to pure zirconia. This implies a strong interaction between zirconia and silica in spite of the low dispersion. Enhanced acidity relative to silica is also evidence of a strong interaction.

Infrared spectroscopy using ammonia to probe the surface acid sites was slightly ambiguous as to whether both Lewis and Bronsted acid sites were formed on the surface of zirconia/silica because of the presence of a broad peak at 1460 cm^{-1} which is often assigned to the asymmetric deformation mode of the ammonium ion. However, the fact that this peak could be removed by evacuation at 100°C , coupled with its breadth suggested that this peak was due to a weaker interaction such as hydrogen-bonding between ammonia and surface

hydroxyl groups. Infrared spectroscopy using pyridine as a probe molecule revealed that only Lewis acid sites were formed. This agrees with predictions based on the models of Tanabe and of Kung that only Lewis acid sites should be generated when zirconia is mixed with silica.

Experiments in which pyridine was used to block certain acid sites prior to ammonia adsorption and subsequent TPD suggested that two different types of Lewis acid sites may be present, only one of which is sterically accessible to the larger pyridine molecule.

Chapter 4:

Characterization of Sulphate-Promoted Zirconia-Silica

Introduction:

In the previous chapter, the surface properties of zirconia-silica were investigated. These materials were used as the substrate from which sulphate-promoted zirconia-silica was prepared by impregnation using aqueous solutions of sulphuric acid. The surface properties of the resultant materials were characterized in a manner similar to that used in Chapter 3 and the results are reported in this chapter. Since these materials have been shown to exhibit superacidic properties, it is appropriate to first present a brief overview of superacids in general.

The term "superacid" was coined by Conant and Hall [97]; in 1927 they discovered that mixtures of sulphuric acid and perchloric acid dissolved in anhydrous acetic acid were able to protonate very weak bases such as ketones and other carbonyl compounds which do not form salts in aqueous solutions of the same acids. The acidity was ascribed to the formation of the $\text{CH}_3\text{CO}_2\text{H}_2^+$ ion which is a stronger proton donor than H_3O^+ . In 1932, Hammett and Deyrup proposed a method for measuring the acidities of aqueous solutions of acids which were more concentrated than those to which the pH scale could be applied [98]. The function that they suggested has since been termed "the Hammett Acidity Function":

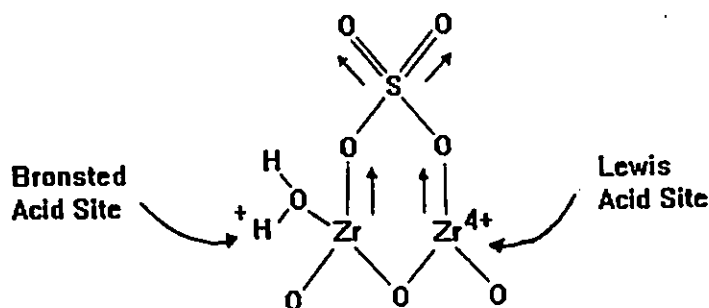
$H_0 = pK_A - \log [BH^+]/[B]$. H_0 was originally measured for the H_2SO_4 - H_2O system; in these solutions the Hammett function varies from zero in 1 M H_2SO_4 to -12.1 for 100 % anhydrous sulphuric acid. As a result, superacids are often somewhat arbitrarily defined as acidic media in which $-H_0$ is equal to or greater than 12 [99]. The above working definition of a superacid is appropriate for Bronsted acids only. Since Lewis acids are also known to exhibit superacidic properties, Olah *et al.* [100] proposed that the anhydrous aluminum chloride be used as the arbitrary reference for these systems and that the Hammett function be modified to: $H_0 = pK_A - \log [AB]/[A]$ where AB represents the Lewis acid-base adduct.

Superacidic properties are not restricted to the solution phase; many types of solid superacid systems have been developed. These systems are more attractive as catalysts from an industrial viewpoint because they are easier to recover, are not as corrosive, and are easier to dispose of than their liquid counterparts. These solid superacid systems include: liquid acids mounted on suitable carriers, such as graphite; combinations of inorganic salts, such as $AlCl_3$ - $CuCl_2$; metal-promoted superacids; and sulphate-promoted metal oxides.

Hino and Arata [101] first reported that a remarkable increase in surface acidity and catalytic activity resulted when $Fe(OH)_3$ or Fe_2O_3 was treated with sulphate ions prior to calcination. Subsequent investigations [102-105] revealed that similar behaviour was obtained with titania and zirconia, but not with alumina, silica, thoria, NiO or MnO_2 . Typically, the oxide or hydroxide was impregnated using 1 N sulphuric acid solution. The resultant material was then calcined at 500°C for 3 hours. These sulphate-promoted metal oxides were capable

of catalyzing the skeletal isomerization of n-butane to isobutane at room temperature. Measurements of their Hammett acidities using appropriate acid-base indicators showed these materials to be superacidic, *ie.* their H_0 values were less than 12; sulphate-promoted zirconia had a measured H_0 value < 16.04 , making it one of the strongest superacids yet discovered [105].

Arata has recently reviewed the progress in the development of solid superacid catalysts in general, and sulphate-promoted metal oxide catalysts in particular [106,107 and references therein]. Studies have shown that similar enhancement in acidity could be achieved using a variety of sulphur compounds as precursors to sulphate ions. Reaction of metal oxides with SO_2 , H_2S , SO_3 , followed by treatment with oxygen at $450^\circ C$ produced similar results to those obtained by impregnation using H_2SO_4 or $(NH_4)_2SO_4$. Infrared analysis in the $S=O$ stretching region showed similar spectra for all methods of preparation. The spectra showed absorption bands at 980-990, 1030-1060, 1120, and at 1220 cm^{-1} . By comparison with the spectra of known compounds, the structure of the surface species was assigned to a bidentate sulphate moiety coordinated to metal atoms. The proposed structure is shown below:



It was proposed that the double bond nature of the complex was much stronger than that normally observed in simple metal sulphates, thus inductive effects are responsible for the enhanced Lewis acidity of the Zr^{4+} and hence for the generation of enhanced acidity. The inductive effects are represented by arrows in the above figure.

Bronsted acidity can be generated by reaction of a Lewis acid site with water. Infrared studies involving pyridine adsorption revealed that both pyridinium ions and coordinated pyridine were present. As the temperature of activation was increased, a decrease in the intensity of the bands due to adsorbed pyridinium ions was observed with a simultaneous increase in the intensity of the bands due to coordinated pyridine. Thus Bronsted acid sites were convertible to Lewis acid sites by desorption of water. Readsorption of water resulted in the recreation of Bronsted sites.

Yamaguchi *et al.* [108] have studied the acidity generation due to sulphate promotion on ZrO_2 , TiO_2 , Fe_2O_3 , Al_2O_3 , SnO_2 , SiO_2 , and Bi_2O_3 . Their results showed that the electronegativity and the coordination number of the metal cation in the metal oxide affected the acid strength. Highly electronegative metals such as ZrO_2 , TiO_2 , and Fe_2O_3 produced the strongest acid sites.

Infrared spectra of sulphate species on silica have been previously reported [109]. It was found that sulphate species on silica could be formed by impregnation of silica using aqueous solutions of either H_2SO_4 or $(NH_4)_2SO_4$. The sulphate species was characterized by

an infrared band at 1412 cm^{-1} which was attributed to the antisymmetric S=O stretching vibration of an $(\text{SiO})_2\text{SO}_2$ species which contained two equivalent, terminal S=O bonds. This structure should also give rise to a band near 925 cm^{-1} , due to an Si-O-S bending mode, however this band was not observed due to the intense background caused by vibrational modes of bulk silica in this region. However, oxygen-18 isotopic exchange experiments further confirmed that both doubly-bonded oxygen atoms were attached to the same sulphur atom. This species was not thermally stable and significant decomposition occurred upon heating beyond 250°C ; all bands due to sulphate species disappeared after heating to 500°C . Unlike Al_2O_3 , TiO_2 [110] and ZrO_2 [111], silica could not be sulphated by heating in the presence of SO_2 with an excess of oxygen. Basic probe molecules such as pyridine, ammonia and dimethyl ether revealed that no surface acidity, either Lewis or Bronsted, was generated by sulphate-promotion of silica.

The infrared spectra of sulphated ZrO_2 are more complex than those of sulphated silica and so far several sulphate species have been observed. The method of preparation of sulphated ZrO_2 strongly influences the structure of sulphate species on the surface of ZrO_2 . Tanabe and his colleagues [112-114] have studied sulphate-promoted ZrO_2 which was prepared by impregnating ZrO_2 with H_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$ by using infrared spectroscopy. They observed four bands at 1390 , 1190 , 1020 and 930 cm^{-1} in the S=O stretching vibration region. The strong band near 1400 cm^{-1} and the band between 1212 and 1190 cm^{-1} were assigned to the antisymmetric and symmetric stretching vibration of O=S=O and the bands at 1020 and 930 cm^{-1} were assigned to stretching modes of O-S-O groups. On the basis of these

assignments these authors were in agreement with the bidentate sulphate structure discussed above.

Bensitel *et al.* have studied the sulphation of ZrO_2 [111] in which the ZrO_2 used was obtained by hydrolysis of zirconium isopropylate and the sulphation was performed by oxidation of SO_2 or by impregnation with $(\text{NH}_4)_2\text{SO}_4$ or H_2SO_4 . The infrared spectra of sulphated ZrO_2 showed a complex spectrum in the 1400 to 800 cm^{-1} region in which there were seven bands observed. At high SO_2 coverages, three species were observed. Oxygen-18 isotopic exchange experiments suggested that two species contained a single $\text{S}=\text{O}$ group and that their structures were possibly of the type $(\text{ZrO})_3\text{S}=\text{O}$ resident on different crystal faces of ZrO_2 . A third species, formed at higher coverage was probably a S_2O_7 type species in which four of the oxygen atoms were bonded to surface zirconium atoms, the proposed species contained one $\text{S}-\text{O}-\text{S}$ bridge and two isolated $\text{S}=\text{O}$ groups. The latter sulphate species was easily decomposed by reaction with water.

Recently, Sohn and Jang have reported the characterization of a series of zirconia-silica catalysts prepared by coprecipitation of zirconyl chloride and sodium silicate from aqueous solution [33]. Sulphate-promoted mixed oxides were also prepared by impregnation of these materials using 1 N sulphuric acid. The materials were then calcined at 400°C .

Infrared analysis of the above sulphate-promoted materials revealed that sulphate was present on the surface as a bidentate species coordinated to Zr^{4+} or Si^{4+} [33]. The acid

strength was measured using Hammett indicators. The Hammett acidity, H_0 , of sulphate-promoted 92 wt. % ZrO_2/SiO_2 was determined to be < 14.5 ; H_0 for sulphated-zirconia and for sulphated-silica were determined to be < 14.5 and < 5.6 , respectively. Therefore, the first two materials were found to be solid superacids while sulphated silica was not. The acid strengths of sulphated materials containing lower zirconia loadings were not reported.

We here report the characterization of sulphated zirconia/silica prepared by impregnation. Since impregnation was used rather than coprecipitation, we have, by necessity, prepared mixtures having lower zirconia loadings (20 wt. % or less) than some of those reported by Sohn and Jang [33]. As will be discussed later in this thesis, since a higher dispersion of zirconia on silica was desired, lower loadings of zirconia would seem preferable.

Experimental:

Preparation of Sulphate-promoted Zirconia-Silica:

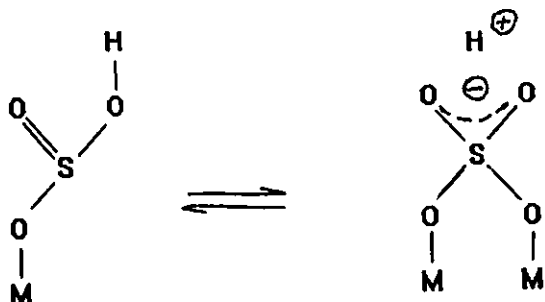
Zirconia-silica samples (5, 10, and 20 wt. % ZrO_2) were prepared by impregnation of silica with aqueous solutions of $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, followed by drying at 100°C , as described in the previous chapter. These materials were calcined at 450°C prior to use. Sulphate-promoted $\text{ZrO}_2/\text{SiO}_2$ samples were prepared by impregnation with sulphuric acid solutions of various molarities. The molarities of the solutions used are expressed in $\mu\text{moles H}_2\text{SO}_4$ per gram of $\text{ZrO}_2/\text{SiO}_2$; concentrations ranged from 100 to 1500 $\mu\text{moles H}_2\text{SO}_4$ per gram. Sulphate-promoted zirconia was prepared in a similar manner. Following impregnation, the samples were dried at 110°C .

