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Direct conversion of methane under non-oxidative conditions

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Abstract

The catalytic conversion of methane into more desirable chemicals is an area of immense interest. This is a consequence of the high relative abundance of methane. This work explores the conversion of methane into hydrogen and benzene under non-oxidative conditions. The experimental work undertaken has focused on two main objectives: to improve the stability and reactivity of the methane dehydroaromatisation catalyst, MoO$_3$/H-ZSM-5 and to understand more fundamental aspects of the MoO$_3$/H-ZSM-5 catalyst.

It has been observed that both the hydrogen and benzene formation rate profiles are similar for MoO$_3$/H-ZSM-5 based catalysts in methane dehydroaromatisation. In all cases the H$_2$:C$_6$H$_6$ formation rate ratio is higher than expected, which is an indication of coke formation. The relative constancy of the ratio implies that the benzene formation and hydrogen producing side reactions decline at similar rates.

On comparing the catalytic activity of MoO$_3$/H-ZSM-5 with Pd/H-ZSM-5, it was observed that these two catalysts exhibit little similarity in behaviour. This implies that either Mo$_2$C is not the active phase of molybdenum in MoO$_3$/H-ZSM-5 or that there are uncertainties in the comparisons that can be drawn between Mo$_2$C and Pd within this system. Pd/H-ZSM-5 was found to be an active methane decomposition catalyst, where the hydrogen produced was free from any CO$_x$ co-products. The carbon deposited on the catalyst during the reaction is in the form of carbon nanotubes with a “herring-bone” structure.

To try and improve the catalytic performance of MoO$_3$/H-ZSM-5 in methane dehydroaromatisation doping with additional metals was investigated. Promotional effects were observed for Fe$^{3+}$, Al$^{3+}$ and Ga$^{3+}$, the impregnation solutions of these dopants were all acidic. Doping with iron increases benzene formation rates at longer times on stream, aluminium doping was also seen to increase the benzene formation rate, although reproducibility effects were observed with this dopant and gallium doping was seen to result in reduced catalyst coking. TEM images of both Fe and Al doped catalysts reveal that some of the carbonaceous deposition on these catalysts is in the form of carbon nanotubes. Doping with Co$^{2+}$ and Ni$^{2+}$ was not seen to produce any promotional effects (aside from an initial high hydrogen formation rate).

Phosphorus doping in the form of a phosphomolybdic acid precursor leads to lower catalytic activity. When 5wt.% phosphorus was added to a ready prepared 3%MoO$_3$/H-
ZSM-5 catalyst, activity was suppressed and hydrogen was observed as the sole gas phase product before the evolution of trace amounts of carbon oxides at longer times on stream. A 5wt.% P doped MoO₃ sample was observed to produce hydrogen as a result of carburisation. In this case carbon oxides were obtained simultaneously with the H₂ maximum. Post reaction XRD of the bulk P/MoO₃ material revealed a mixture of molybdenum carbide and molybdenum phosphide.

A novel method for the production of phosphides through the reduction under methane from the corresponding phosphate doped oxide has been observed. Although, the preparation of phosphides via reduction of phosphates using more reactive hydrocarbons i.e. propane and propene, as the reducing agents has proved more difficult.

A study on the activation of MoO₃/H-ZSM-5 dehydroaromatisation catalysts using Al K-edge EXAFS in conjunction with ⁷⁷Al MAS NMR found that there is a significant distortion of the tetrahedral framework Al environment, with Al species being drawn towards molybdenum centres. *In-situ* FTIR verifies that molybdenum remains in the +VI oxidation state under the conditions employed in the EXAFS experiments.

²⁷Al and ²⁹Si MAS NMR experiments conducted on H-ZSM-5 and MoO₃/H-ZSM-5 catalysts demonstrated that there is an extraction of framework Al upon incorporation of Mo species into H-ZSM-5. The appearance of a sharp signal in the ²⁷Al MAS NMR spectra of MoO₃/H-ZSM-5 catalysts is notable. This implies that such species are “liquid-like” in nature and may be present as either highly disordered species or possibly as hydrated cations.
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Publications


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Author’s declaration

The work contained in this thesis, submitted for the degree of doctor of philosophy, is my own original work, except where due reference is made to others. No material within has been previously submitted for a degree at this or any other university.
1 Introduction

1.1 General background

Natural gas exists in gaseous form or as a mixture with oil in natural underground reservoirs all around the world. It is an abundant, low cost carbon based feedstock. Methane is the primary component of natural gas and it is a greenhouse gas. It is the simplest and most stable hydrocarbon molecule, and its conversion into more useful compounds has been studied extensively in both homogeneous and heterogeneous catalysis[1]. The challenge that faces catalytic chemists is to develop a route to more desirable chemicals in the conversion of methane that is efficient, commercially viable and most important environmentally benign[2].

1.1.1 Methane activation

Extensive research on methane activation over the past several decades has resulted in both indirect and direct routes of methane conversion. A schematic representation of different methods of activating methane adapted from reference[11] is shown in Figure 1.1-1. The direct route involves the generation of hydrocarbons from the coupling of methane in either oxidative or non-oxidative conditions, while the indirect route generates hydrocarbons via intermediates, which come from methane reacting with steam or oxygen[1].