These materials were studied by: FTIR using ammonia and pyridine as probe molecules; TPD of ammonia; gravimetric ammonia adsorption; and XRD. Unless otherwise stated the experimental procedures used were as described in Chapter 3.

Results:

FTIR Characterization of sulphated-promoted $\text{ZrO}_2/\text{SiO}_2$:

The infrared spectra in the S=O stretching region obtained from sulphate-promoted 10 wt. % $\text{ZrO}_2/\text{SiO}_2$ with loadings of 100, 500, 1000, and 1500 $\mu\text{mol H}_2\text{SO}_4/\text{g}$ previously activated by evacuation at 200°C and 500°C are shown in Figure 4.1. It can be seen that the spectra following 200°C activation are different than those recorded after 500°C evacuation. Upon 200°C evacuation, samples with higher sulphate loadings showed a broad band at 1354 cm^{-1} and a shoulder at 1425 cm^{-1} . At lower sulphate loadings only a small band at 1354 cm^{-1} was observed. The shoulder at 1425 cm^{-1} at high sulphate loadings is assigned to the asymmetric stretching mode of O=S=O on silica as discussed previously [109]. The corresponding mode on zirconia is normally found at 1390 cm^{-1} [112], thus the broad band at 1354 cm^{-1} would seem too low to be due to such a species. Previous studies on sulphated alumina and titania [110] have found a similar band after exposure to water vapour. It was proposed that water reacts with the sulphate moiety to produce a species of the type:



This interaction with water would cause a lowering and broadening of the O=S=O stretching mode. This species is also expected to exhibit Bronsted acidity. A similar type of species is proposed to be responsible for the band at 1354 cm^{-1} .

For 500°C evacuation, the samples with higher loadings have a band at 1385 cm^{-1} and a band at 1425 cm^{-1} while the samples with lower loadings only have a band at 1375 cm^{-1} . Again, the band at 1425 cm^{-1} is assigned to sulphated silica. The band at 1375-1385 cm^{-1} is assigned to the asymmetric stretching mode of O=S=O on zirconia. As expected, the band at 1354 cm^{-1} , observed following 200°C activation, is greatly diminished by activation at 500°C. This is consistent with a larger degree of dehydration of the sample and supports the assignment of this band to an interaction with surface hydroxyl groups.

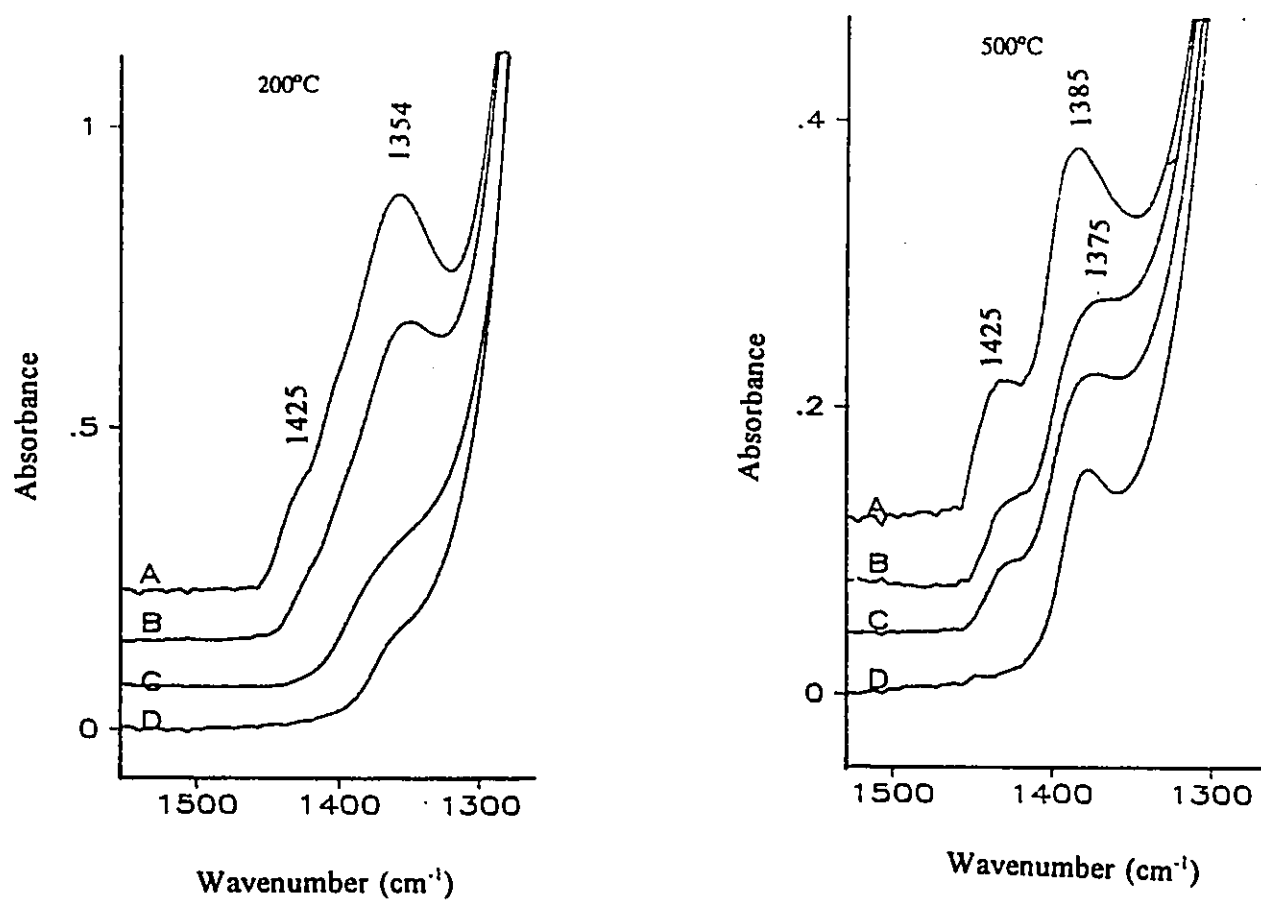


Figure 4.1: Infrared spectra of sulphate-promoted 10 wt. % $\text{ZrO}_2/\text{SiO}_2$ following activation by evacuation at 200°C and 500°C for various loadings of sulphate.

- A. 1500 $\mu\text{mol H}_2\text{SO}_4/\text{g}$
- B. 1000 $\mu\text{mol H}_2\text{SO}_4/\text{g}$
- C. 500 $\mu\text{mol H}_2\text{SO}_4/\text{g}$
- D. 100 $\mu\text{mol H}_2\text{SO}_4/\text{g}$

Effect of activation temperature on sulphate species:

In order to investigate the thermal stability of the sulphate species on the surface of $\text{ZrO}_2/\text{SiO}_2$, a sample of $1500 \mu\text{mol H}_2\text{SO}_4/\text{g}$ 10 wt % $\text{ZrO}_2/\text{SiO}_2$ was activated by evacuation at various temperatures ranging from 200°C to 700°C . The sample was first activated at 200°C for 60 minutes, then cooled to room temperature and its IR spectrum was recorded. This process was repeated several times, each time increasing the activation temperature by 100°C until 700°C was reached. The resulting spectra are shown in Figure 4.2. It can be seen that following 200°C activation there is a strong band at 1354 cm^{-1} and shoulders at 1385 cm^{-1} and 1425 cm^{-1} . The 1354 cm^{-1} band decreased in intensity with increasing activation temperature and disappeared at 500°C ; as its intensity decreased, the shoulder at 1385 cm^{-1} developed into a distinct band. Following 600°C activation, the band at 1385 cm^{-1} decreased in intensity and simultaneously shifted to 1375 cm^{-1} and the band at 1425 cm^{-1} had almost disappeared. All bands disappeared at above 700°C evacuation.

These results are consistent with the previous assignments. The band at 1354 cm^{-1} , due to interaction of the sulphate species with water, decreases with increasing activation temperature. The bands at $1385\text{-}1375 \text{ cm}^{-1}$ and 1425 cm^{-1} , due to the asymmetric stretching modes of $\text{O}=\text{S}=\text{O}$ on zirconia and silica respectively, diminish in intensity as the activation temperature increases. This is due to loss of sulphate from the sample. It can be seen that sulphated zirconia is thermally more stable than sulphated silica since the latter is removed at 700°C while some of the former remains.

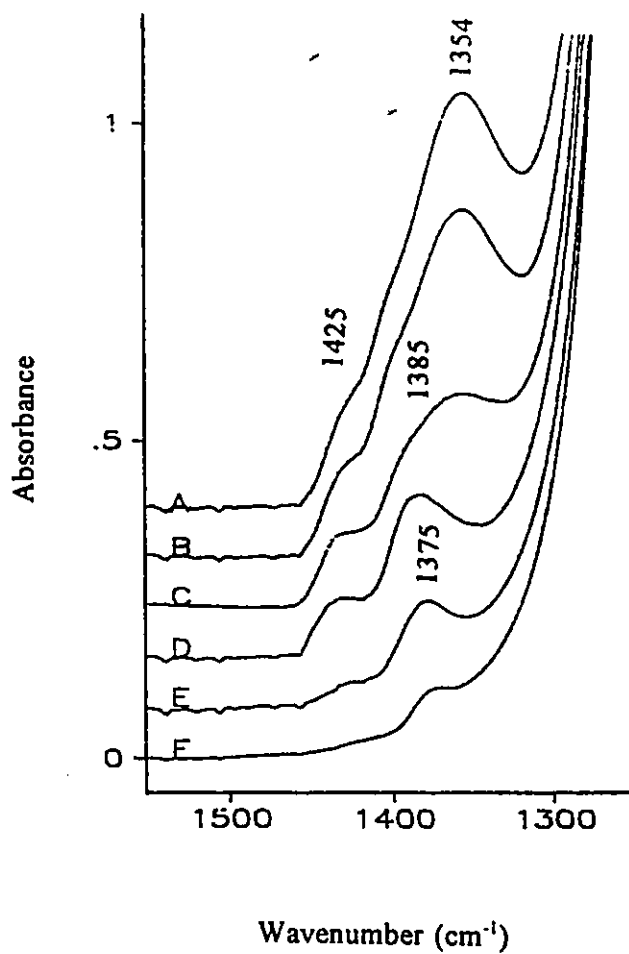


Figure 4.2: The effect of activation temperature on the infrared spectrum of 1500 $\mu\text{mol H}_2\text{SO}_4/\text{g}$ 10 wt % $\text{ZrO}_2/\text{SiO}_2$ in the S=O stretching region.

A. 200°C; B. 300°C; C. 400°C; D. 500°C; E. 600°C; F. 700°C

Adsorption of ammonia on sulphated $\text{ZrO}_2/\text{SiO}_2$:

In this experiment, 100 μmol , 500 μmol , 1000 μmol and 1500 μmol $\text{H}_2\text{SO}_4/\text{g}$ 10 wt.% $\text{ZrO}_2/\text{SiO}_2$ samples were first activated by evacuation at 500°C and then ammonia (8.5 torr) was added to the cell at room temperature. After adsorption for 40 minutes and evacuation for 40 minutes, the infrared spectra of ammonia adsorbed on sulphated 10 wt.% $\text{ZrO}_2/\text{SiO}_2$ were obtained. The spectra obtained in the region 3800 to 2600 cm^{-1} are shown in Figures 4.3 and those obtained in the region 1800 to 1300 cm^{-1} are shown in Figure 4.4. In Figure 4.3, the background spectra of the sample measured prior to ammonia adsorption has been subtracted. The negative bands at 3745 cm^{-1} are due to loss of intensity of isolated SiOH groups following ammonia adsorption. In Figure 4.3, it can be seen that there are two absorption bands at 3381 and 3288 cm^{-1} . As discussed in Chapter 3, absorption bands at 3381 , 3288 cm^{-1} are attributed to the asymmetric stretching vibration, ν_3 , and to the symmetric stretching vibration, ν_1 , of adsorbed ammonia molecules on Lewis acid sites, respectively. With increasing the sulphate coverage, the 3381 and 3288 cm^{-1} increased in intensity rapidly and their peak maximum shifted to lower wavenumber, to 3360 and 3275 cm^{-1} respectively. With a higher sulphate coverage, there were two shoulders at 3209 and 3178 cm^{-1} and a broad band at 3045 cm^{-1} which were unresolved for lower sulphate coverages.

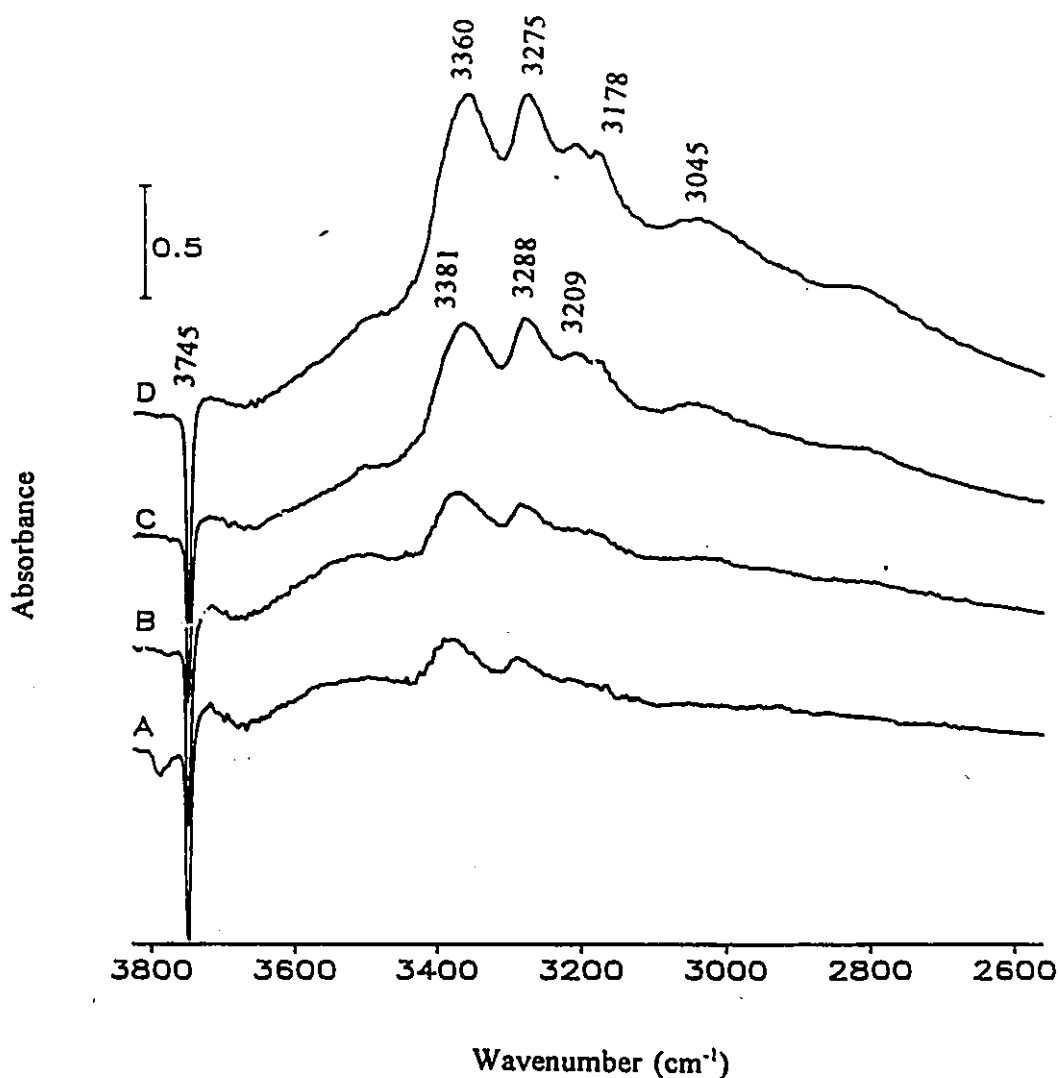


Figure 4.3: Infrared spectra in the N-H stretching region following the room temperature adsorption of ammonia (8.5 torr) and room temperature evacuation on sulphate-promoted 10 wt. % ZrO₂/SiO₂ with different loadings of sulphate. Samples were previously activated at 500°C.

- A. 100 $\mu\text{mol H}_2\text{SO}_4/\text{g}$.
- B. 500 $\mu\text{mol H}_2\text{SO}_4/\text{g}$
- C. 1000 $\mu\text{mol H}_2\text{SO}_4/\text{g}$
- D. 1500 $\mu\text{mol H}_2\text{SO}_4/\text{g}$

In Figure 4.4, two absorption bands appeared at 1608 and 1450 cm^{-1} in the N-H bending region at lower sulphate coverages. The intensity of the 1608 cm^{-1} band increased with increasing sulphate loading; this band is assigned to the asymmetric bending mode of N-H bonds of Lewis acid-coordinated ammonia. The broad band at 1450 cm^{-1} increased in intensity more rapidly than the 1608 cm^{-1} band and its peak maximum shifted to lower wavenumber, to 1433 cm^{-1} . A new band appeared at 1553 cm^{-1} ; this band is known to be due to the deformation of NH_2 species produced by dissociative adsorption of ammonia molecules on the surface of silica. In addition, after ammonia adsorption the absorption bands of sulphate species at 1385 and 1432 cm^{-1} shifted to lower wavenumber. As a result they could no longer be observed because of the strong absorption band of the support silica in the 1250-1000 cm^{-1} region.

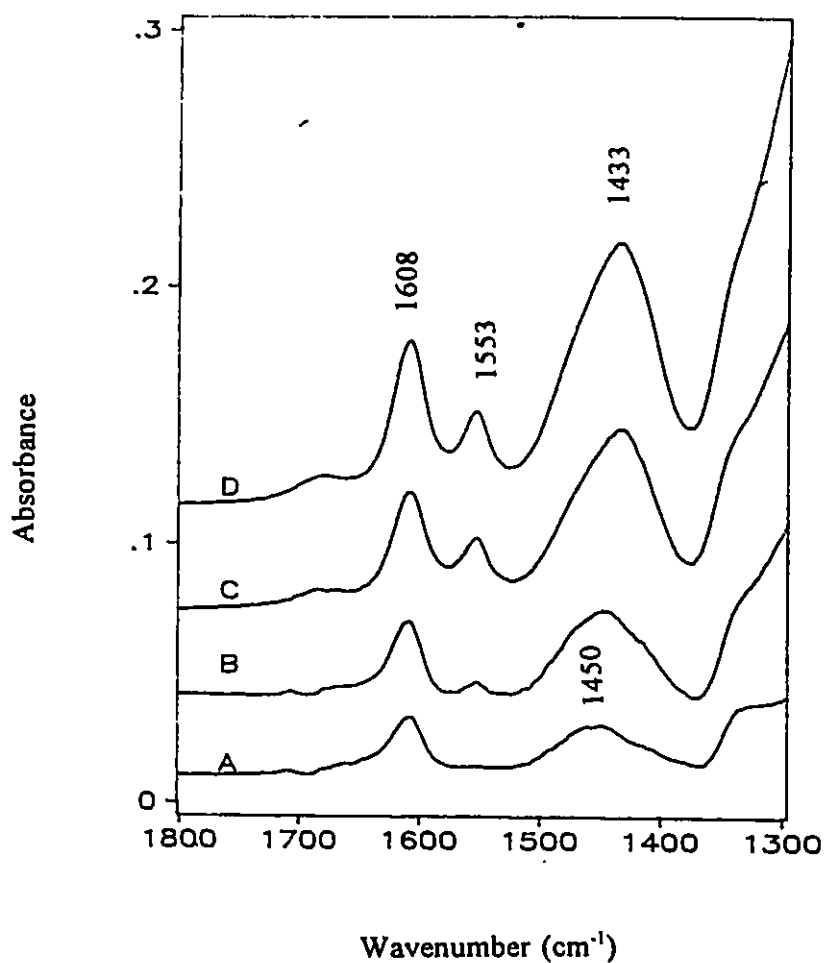


Figure 4.4: Infrared spectra in the N-H bending region following the room temperature adsorption of ammonia (8.5 torr) and room temperature evacuation on sulphate-promoted 10 wt. % ZrO₂/SiO₂ with different loadings of sulphate. Samples were previously activated at 500°C.

- A. 100 $\mu\text{mol H}_2\text{SO}_4/\text{g}$
- B. 500 $\mu\text{mol H}_2\text{SO}_4/\text{g}$
- C. 1000 $\mu\text{mol H}_2\text{SO}_4/\text{g}$
- D. 1500 $\mu\text{mol H}_2\text{SO}_4/\text{g}$

It is well known that a free ammonium ion with T_d symmetry would have two fundamental vibrations active in the infrared: the asymmetric stretching and the asymmetric bending modes, ν_3 and ν_4 , respectively. These modes are both triply degenerate. However, when adsorbed or subjected to a crystal field, the degeneracy of ν_3 and ν_4 is removed and is split into several bands, depending upon the symmetry of the ammonium ion in its environment [115]. Therefore, the absorption bands at 3209 and 3178 cm^{-1} are assigned to the asymmetric stretching vibration, ν_3 , of the N-H bonds of ammonium ions adsorbed on Bronsted acid sites. The two bands probably resulted from the splitting of the ν_3 mode due to the decrease in the symmetry of the ammonium ion from T_d to C_{3v} symmetry as a result of adsorption. The band at 3045 cm^{-1} is assigned to the combination band of the ν_2 and ν_4 absorption bands of ammonium ions [115]. The strong and asymmetric band at 1450-1433 cm^{-1} is assigned to the ν_4 , bending mode of N-H bands of ammonium ions. It is apparent that the increase in intensity of all absorption bands of both coordinated adsorbed ammonia and protonated ammonium ions with increase of sulphate coverage indicates that both Lewis and Bronsted acid sites increase with increase of sulphate coverage. The shift of the bands at 3381 and 3288 cm^{-1} to lower wavenumber with increasing sulphate coverage suggests that the Lewis acid strength increases with an increasing sulphate coverage. This is probably due to the increase of the inductive effect of sulphate species on Lewis acid sites as a result of increasing sulphate coverage. The increase of the intensity of 1554 cm^{-1} band with sulphate coverage seems to suggest that the formation of NH_2 species would be related to the sulphate coverage because, generally, the ammonia adsorption on dehydrated silica leads to the formation of NH_2 species, which presents absorption bands at 3540, 3432 and 1550 cm^{-1} ,

due to the dissociation of ammonia molecules [78]. In our sample the active sites on which NH_2 species are formed would be largely hampered by loading zirconia and sulphate ions.

Adsorption of Pyridine on Sulphate-Promoted Zirconia/Silica:

In this experiment, 1000 $\mu\text{mole H}_2\text{SO}_4/\text{g}$ 10 wt.% $\text{ZrO}_2/\text{SiO}_2$ was activated at 200°C , and then exposed to pyridine (2.2 torr) at room temperature. The sample was first evacuated at room temperature and then at 200°C . Figure 4.5 shows the infrared spectra obtained at each stage. The absorption bands at 1595, 1579 and 1445 cm^{-1} , which are assigned to the hydrogen-bonded pyridine, decrease in intensity with evacuation at room temperature and disappear upon evacuation at 200°C . The bands at 1612 and 1445 cm^{-1} , which are assigned to the coordinately adsorbed pyridine on Lewis acid sites, also decrease in intensity with evacuation at room temperature and become very weak following evacuation at 200°C . The bands at 1640 and 1543, 1491 cm^{-1} , which are characteristic absorption bands of pyridinium ions on Brønsted acid sites, have strong absorption intensity upon evacuation at room temperature and at 200°C . It would appear that the Brønsted acid sites on the surface of the catalyst were predominant; a relatively small amount of Lewis acid sites did however exist.

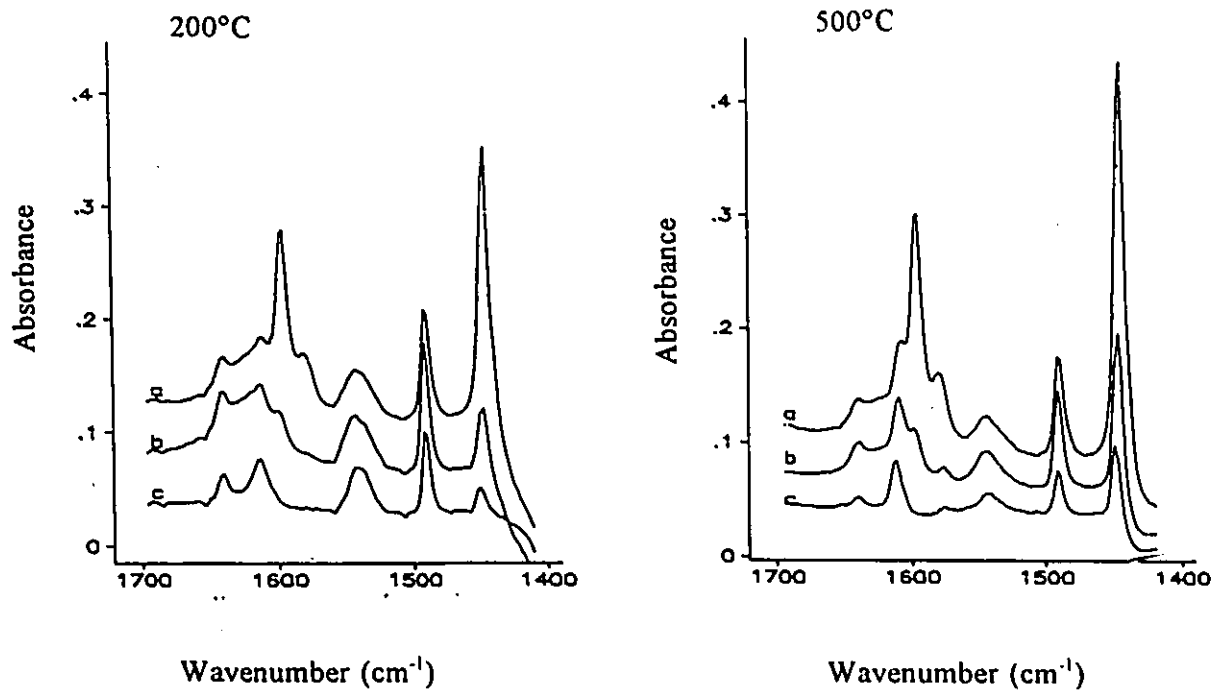


Figure 4.5: Infrared spectra of 1000 $\mu\text{mole H}_2\text{SO}_4/\text{g}$ 10 wt. % $\text{ZrO}_2/\text{SiO}_2$ following room temperature adsorption of pyridine (2.2 torr). The sample was previously activated at 200°C or at 500°C prior to adsorption.

- a) following adsorption
- b) following room temperature evacuation
- c) following evacuation at 200°C

The experiment was repeated with the sample activated at 500°C. The spectra are also shown in Figure 4.5. It can be seen that the strong absorption bands at 1595 and 1445 cm^{-1} , which are assigned to hydrogen-bonded pyridine, decrease rapidly in intensity with evacuation at room temperature and were removed upon evacuation at 200°C. The strong absorption bands at 1612 and 1448 that appeared upon evacuation at room temperature and 200°C are assigned to the coordinately adsorbed pyridine on Lewis acid sites while there were the weak absorption bands at 1640 and 1543 cm^{-1} , which are assigned to the pyridinium ions on Brønsted acid sites. This result suggests that activation at 500°C resulted in the production of more Lewis acid sites than Bronsted sites. Thus, the relative amount of Lewis and Bronsted acid sites is dependent upon the temperature of activation. As the activation temperature is increased, the number of Bronsted sites decreases while the number of Lewis acid sites increases. This result is consistent with the increasing degree of dehydration of the surface at higher activation temperatures.

TPD of Ammonia on Sulphate-Promoted Zirconia/Silica:

Kumbhar *et al.* [91] have studied the influence of the treatment of ZrO_2 by sulphuric, phosphoric, and boric acids on surface properties. Acidity measurements were performed by temperature programmed desorption (TPD) experiments following room temperature NH_3 adsorption. They divided the TPD spectra obtained into four regions representing different acid strengths based on the temperature desorption maxima: weak (below 100°C); intermediate (100°C - 200°C); strong (200°C - 400°C); and very strong ($>400^\circ\text{C}$). Only $\text{SO}_4^{2-}/\text{ZrO}_2$ produced a weak peak at 415°C , which was postulated to be due to superacidic sites. In addition to this peak $\text{SO}_4^{2-}/\text{ZrO}_2$ showed strong peaks at 160°C and 210°C , whereas pure ZrO_2 produced only weak peaks at 77°C and 230°C . These authors refer to a recent study by Yori *et al.* [116] which reported that a linear correlation exists between the Hammett acidity (H_0), as determined by indicators, and the reciprocal of the NH_3 desorption temperature for alumina and silica-aluminas. Kumbhar *et al.* suggest that a similar relationship exists for ZrO_2 and acid treated ZrO_2 , hence their division into weak, intermediate, strong, and very strong acid sites as stated above. Apart from the correlation of the 415°C peak with superacid sites no discussion of the type of acidic interaction (Lewis or Bronsted) of the other peaks was given. The total amount of NH_3 desorbed from the sample was estimated from the areas under the peaks and the TCD response factor. The measured total acidity was $134.3 \mu\text{moles/g}$ for ZrO_2 and $604.0 \mu\text{moles/g}$ for $\text{SO}_4^{2-}/\text{ZrO}_2$.

Recently Sohn and Jang [33] have characterized $\text{ZrO}_2/\text{SiO}_2$ and sulphuric acid

modified $\text{ZrO}_2/\text{SiO}_2$ by XRD, IR, XPS, surface area measurements, acidity, acid strength. $\text{ZrO}_2/\text{SiO}_2$ was prepared by coprecipitation of zirconium oxychloride and sodium silicate with aqueous NH_3 solutions. Because coprecipitation was used the entire composition range from pure SiO_2 to pure ZrO_2 could be studied. The acidity of $\text{ZrO}_2/\text{SiO}_2$ and $\text{SO}_4^{2-}/\text{ZrO}_2/\text{SiO}_2$ was measured gravimetrically by determination of the amount of NH_3 irreversibly chemisorbed by the samples at 230°C according to the procedure of Ai [117-119]. No reason was given for the choice of this temperature.

Figure 4.6a shows the TPD spectrum obtained following room temperature adsorption of NH_3 on a sample of sulphated 10 wt.% $\text{ZrO}_2/\text{SiO}_2$ (1500 $\mu\text{mole SO}_4^{2-}/\text{g}$). The sample had been previously activated at 450°C for one hour. For comparison, the spectrum obtained from 10 wt.% $\text{ZrO}_2/\text{SiO}_2$ is shown in Figure 4.6b. The two spectra show identical peaks at 92°C due to physisorbed or hydrogen-bonded NH_3 . The peak at 240°C decreases upon sulphation, *ie.* the number of Lewis acid sites is diminished by sulphation.

The most distinct difference between Figures 4.6a and 4.6b is the presence of the high temperature peak in sulphated spectrum, 4.6a. The peak begins at about 415°C and increases monotonically to the original dehydration temperature of 450°C . This peak is not due to water desorbing from an incompletely dehydrated sample near the activation temperature because an experiment in which the sample was first activated at 600°C gave exactly the same result. This peak is attributed to very strongly adsorbed, possibly "superacidic" sites. A similar peak at 415°C was observed by Kumbhar *et al.* [91] on sulphuric acid-treated ZrO_2 .

These authors also attributed it to superacidic sites.

Since the high temperature peak extends past the maximum temperature used for TPD, adsorbed NH_3 must remain on the sample at temperatures greater than 450°C . An estimate of the amount of NH_3 irreversibly adsorbed at 450°C can be made from the difference in the amount adsorbed prior to TPD and that desorbed during the experiment. The amount of NH_3 irreversibly adsorbed at 450°C is estimated to be $193\ \mu\text{moles/g}$ based on the measured amount of NH_3 desorbed and $118\ \mu\text{moles/g}$ based on the amount desorbed calculated by from the integrated area of the spectrum. These estimates differ by 39%. However approximate, these calculations show that the amount of irreversibly adsorbed NH_3 at 450°C is substantial therefore supporting the presence of a considerable amount of very strong adsorption sites.

TPD of Pyridine on Sulphated- $\text{ZrO}_2/\text{SiO}_2$:

To date attempts to characterize sulphated- $\text{ZrO}_2/\text{SiO}_2$ by room-temperature adsorption of pyridine and subsequent TPD have proven unsuccessful; the results obtained are irreproducible. Attempts have been made to purify pyridine by vacuum distillation from an alcohol/dry ice bath (melting point pyridine = -42°C) to a liquid nitrogen bath to avoid moisture contamination. Purification did not solve the problem. It appears that pyridine may contaminate the vacuum/reactor system, being very tenaciously adsorbed at room temperature. Subsequent experiments with NH_3 , days after pyridine exposure, show traces of pyridine.

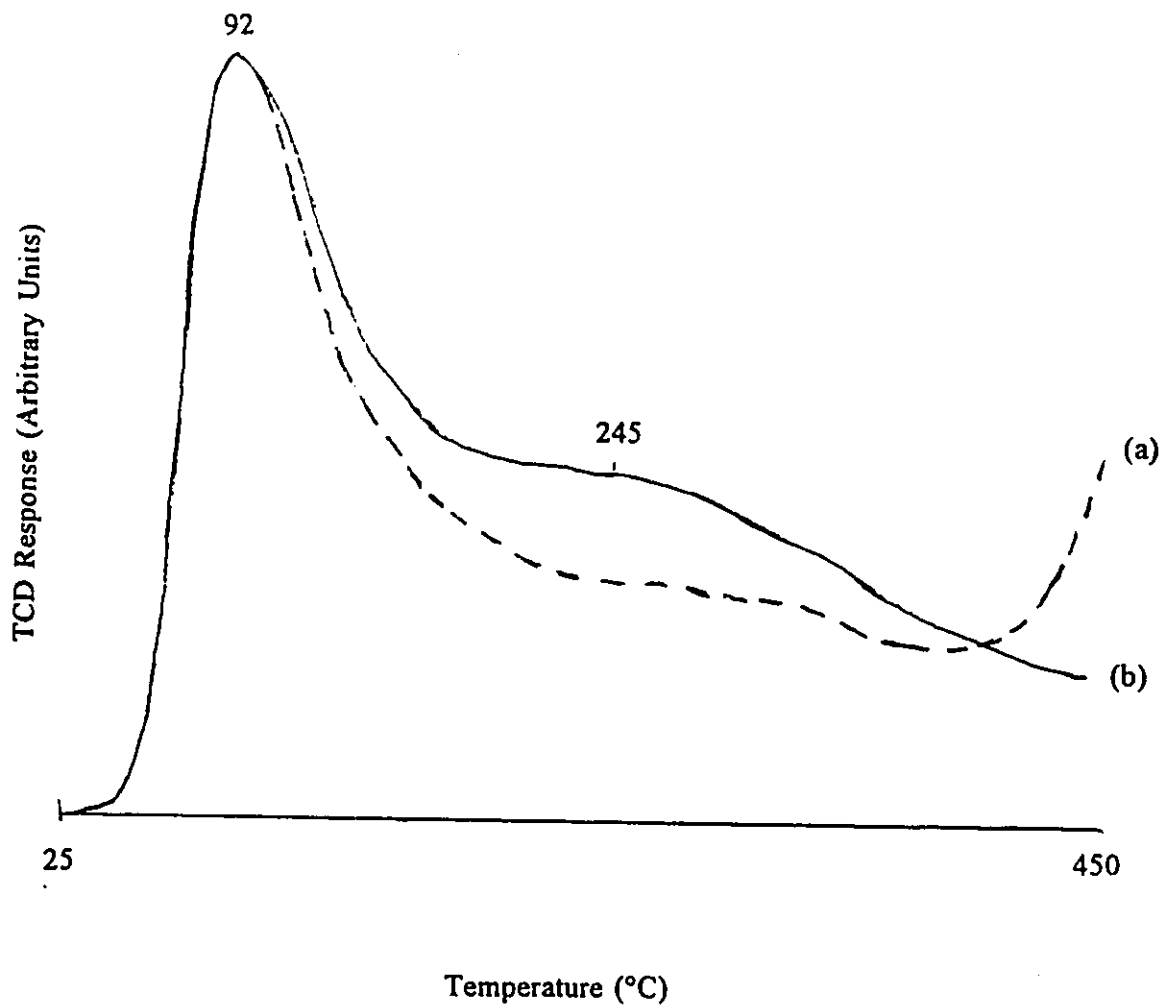


Figure 4.6: TPD spectra following room temperature adsorption of ammonia (8 torr) on 10 wt. % $\text{ZrO}_2/\text{SiO}_2$ and 1500 $\mu\text{mole H}_2\text{SO}_4/\text{g}$ 10 wt. % $\text{ZrO}_2/\text{SiO}_2$ following 450°C activation.

- a) 1500 $\mu\text{mole H}_2\text{SO}_4/\text{g}$ 10 wt. % $\text{ZrO}_2/\text{SiO}_2$
- b) 10 wt. % $\text{ZrO}_2/\text{SiO}_2$

Gravimetric Ammonia Adsorption Measurements:

As discussed previously, TPD revealed that some ammonia remained on the surface of sulphated-ZrO₂/SiO₂ at 450°C making direct measurement of the total acidity by NH₃ desorption less accurate. Experiments were therefore performed in which the amount of ammonia adsorbed was measured directly. Gravimetric ammonia measurements were performed using a Satorius Model 4433 electronic microbalance.

A 100 mg pressed disk of sample was loaded on the right arm of the two-arm compensating balance. A 100 mg counterweight was placed on the left. The balance was connected to a vacuum manifold and evacuated. The sample was then activated at 450°C for 60 minutes using a resistive heating element. The sample was cooled to room temperature and the balance was tared. Ammonia was introduced into the cell. Approximately 95 % of the total weight increase occurred within the first minute of contact. Constant weight was achieved within 60 minutes. The balance was then evacuated at 25°C for 60 minutes until constant weight was obtained. The sample was heated under vacuum at 100°C for 60 minutes then cooled to room temperature and the weight of irreversibly adsorbed ammonia at 100°C was recorded. The process was repeated at 200°C. For the samples with large sulphate loadings (eg. 1500 μmole/g), difficulties were encountered due to weight loss upon heating at 200°C. This was attributed to loss of adsorbed sulphate. Efforts to measure the amounts of ammonia irreversibly adsorbed at temperatures greater than 200°C proved impossible for all sulphated samples, again due to loss of sulphate.

Table 4.1 gives the amounts of adsorbed ammonia irreversibly adsorbed on sulphated 10 wt. % zirconia-silica at various temperatures.

Table 4.1: The amount of irreversibly adsorbed NH_3 at different temperatures on 10 wt. % $\text{ZrO}_2/\text{SiO}_2$ with various sulphate loadings as determined by gravimetric means.

Sulphate Loading ($\mu\text{mole/g}$)	Amount of NH_3 Irreversibly Adsorbed ($\mu\text{mole/g}$)		
	25°C	100°C	200°C
0	480	190	80
500	830	160	120
1000	920	230	170
1500	970	300	250
1000(ZrO_2)	950	270	200

Good agreement was found between the amount of ammonia adsorbed on 10 wt. % $\text{ZrO}_2/\text{SiO}_2$ as measured by gravimetric means and by TPD (compare data in Tables 4.1 with 3.1 and 3.2). The difference between the amounts of ammonia irreversibly adsorbed at 25°C was 16 %.

The value obtained for the amounts of NH_3 irreversibly adsorbed at 200°C for 1500 $\mu\text{mole/g}$ 10 wt. % $\text{ZrO}_2/\text{SiO}_2$ was 250 $\mu\text{mole NH}_3/\text{g}$. Recall that the value estimated for the amount of ammonia remaining at 450°C by TPD was between 118 and 193 $\mu\text{moles/g}$. These values seem consistent since some NH_3 does desorb between 200°C and 450°C (see Figure 4.6). The amount of ammonia irreversibly adsorbed at 200°C is not a precise measure of the number of superacid sites alone; it also contains some weaker sites. Again, attempts to directly measure the amount of NH_3 irreversibly adsorbed at 400°C were hampered by a weight loss due to sulphate.

X-ray Diffraction Analysis of Sulphate-Promoted Zirconia-Silica:

XRD analysis of 1000 $\mu\text{mol/g}$ 10 wt. % $\text{ZrO}_2/\text{SiO}_2$ previously calcined at 500°C revealed no diffraction peaks. Thus the addition of sulphate does not promote crystallization of the amorphous zirconia-silica. This result is consistent with those reported by Sohn and Jang [33] for sulphate-promoted zirconia-silica prepared by coprecipitation.

Conclusions:

Infrared analysis of 10 wt. % $\text{ZrO}_2/\text{SiO}_2$ with sulphate loadings ranging from 100 to 1500 $\mu\text{mole/g}$ revealed that the nature of the surface sulphate species was dependent on the temperature of activation. For low activation temperatures, eg. 200°C, adsorbed sulphate species appeared to interact with surface hydroxyl groups to form a hydrogenosulphate species. This species possessed Bronsted acidity. At 500°C activation, the adsorbed sulphate existed as a bidentate sulphate species coordinated to Zr^{4+} . A small amount of a similar type of species coordinated to Si^{4+} was also present. The sulphated-zirconia species was found to be thermally more stable than sulphated-silica; some species still remained after activation at 700°C while sulphate was removed from the surface of silica.

IR analysis of acid sites using NH_3 as a probe molecule suggested that both Lewis and Bronsted acid sites existed after 500°C activation. The amount of each type of site appeared to increase with increased sulphate loading. Similar experiments using pyridine supported this conclusion. The relative number of each type of acid site was dependent on the activation temperature. Activation at 200°C resulted in mainly Bronsted acid sites while Lewis acid sites predominated after 500°C activation.

TPD of NH_3 on 1500 $\mu\text{mole H}_2\text{SO}_4/\text{g}$ 10 wt. % $\text{ZrO}_2/\text{SiO}_2$ activated at 450°C revealed peaks at 92°C and at 240°C. These peaks were similar to those obtained on 10 wt. % $\text{ZrO}_2/\text{SiO}_2$. The intensity of the band at 240°C was reduced by sulphation. This band was

assigned to Lewis acid coordinated NH_3 . In addition to these peaks, a peak was observed which began at 410°C and increased monotonically to the temperature of activation of the sample. The appearance of a similar peak following activation at 600°C suggested that this peak was not due to desorption of water, but rather that it was due to desorption of very strongly bound NH_3 . Thus, this peak was assigned to ammonia adsorbed on very strong, perhaps superacid sites.

Direct measurements of the number of these strong acid sites by TPD was hampered by the fact that not all of the ammonia was desorbed prior to reaching the original activation temperature of the sample. It was estimated that the number of these sites was between 118 and 190 $\mu\text{mole/g}$ for 1500 $\mu\text{mole/g}$ 10 wt. % $\text{ZrO}_2/\text{SiO}_2$, previously activated at 450°C .

The acidity of 10 wt. % $\text{ZrO}_2/\text{SiO}_2$ samples with various sulphate loadings was measured by gravimetric ammonia adsorption following varying evacuation temperatures. The amounts of irreversibly adsorbed ammonia were found to increase with increased sulphate loading at 25°C , 100°C , and 200°C . Attempts to measure the amount of irreversible adsorption at temperatures greater than 200°C were hampered by weight loss due to sulphate. Thus, precise measurement of the total number of acid sites alone was not possible.

Chapter 5:

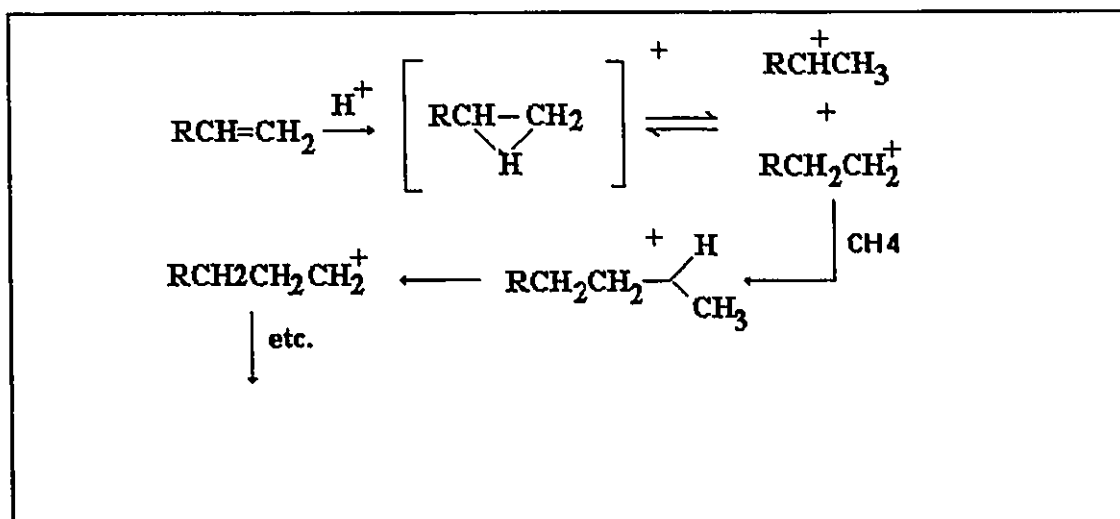
Reactions of Methane and Ethylene (or Propylene)

over Sulphate-Promoted $\text{ZrO}_2/\text{SiO}_2$:

In the late 1960's Olah and coworkers [120-123] reported that gaseous alkanes, including methane, could be polycondensed in an autoclave at room temperature by solutions of superacids, such as $\text{HSO}_3\text{F-SbF}_5$, to form various cations and highly branched low molecular weight alkanes. Later, Roberts and Calihan [124] reported that alkanes could be polymerized to compounds ranging from monomeric units to molecular weights around 700 using similar catalytic systems. In an effort to improve the yield of polycondensed products from methane these same authors added 1 to 2 wt.% of various olefins to the reaction mixtures [125]. In addition to improved yields, the molecular weight distribution was narrowed to between 100 and 700.

The results above have been explained by the ability of these strong acids to protonate even extremely weak bases such as alkanes and alkenes. For example, the protonation of alkanes produces the family of alkonium ions, $(\text{C}_n\text{H}_{2n+3})^+$, of which methonium, CH_5^+ , is the parent [126]. These are "non-classical ions" in the sense that they possess two-electron, three-centre bonds. The protonation of alkenes produces carbenium ions, $(\text{C}_n\text{H}_{2n+1})^+$.

The carbenium ion intermediates are extremely reactive and are capable of electrophilic attack on the carbon-hydrogen sigma bond of methane, thus resulting in alkylation of methane as follows:



The ethylation of methane by superacids in solution has been reported by Siskin [127] and by Sommer *et al.* [128].

Unfortunately, the extreme reactivity of the carbonium ion intermediates formed also enable side-reactions such as oligomerization to occur. These oligomers may also be "cracked" down to lower molecular weight compounds. Hydride transfer is also possible between the alkylation product and the reactive cation, resulting in the reduction of the starting alkene, however, oligomerization-cracking is the larger problem. "The difficulty lies in generating in a controlled way a very energetic primary carbenium ion in the presence of excess CH₄ and at the same time avoiding oligocondensation of C₂H₄ itself "[126].

As a result, several points must be addressed in order to use superacid catalysts [31,128]:

- (a) the tendency for the alkene to react with itself by oligomerization must be countered;
- (b) the alkylation product must be rapidly removed from the reaction medium before hydride transfer to the reactive cation takes place; and
- (c) hydride transfer from the reactant alkane should be relatively difficult.

In light of the above several recommendations have been stated [31]:

- (a) Large alkane:alkene ratios should be used;
- (b) a continuous flow arrangement with, for example, a fixed bed of catalyst should be employed; and
- (c) the most suitable alkanes for use as reactants are methane and ethane.

The first report of heterogeneous alkylation of methane in a flow system was published by Olah *et al.* [28] in 1983 using solid superacids such as: SbF_5 intercalated into graphite; TaF_5 on AlF_3 ; and TaF_5 (all activated by HF). In order to minimize oligomerization-cracking, the system was pressurized to 138-414 kPa (20-60 psig). Mixtures of CH_4 and C_2H_4 , containing about 1 mole % C_2H_4 , were flowed through the catalyst at 5-10 mL/min. and ambient temperature. Isotopically labeled methane was used and the presence of singly labeled propane proved that reaction between methane and ethylene had indeed occurred; propane can also be formed by cracking of oligomers. The small scale of the reaction, limited by the amount of $^{13}\text{CH}_4$, made accurate determination of the turnover numbers difficult, although for the case of SbF_5 -intercalated graphite the reaction was determined to be

catalytic rather than stoichiometric. The formation of propane was found to be extremely sensitive to the $^{13}\text{CH}_4$ - ethylene ratio. Increasing the amount of ethylene to greater than 2 mole % greatly reduced the amount of singly labeled propane produced. No singly labeled propane was found when larger amounts of ethylene (8 mole %) were used.

The coupling of methane and ethylene mixtures has been reported in a flow system over sulphated-zirconia catalysts at 300°C [29,31]. Thermal pretreatment of these catalysts (approximately 3 wt.% sulphate) at around 500°C was found to be necessary for activity at 300°C; thermal activation was regarded as generating superacidity in these catalysts. Mixtures of CH_4 and C_2H_4 (with mole ratios between 2:1 and 3:1) were passed through the reactor at 1.96 MPa (19.3 atmospheres) and a gaseous hourly space velocity (GHSV) of 960 hr^{-1} (m^3 reactant at 0°C and 0.1 MPa per m^3 catalyst bed per hour). The catalyst behaviour was found to vary greatly with increasing time on stream. After one hour the conversion of ethylene was high (80-90 %) and C_6 and C_7 hydrocarbons dominated. However, as the time on stream increased the products became lighter (propane, C_4 's and C_5 's dominated). Also deactivation of the catalyst occurred. After 23 hours on stream the total conversion of methane and ethylene was only 3 %. Ethylene oligomerization was found always to be a competing process, but experiments performed with and without CH_4 revealed that methane did have a marked affect on the product spectrum obtained.

Recently, Ng and coworkers [30] reported results obtained from experiments in which methane/ethylene mixtures were reacted over zeolite-supported TaF_5 . The zeolites tested

were LZY52, LZY82, and 13X. Experiments were performed in a downflow tubular reactor at 2.86 MPa and 4.24 MPa and temperatures of 150°C and 175°C. The feed gas was approximately 3 mole % C_2H_4 in CH_4 . Mixtures of alkanes and alkenes up to C_6 were obtained, with isobutane and isopentane being the predominant products. The amount of products formed by all three catalysts was low (ranging from 0.006 to 1.26 mol.%). All three catalysts showed rapid deactivation attributed to coke formation.

Sulphate-promoted ZrO_2/SiO_2 as a Catalyst for the CH_4 /Olefin Coupling:

As previously discussed, sulphate-promoted ZrO_2/SiO_2 has been found to possess superacid properties. This is based on its ability to catalyze such reactions as: ring-opening of cyclopropane at 100°C [32]; dehydration of 2-propanol at 180°C; and dealkylation of cumene at 400°C [33]. The catalysis of such reactions under mild conditions is evidence of superacidity [34]. In addition, we have shown in Chapter 4, on the basis of adsorption studies of NH_3 and pyridine using infrared spectroscopy and TPD, that these materials possess very strong acid centres once activated. We have considered the possibility that dispersion of zirconia on an inert substrate such as silica, at low loadings of zirconia (10 wt.%), prior to sulphation, might lower the catalytic activity for olefin oligomerization reactions. As discussed, these reactions caused rapid deactivation of sulphate-promoted zirconia during CH_4 /olefin coupling at 300°C [29]. If oligomerization can be alleviated, while maintaining the ability to catalyze coupling, the lifespan of these catalysts would be extended. In light of

the above, we have performed several experiments to test sulphate-promoted $\text{ZrO}_2/\text{SiO}_2$ as a catalyst for the coupling of $\text{CH}_4/\text{C}_3\text{H}_6$ and $\text{CH}_4/\text{C}_2\text{H}_4$ mixtures.

Experimental:

Materials:

Methane (Instrument Grade, 99.7 % min.) and ethylene (C. P. Grade, 99.5 % min.), and helium (Ultra-high carrier grade, < 1 ppm O₂ and H₂O) were obtained from Air Products Ltd. Helium was further deoxygenated by passing it through a Model OT-1 oxygen trap from Chromatographic Specialties Ltd. Propylene (C. P. Grade, 99.0 % min.) was obtained from Matheson Ltd.

The catalysts used: 1000 μ mole and 1500 μ mole SO₄²⁻/g 10 wt.% ZrO₂/SiO₂; 1000 μ mole SO₄²⁻/g ZrO₂; and 10 wt.% ZrO₂/SiO₂ were the same catalysts as those characterized in Chapters 3 and 4. Hence, the reader is referred to those chapters for their methods of preparation. These materials were pressed into disks, in a manner identical to that used for study by infrared spectroscopy. The disks were then broken into pieces and sieved. Fragments having a diameter between 0.5 and 1.0 mm (16-32 mesh) were used. Typically, about 200 mg of catalyst was used for each experiment. Fresh catalyst was used for each run.

Apparatus:

Experiments were conducted at atmospheric pressure using the single-pass flow system described in Chapter 2. The system was identical to that described except for the following modification. The capacitance manometer previously used (0-13 kPa or 0-100 torr) was replaced by an MKS Baratron Model 122AA capacitance manometer with a 0-133 kPa (0-1000 torr) measurement range. This allowed the total pressure within the system to be monitored during the course of the experiment by leaving valve V2 open (see Figure 2.2). This was a safety precaution, since the possibility existed that high molecular weight compounds might be formed during reaction. Condensation of these products within the system could potentially cause blockage leading to dramatic pressure increase and eventual system rupture.

Catalyst Activation:

All catalysts were activated in flowing helium (10 mL/min.) at 500°C for at least 16 hours. These conditions are similar to those used by Scurrrell *et al.* [29]. Following activation the catalysts were isolated in helium and the temperature was reduced to that used during the experiment, between 225°C and 275°C. During this time gaseous reactant mixtures were flowed through the bypass at room temperature, as described in Chapter 2.

Gas Chromatographic Analysis:

Reaction mixtures and product effluents were analyzed by on-line gas chromatography. All parameters were identical to those used previously (see Chapter 2).

Reaction Conditions:

Following catalyst activation, reactant gas mixtures were diverted through the reactor. Reactant mixtures included : C_3H_8/CH_4 ; C_2H_4/CH_4 ; C_2H_4/He ; and pure CH_4 . The experimental conditions are listed in Table 5.1.

Although the coupling reaction between methane and olefins is thermodynamically more favourable and the tendency for olefins to undergo oligomerization-cracking reactions is minimized at increased pressures, as previously discussed, the following experiments were conducted at atmospheric pressure. These experiments were intended as a preliminary investigation to determine if results warranted the considerable modification of the flow system that would be necessary to operate at higher pressures, between 2 MPa and 4 MPa, such as those used in previous studies [29,30]. Safety considerations were also a determining factor in the decision to operate at atmospheric pressure.

Table 5.1. Experimental Conditions for Methane/Olefin Reactions over Superacid Catalysts.

Expt. No.	Catalyst	Weight (mg)	Flow Rate (mL/min)	Feed Gas	Mole Ratio	Reaction Temperature (°C)
2	1500 [#] , 10 wt.% ZrO ₂ /SiO ₂	170	10	C ₃ H ₆ /CH ₄	0.50	275
3	1000 [#] , 10 wt.% ZrO ₂ /SiO ₂	193	5	C ₃ H ₆ /CH ₄	0.10	275
4	"	227	5	C ₂ H ₄ /CH ₄	0.10	275
5	"	200	5	C ₂ H ₄ /CH ₄	0.10	225
6	"	202	5	C ₂ H ₄ /He	0.10	275
7	"	212	5	CH ₄	0.00	275
8	"	199	5	C ₂ H ₄ /CH ₄	0.50	275
9	1000 [#] , ZrO ₂	216	5	C ₂ H ₄ /CH ₄	0.10	275
10	10 wt.% ZrO ₂ /SiO ₂	207	5	C ₂ H ₄ /CH ₄	0.10	275

[#] loading of sulphate (μmole/g substrate)

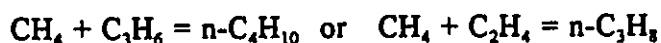
Results and Discussion:

As shown in Table 5.1, in Expt. # 2, a propylene/methane mixture (mole ratio= 0.5; flow rate= 10 mL/min.) was reacted over 1500 $\mu\text{mole SO}_4^{2-}/\text{g}$ 10 wt.% $\text{ZrO}_2/\text{SiO}_2$ at 275°C. Table 5.2 lists the equilibrium compositions for the methane/olefin coupling reaction under these, and other reaction conditions. The equilibrium conversions for propylene and methane are 12.9 % and 6.4 %; the equilibrium partial pressure of n-butane is 4.36 kPa (32.7 torr).

Table 5.2. Equilibrium Compositions for the methane/olefin coupling reaction at atmospheric pressure.

Temperature (°C)	Composition	Mole Ratio	Conversion CH ₄ (%)	Conversion Olefin (%)	Pressure n-alkane [*] / kPa (torr)
275	C ₃ H ₆ /CH ₄	0.50	6.4	12.9	4.36 (32.7)
275	C ₃ H ₆ /CH ₄	0.10	1.7	17.5	1.62 (12.2)
275	C ₂ H ₄ /CH ₄	0.10	7.9	78.5	7.24 (54.3)
225	C ₂ H ₄ /CH ₄	0.10	9.6	95.6	8.80 (66.0)
275	C ₂ H ₄ /CH ₄	0.50	33.0	66.1	22.3 (167.4)

* n-alkane is either butane or propane according to the reactions:



The initial conversions of propylene and methane (measured at 5 minutes on stream) were 2.7 % and 2.1 % respectively. No products (C_4+) were detected. In spite of this apparent low activity, the catalyst was totally deactivated within 35 minutes on stream. The reaction was stopped following only 45 minutes on stream. Upon visual examination, the catalyst appeared deeply blackened. Deactivation was therefore attributed to oligomerization.

In an attempt to alleviate oligomerization, the amount of propylene in the initial reactant mixture was reduced (mole ratio= 0.10). The total flow rate was also decreased to 5 mL/min. The catalyst used was 1000 $\mu\text{mole SO}_4^{2-}/\text{g}$ 10 wt.% $\text{ZrO}_2/\text{SiO}_2$ (see Expt.#3). The observed, initial C_3H_6 and CH_4 conversions were much higher than in the previous experiment (66 % and 61 %, respectively); however, no products higher than C_3 were observed. Again the catalyst deactivated within 35 minutes on stream. From Table 5.2, the initial conversions were much larger than thermodynamically possible for methane/propylene coupling. For example, the equilibrium methane conversion is only 1.7 % under these conditions. Obviously, reactions other than coupling were occurring, such as oligomerization, leading to rapid deactivation.

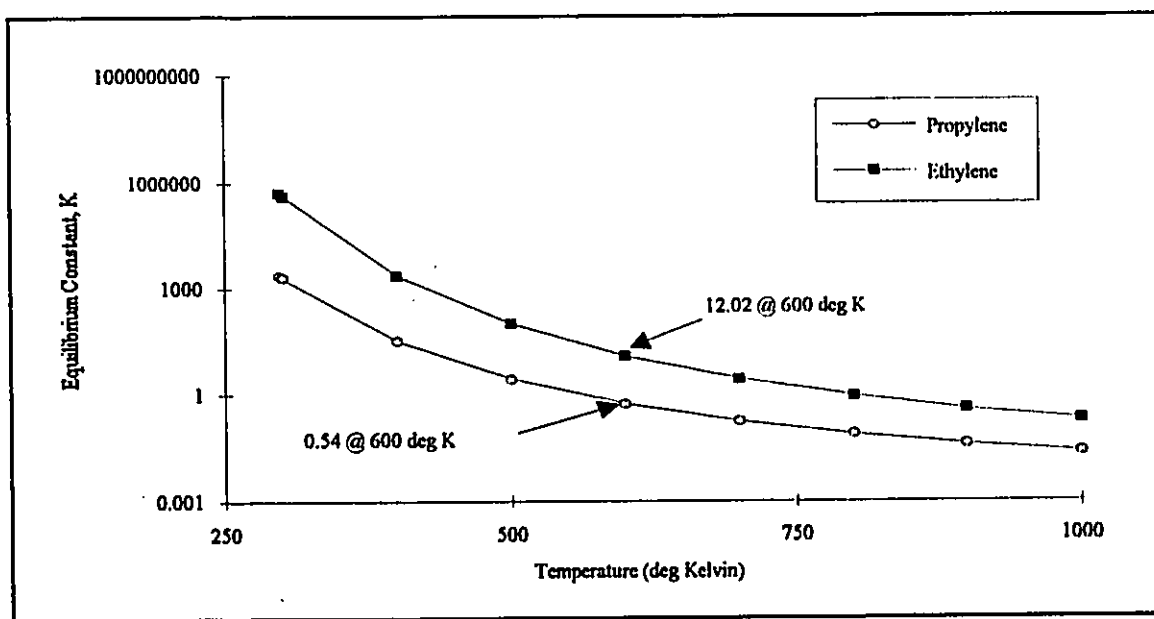
Reactions using Methane/Ethylene Mixtures:

In light of the poor results obtained above, it was decided to use ethylene rather than propylene in subsequent experiments. There were two reasons for this decision. Firstly, as shown previously in Figure 1.2, the equilibrium constant for the coupling of methane and

ethylene is approximately 100 times larger than that for methane/propylene coupling. The second, and more significant reason, is the lesser tendency for ethylene to oligomerize in the presence of acid catalysts than propylene.

Figure 5.1 shows the equilibrium constants, K , for ethylene dimerization to 1-butene and for propylene dimerization to 1-hexene as a function of temperature. As shown, the equilibrium constant for ethylene dimerization is larger (approximately 20 times larger at 600 K) than that of propylene. Hence, from a purely thermodynamic viewpoint, the tendency for ethylene to dimerization is larger than for propylene. Similar calculations show that the same is also true for higher degrees of oligomerization *ie.* trimerization, tetramerization, *etc.*

Figure 5.1: Equilibrium Constant, K , versus Temperature for the Dimerization Reactions of Ethylene and Propylene.



Kinetically ethylene is more difficult to oligomerize in the presence of acid catalysts than propylene. This behaviour is due to the reaction mechanism. Since oligomerization involves carbonium ion intermediates, the relative stability of these ions determines the ease of reaction. The propylenium cation, $C_3H_7^+$, is more stable than the ethylenium cation, $C_2H_5^+$; the former exists in a dynamic equilibrium between a primary and a secondary carbocation, whereas the latter can only exist as a primary carbocation [31]. Therefore, in all subsequent experiments ethylene was used rather than propylene.

As shown in Table 5.1, in Expt.#4 an ethylene/methane mixture (initial mole ratio = 0.1) was reacted at 275°C. Since propane became the lowest possible coupling product, rather than butane, it became possible to monitor the production of propane at 10 minute intervals by GC rather than at 30 minute intervals. It should be recalled that propane had a retention time of 6.9 minutes; n-butane had a retention time of 25 minutes. This allowed us to obtain a larger number of data points.

The percent conversions of ethylene and methane obtained at various times on stream during various experiments are listed in Tables 5.3 and 5.4 respectively.

Table 5.3: Percent Ethylene Conversion as a Function of Time on Stream.

Expt.#	Time on Stream (minutes)			
	5	15	25	35
4	18.14	4.53	2.03	0.0
5	69.56	2.77	0.0	0.0
6	19.03	5.34	2.61	0.53
7	N/A	N/A	N/A	N/A
8	89.58	2.08	0.26	0.0
9	84.94	6.44	0.0	0.0
10	2.53	2.42	2.18	2.96

N/A not applicable

Table 5.4: Percent Methane Conversion as a Function of Time on Stream.

Expt.#	Time on Stream (minutes)			
	5	15	25	35
4	17.07	1.37	0.0	0.0
5	66.10	1.50	0.0	0.0
6	N/A	N/A	N/A	N/A
7	25.65	0.29	0.0	0.0
8	87.21	1.98	0.0	0.0
9	80.86	1.58	0.0	0.0
10	1.47	1.30	1.86	1.52

N/A not applicable

From Tables 5.3 and 5.4, the data indicate that a methane/ethylene mixture flowed over 1000 $\mu\text{mole SO}_4^{2-}/\text{g}$ 10 wt.% $\text{ZrO}_2/\text{SiO}_2$ at 275°C (Expt.#4) also led to deactivation within 35 minutes on stream. The conversion of ethylene dropped quickly from 18 %. Minute amounts of propylene and propane were initially detected (at 5 minutes on stream) but not in sufficient quantities for reliable measurements. Higher hydrocarbons could not be monitored because of the short interval between GC samples as stated above.

Since the coupling reaction is thermodynamically favoured at lower temperatures, see Figure 1.2, the reaction temperature was lowered to 225°C (Expt.#5). The initial conversions of ethylene and methane both increased four-fold from those obtained at 275°C (Expt.#4). Again only trace amounts of propylene and propane were obtained. Increased conversions only led to more rapid catalyst deactivation, within 25 minutes.

In Expt.#6, the effects of reacting ethylene alone, without methane, were investigated. A mixture of C_2H_4 in helium (mole ratio= 0.1) was introduced at the same temperature and flow rate as Expt.#4. From Table 5.3, the ethylene conversion was very similar to that obtained with ethylene/methane mixtures *ie.* the initial conversion was 19 % and fell to zero within 35 minutes on stream. This suggests that ethylene is responsible for deactivation, which is of course consistent with oligomerization. Of interest however, is the fact that trace amounts of propylene, but no propane, were obtained in this experiment, whereas trace amounts of both were formed in Expts.# 4 and #5. The formation of propylene can be explained by the cracking of oligomers. The absence of propane, however trace, may suggest

that methane/ethylene coupling did occur to a small extent in Expts.#4 and #5.

In Expt.#7, methane (5 mL/min) was reacted alone over 1000 $\mu\text{mole SO}_4^{2-}/\text{g}$ 10 wt.% $\text{ZrO}_2/\text{SiO}_2$ at 275°C. The initial methane conversion was 25 %. The catalyst deactivated within 25 minutes. This suggests, contrary to the evidence provided by Expt.#6, that methane also interacts strongly with the catalyst. Superacids are known to polymerize methane [124] and therefore deactivation was again attributed to formation of high molecular weight hydrocarbons. No C_2 's, propane or propylene were detected. This further suggests that coupling of methane and ethylene was occurring in previous experiments, albeit to a very small extent.

In Expt.#8, an equimolar mixture of methane and ethylene was reacted at 275°C. Initial conversions of both methane and ethylene were quite large, 80 % and 90 % respectively. Again, trace amounts of both propane and propylene were measured. The catalyst deactivated within 25 minutes on stream. When the mole ratio of ethylene-to-methane was decreased to 0.1 (Expt.#4) the initial conversion of ethylene was decreased to 18 %. Deactivation occurred more slowly than in Expt.#8 where equimolar quantities of ethylene and methane were used; after 45 minutes the ethylene conversion was still 6 %. Only trace amounts of propylene were formed; no propane was detected.

The effects of dispersing ZrO_2 in silica can be examined by comparing Expts.#8 and 9. In Expt.#9 ethylene/methane (mole ratio= 0.10) was reacted over 1000 $\mu\text{mole/g SO}_4^{2-}$

promoted ZrO_2 (no silica). The results of this experiment were very similar to those obtained in Expt.#8 *ie.* in both experiments the initial conversions of methane and ethylene were above 80 % with deactivation occurring within 25 minutes. However, in Expt.#8 a substantially larger amount of ethylene was used. This suggests that dispersion of zirconia on silica may in fact slightly lower the tendency for oligomerization, as initially predicted. Unfortunately, there is no evidence of enhancement of the coupling of methane and ethylene.

Finally, ethylene and methane were reacted over 10 wt.% $\text{ZrO}_2/\text{SiO}_2$ (no sulphate promotion). The conditions for this experiment (#10) were otherwise the same as those used in Expt.#4. From Tables 5.3 and 5.4, there was a small interaction between this material and both methane and ethylene. The conversions remained fairly constant at approximately 2 % over the course of the experiment. This experiment was allowed to run for six hours; no deactivation occurred. No traces of propane or propylene were detected. This suggests that sulphate promotion of $\text{ZrO}_2/\text{SiO}_2$ is indeed responsible for the activity observed in the above experiments.

In summary, all experiments were hampered by rapid deactivation (within 35 minutes on stream). Only minute quantities of propane were detected. Lowering the reaction temperature from 275°C to 225°C increased the rate of deactivation due to oligomerization. When ethylene was reacted alone, only trace amounts of propylene were detected; no propane was formed. This may suggest that some coupling of methane and ethylene, however slight, did occur in other experiments. Reactions of methane alone showed that it also interacted

strongly with the catalyst, leading to deactivation; however no C₃ hydrocarbons were detected. This implies that some amount of methane/ethylene coupling did occur. Reactions over 1000 $\mu\text{mole SO}_4^{2-}/\text{g}$ 10 wt.% ZrO₂/SiO₂ showed that the initial conversions of ethylene and methane were larger when a larger fraction of ethylene was used, however deactivation occurred more quickly. The similarities between reactions of methane and ethylene mixtures over 1000 $\mu\text{mole SO}_4^{2-}/\text{g}$ 10 wt.% ZrO₂/SiO₂ and more dilute ethylene mixtures reacted over 1000 $\mu\text{mole SO}_4^{2-}$ - promoted ZrO₂ implies that dispersion of the zirconia in silica may alleviate oligomerization to a small degree. The inactivity of 10 wt.% ZrO₂/SiO₂ toward ethylene/methane mixtures confirms the necessity for sulphate promotion.

Directions for Further Study:

Several directions for continued study of CH₄- C₂H₄ coupling using sulphate- promoted zirconia catalysts are listed below:

#1. Catalyst Composition:

The effects of varying the composition of the catalyst should be investigated.

- (a) The results of characterization studies presented in Chapter 3 suggest that the monolayer capacity of zirconia on silica is approximately 10 wt.% zirconia. In terms of alleviating the problems due to deactivation by oligomerization of ethylene, it may prove

advantageous to use sulphate-promoted $\text{ZrO}_2\text{-SiO}_2$ catalysts which contain a smaller amount of zirconia, for example 1 wt. %. A higher dispersion of zirconia on silica than currently used may be necessary.

(b) The effects of loading of sulphate could also be investigated.

#2. Study of Effects of Increased Pressure:

As mentioned previously, from a thermodynamic standpoint, the coupling of methane and olefins is favoured by increased pressure (see Figure 1.3). It has also been stated that increased pressure suppresses the oligomerization of olefins [28]. Indeed, previous studies [29-31] have been conducted at pressures ranging from 2 to 4.5 MPa. Modification of the current flow system to operate in this pressure region may well prove necessary if continued study of this system is desired.

#3. Addition of Platinum to Sulphate-Promoted Zirconia:

The problems encountered in this work due to deactivation are not unique to the methane-olefin coupling reaction. Rather, deactivation is a difficulty encountered in all hydrocarbon reactions currently catalyzed by solid superacids. The skeletal isomerization of n-butane over sulphated- ZrO_2 is a case in point. As discussed by Garin *et al.* [129], "Despite the large number of papers devoted to the ability of sulphate-treated zirconium-oxide

and other related oxides to convert n-butane to isobutane, the question of the rapid deactivation of these catalysts under usual experimental conditions has not been stressed." In an effort to alleviate this ubiquitous problem, these authors have added 0.3 wt. % Pt to sulphated ZrO_2 , and have found that the catalyst lifespan could be increased if hydrogen was also co-fed. This procedure presumably reactivates the catalyst by in situ hydrogenation of the carbonaceous deposits. Hosoi *et al.* have also found that addition of 0.5 wt. % Pt to sulphated-zirconia proved useful in increasing the research octane number (RON) of straight run naphtha [130]. The utility of platinum addition has sparked an increase in interest in these materials and subsequently studies involving infrared and XPS characterization, as well as catalytic testing, have recently been published [131-133].

The addition of platinum to sulphated- ZrO_2 may alleviate the deactivation during methane-olefin coupling and thus should be investigated. Cofeeding hydrogen may also prove beneficial.

#4. Cofeeding Hydrogen over Sulphated-Zirconia or Sulphated-Zirconia/Silica:

Cofeeding hydrogen during methane-ethylene coupling reactions could also prove beneficial however this is not certain. Yori *et al.* [134] found that deactivation of sulphated-zirconia catalysts during n-butane isomerization was not alleviated by cofeeding equimolar mixtures of hydrogen and n-butane at 300°C. Rather, deactivation occurred more quickly. These authors suggested that deactivation was due to reduction of the oxidation state of

sulphur from +6 in the sulphate ion to -2 in $\text{Zr}=\text{S}$. Reduction resulted in the loss of enhanced Lewis acidity of the Zr^{4+} ions (the active sites according to these authors). They found instead that activity could be restored by an intermediate reoxidation step using air. These authors suggested that reoxidation of sulphur was responsible for regeneration. We wonder if the removal of carbonaceous material by oxidation might have been (at least partially) responsible.

#6. Reactivation of Catalyst by Oxidation:

Given the results of Yori et al. [134] discussed above, it may well prove fruitful at some future stage to undertake experiments in which an intermediate reoxidation step, using air or oxygen, is added to attempt to regenerate the catalyst. Of course, before this is necessary one must first find a set of experimental conditions that yield the desired product(s) in sufficient quantities to make the whole process feasible.

Appendix 1:

Development of a Flow Reactor System with an On-line Mass Spectrometer Detector:

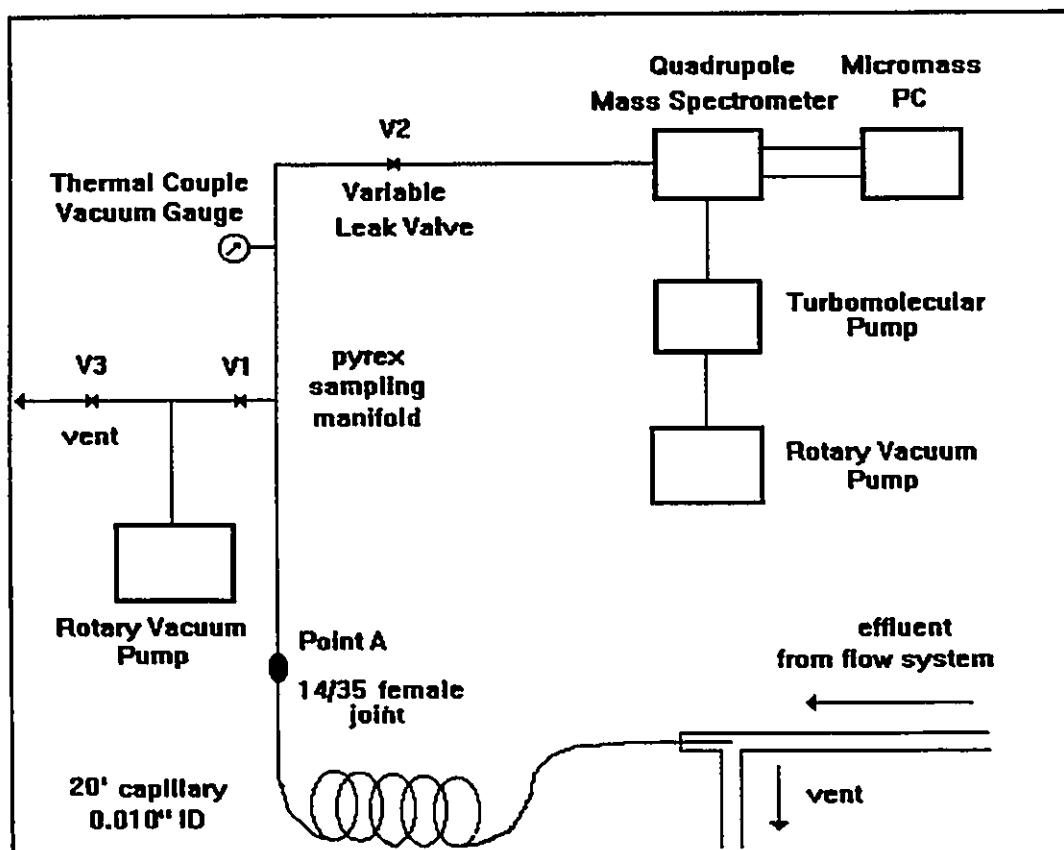
The single-pass, flow system has been described previously in this thesis. A schematic diagram is shown in Figure 2.1. As described, the system had an on-line gas chromatograph for analysis of effluent gas mixtures. A gas chromatograph is necessary for analysis when the mixtures contain multiple components. If however the mixtures have relatively simple composition, or if isotopic labelling is used, detection using a mass spectrometer may prove advantageous. In this section we describe the interfacing and calibration of a quadrupole mass spectrometer as a means of analysis of the flow system effluents.

Description of Mass Spectrometer Detection System:

A schematic diagram of the detection system is shown in Appendix 1.1. As shown, the majority of the effluent gas stream was vented to the atmosphere. A portion of the gas stream was split off to the mass spectrometer for analysis. This was achieved by inserting a

1/16" OD capillary tube into a 1/8" Swagelok tee using a 1/8" bored-through (BT) fitting and a 1/8" to 1/16" reducer.

Appendix 1.1: Schematic Diagram of On-Line Mass Spectrometer Detector System.



The stainless steel capillary had an internal diameter of 0.010" and was 20 feet (6.1 m) in length. It was connected to the pyrex intake manifold of the mass spectrometer via a 1/8" Kovar glass-to-metal seal fitted with a male, No. 14 ground glass joint.

By means of the capillary the sample pressure was reduced from atmospheric pressure at the inlet to approximately 0.13 kPa (1 torr) in the manifold as measured by a thermocouple vacuum gauge. The sample pressure could be further reduced by opening a Teflon stopcock (V1) that connected the manifold to a rotary vacuum pump. The sample was introduced to the mass spectrometer through a Granville-Phillips Series 203 variable leak valve (V2).

The quadrupole mass spectrometer (VG) employed a 15 cm long mass filter and had a resolution of 1 atomic mass unit (amu) across its range of 1- 200 amu. The spectrometer was evacuated via a Pfeiffer Type TPU turbo molecular pump (pumping speed 50 L/s) backed by an Edwards Model E2M2 rotary pump. Background pressures of 10^{-5} - 10^{-4} Pa (10^{-7} - 10^{-6} mbarr) were obtained. The instrument was equipped with both a Faraday cup detector and a Secondary Electron Multiplier (SEM) detector; the former was used most frequently since sample pressures were typically in the 10^{-3} Pa region (too high for the SEM detector to be safely used).

In Multi-Ion Monitoring (MIM) mode the instrument was capable of measuring 16 different masses simultaneously. Typically data points were acquired every 30 seconds; signal-averaging of 16 or 256 times at each mass was used.

The spectrometer was interfaced to a VG Micromass PC, a dedicated PC-based computer. A program called "Quasar", also from VG, controlled data acquisition and processing. This program could also be run on any IBM-compatible PC for the data manipulation and display purposes.

Calibration of the Mass Spectrometer System:

Ultimately quantitative analysis of mixtures of gaseous hydrocarbons such methane and ethane in an argon carrier gas was desired. In order to convert from partial pressures, as measured by the mass spectrometer, into percent composition in the mixture calibration was required.

For the purposes of calibration argon was used not only as a carrier gas but as an internal standard; using the MIM mode, the partial pressure of its molecular ion, Ar^+ , mass-to-charge ratio (m/e) = 40, was measured. In addition, the partial pressures of other selected masses were monitored. The ratio of the partial pressure of monitored mass to that of m/e 40 was then determined. Once an appropriate calibration curve was measured (*ie.* ratio $m/e = x$ to m/e 40 versus percentage hydrocarbon in mixture) then quantitative measurement was possible.

The mass-to-charge ratios of 2, 16, and 30 amu were selected to monitor hydrogen, methane and ethane respectively. Although the base peak for ethane occurs at 28 amu, significant interference from residual N_2 existed at this mass. Thus in spite of the fact that m/e 30 was only 23.5% as intense as the base peak, the lower background lead to increased sensitivity for ethane.

Calibration using Static Gas Sample Mixtures:

Samples of methane, ethane, and hydrogen in argon (each at 1, 5, and 10 volume %) were prepared by expanding measured amounts of each gas within a calibrated gas manifold into a pyrex gas sampler (volume 10 mL); the sampler was connected by a #14 male ground glass joint. The total sample pressure was 93.3 kPa (700 torr). The sampler was isolated via Teflon stopcock and was connected to the mass spectrometer system (see Appendix 1.1, point A).

Experiments revealed that the ratio (m/e of interest to m/e 40) obtained depended on the following parameters:

1. Sample pressure within spectrometer:

The ratio was found to decrease as the sample pressure within the spectrometer increased. This can be explained by collision-induced (CI) fragmentation of the hydrocarbon ion products within the spectrometer; CI fragmentation should increase with increased internal pressure as observed. Thus the leak valve was adjusted such that the sample pressure within the spectrometer was constant for each measurement (approximately 10^{-3} Pa);

2. Leak valve opening:

Although the leak valve was adjusted to maintain a constant pressure as discussed above, limits did exist. The size of the orifice through the leak valve was found to affect the ratio as the opening became small. The effect was greatest for H_2 , followed by CH_4 , and then C_2H_6 . This dependence can be explained by diffusional effects which become important at small orifice openings. Therefore the orifice was kept as wide as possible to eliminate this phenomenon.

The source pressure, ie. the pressure within the sampling manifold did not affect the the measured ratio within the range 0.13- 133 Pa (100 mtorr to 1 torr).

Calibration of Flowing Gas Mixtures:

Mixtures of 1 to 25 vol.% CH₄/Ar and 5 % and 10 % H₂/Ar were prepared by appropriate adjustment of the mass flow controllers. The total flow rate of the gas mixture was kept constant at 50 mL/min. As described previously a 20 foot long, 0.010" ID. capillary was used to introduce a sample of the effluent to the mass spectrometer manifold. Using this flow rate and length of capillary the source pressure could be varied from approximately 46.7 Pa (350 mtorr) to atmospheric pressure by adjusting the stopcock to the rough pump (V1 in Appendix 1.1).

As observed with static samples, the calibration ratios were observed to depend on the sample pressure within the spectrometer. The ratios also varied at small leak valve settings. In summary, a calibration curve for CH₄/Ar mixtures [ratio m/e 16/40 versus % CH₄ in Ar] was obtained under the following conditions: total flow rate = 50 mL/min.; source pressure approximately 53 Pa (400 mtorr); leak valve setting = 100; pressure of sample within spectrometer = 1×10^{-3} Pa (10^{-5} mbarr).

Determination of the Sensitivity of the Flow System with Mass Spectrometer Detector:

In order to determine the lower detection limit of a component in a mixture such as CH_4 , C_2H_6 , in argon in following procedure was performed. Samples of (1.0 volume % C_2H_6 , 10 % CH_4 , bulk Ar) and (0.1 % C_2H_6 , 10 % CH_4 , bulk Ar) were prepared in a sampling bulb using the gas manifold as previously described. The samples (total pressure about 40 kPa (300 torr)) were then analyzed by the mass spectrometer in MIM mode using the Faraday cup detector.

Analysis showed that at least 1.0 volume % C_2H_6 in the total mixture was necessary to obtain a signal-to-noise ratio of 10 at m/e 30. The sample containing 0.1 % C_2H_6 produced a signal-to-noise ratio of approximately 2, even when signal averaging of 1024 times was employed.

The lower detection limit of a compound such as ethane in the mixture is approximately 1 volume percent. Similar detection limits have been reported by researchers studying the oxidative coupling of methane using a similar type of flow reactor system with mass spectrometric detection [145] .

System Evaluation By Analysis of the Hydrogenation of Propylene over 1.0 % Pt/Al₂O₃:

The hydrogenation of propylene to propane is a thermodynamically favourable reaction over the temperature range 300 K to 800 K. The equilibrium constant, K , is 10^5 at 600 K. Thus, the equilibrium conversion of propylene is near 100% for an equimolar mixture of propylene and hydrogen at this temperature. In addition to favorable thermodynamics the hydrogenation is known to be catalyzed by platinum with very high selectivity.

It was decided that propylene hydrogenation over 1.0 % Pt/Al₂O₃ would serve nicely as a test reaction with which to characterize the system. The hydrogenation of ethylene to ethane was dismissed as a test reaction because of the great similarities in the mass spectra of these two compounds, thus severely hampering quantitative analysis of their mixtures. By contrast the mass spectra of propylene and propane are quite distinct. If proper account is taken of the minor overlap of at $m/e = 29$, the base peak of propane, and at $m/e = 41$, the base peak of propylene, these two masses can be used to monitor propane and propylene respectively.

Calibration curves for the ratio of intensities of m/e 29/ m/e 40 versus % composition for propane/argon mixtures and m/e 41/40 for propylene/argon mixtures were measured in a constant at 50 mL/min.

A minor modification was necessary to the flow system in order to provide mixtures of propylene, argon, and hydrogen for reaction. A Swagelok tee was inserted into the hydrogen line just above valve V6 (see Appendix 1.1). The 1/4" Swagelok tee below valve V8 was replaced by a 1/4" Swagelok cross. The hydrogen line was then connected at this point. Hence, hydrogen could be used alone for initial reduction of the catalyst, or, by switching the position of the three-way valve, V6, it could be mixed with propylene and argon.

Prior to experiments, the catalyst was reduced in flowing hydrogen (80 mL/min.) at 400°C for two hours. Hydrogenation reactions were then performed at 325°C and atmospheric pressure. Mixtures of C₃H₆ and H₂, with ratios of C₃H₆/H₂ = 5.0, 1.0, and 0.20, diluted in argon (either 50% or 75% argon) were flown through the catalyst at 50 mL/min.

Product effluents were analyzed by the mass spectrometer in MIM mode. In all cases, analysis revealed very good agreement between the amounts of C₃H₆ and C₃H₈ measured and the equilibrium compositions calculated under the experimental conditions used. Agreement was always better than 2-3%. Thus equilibrium was established under all conditions used.

In summary, a system by which effluents from the flow reactor system can be quantitatively analyzed by an on-line mass spectrometer has been calibrated, and tested. Provided that the effluent mixtures are simple enough and/or that the mass spectra of the components do not significantly overlap, and that appropriate calibrations have been run

beforehand, quantitative analysis is possible. The lower detection limit for a compound such as ethane was determined to be 1 volume percent for this particular system.

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