Figure 1.1-1 Schematic representation of different methods of activating methane[11].
Thermodynamic constraints on reactions where all the C-H bonds of methane are broken, i.e. CH$_4$ reforming into synthesis gas or CH$_4$ decomposition, are far easier to overcome than reactions where only one or two C-H bonds of methane are broken.

At present, steam reforming of methane is the primary route of methane conversion (CH$_4$ + H$_2$O $\rightarrow$ CO + 3H$_2$). This process is highly endothermic and results in the formation of synthesis gas that can be further processed into methanol and ammonia$^{[3]}$. The methanol to gasoline (MTG) process can then be utilised for the production of gasoline$^{[4]}$. Alternatively, synthesis gas can be directly processed into hydrocarbons via the Fischer-Tropsch process$^{[3, 5]}$. Steam reforming of methane is by far the most researched route of methane conversion but it is an expensive process to produce hydrocarbons in this way$^{[1]}$.

In homogeneous catalysis, it was first reported as early as the 1970s that methane could be converted into higher hydrocarbons via the homologation reaction in a superacid medium$^{[6]}$. More recently, the direct conversion of methane to higher hydrocarbons has been extensively studied in heterogeneous catalysis. In the early eighties, the oxidative coupling of methane (OCM) was first reported by Keller and Bhasin$^{[7]}$. The products of the reaction are ethane and ethylene. The reaction is normally carried out at atmospheric pressure and temperatures ranging between 900 and 1200 K. Since the report by Keller and Bhasin this reaction has been extensively researched with many developments being made$^{[8, 9]}$. The OCM reaction has become one of the most pursued topics of research in methane activation$^{[1]}$. However, no catalyst has been able to meet the conditions required for industrial application, as no catalysts were found to have a selectivity to C$_2$ higher than 80% and per pass C$_2$ yield greater than 25% (C$_2$ products are easily further converted into the undesired CO$_x$ species formed due to the presence of oxygen in the feed). Therefore the research for this route has gradually diminished and other routes were investigated$^{[10]}$.

In view of the fact that the conversion of methane with the aid of oxidants is thermodynamically more favourable than under non-oxidative conditions, methane conversion with the aid of oxidants has received far greater attention than that under non-oxidative conditions$^{[11]}$.

1.1.2 Direct conversion of methane under non-oxidative conditions

As already mentioned, the direct conversion of methane under non-oxidative conditions is thermodynamically unfavourable. However this alternative approach to methane
conversion has generated considerable attention over recent years. A particular advantage for this route compared to oxidative conversion is the absence of pathways to COx involving gas-phase oxidants. In addition, it can also be seen as a possible pathway to generate hydrogen.

Two research groups in particular, van Santen and co-workers, and Amariglio and co-workers, simultaneously and independently discovered a two-step procedure for the direct non-oxidative conversion of methane\(^{12-14}\). They both reported that the first step consists of contacting methane with dispersed metallic particles leading to hydrocarbonaceous residues, which in the second step are hydrogenated off yielding higher hydrocarbons. The two groups' procedures differ in the following ways: (1) the relative temperature of the first step and (2) the partial pressure of methane applied. The van Santen group use a two-temperature cycle. Dissociative methane adsorption takes place on a silica supported transition metal catalyst (Ru, Rh or Co) at 700 K, and then hydrogenation is carried out below 400 K and at atmospheric pressure. The Amariglio group carry out the two-step procedure under isothermal conditions and at a moderate temperature on Pt (including EUROPT-1), Ru and Co, e.g. 533, 433 and 553 K respectively, using methane and hydrogen sequentially at atmospheric pressure\(^{12, 14}\). Under the conditions applied, thermodynamics prevent the direct formation of ethane (as well as, propane and butane, which are also products of the reaction) from methane, therefore to avoid this thermodynamic limitation, van Santen and co-workers operated the process at two different temperatures\(^{14}\). The Amariglio group overcame the thermodynamic limitation in the isothermal process by removing hydrogen from the surface in the first step at low pressures, where high flow rates of methane were used, and then supplying it in the hydrogenation step at 1 bar. van Santen and co-workers suggested that methane first dissociated on a precious metal to form a carbide and hydrogen, then the carbide is hydrogenated to form hydrocarbons. In this case C-C bonds were suggested to form during the hydrogenation step\(^{14}\). Temperature-programmed surface reaction (TPSR) carried out after the chemisorption step showed that there were three different types of carbonaceous species on the surface. The highly active C\(_a\) phase was held accountable for the formation of higher hydrocarbons. C\(_r\), which was unreactive, and gas-graphitic in nature, had a tendency for methane formation at higher temperatures. C\(_g\) had intermediate activity producing mainly methane with very small amounts of C\(_2+\) hydrocarbons. Amariglio and co-workers suggested that C-C bonding could take place between H-deficient CH\(_x\) formed during the first step of methane chemisorption, while hydrogen saturated the C\(_2\) precursors in the second step and removed them from the surface\(^{15-18}\). This two-step route has been found to be possible over many oxide or zeolite supported
transition metal and bimetallic catalysts, such as Cu-promoted Rh/SiO₂, and Co-Pt/NaY\textsuperscript{[19-21]}. Solymosi et al. demonstrated that a Cu-promoted Rh/SiO₂ catalyst resulted in an enhanced formation of C₂H₆ and that higher hydrocarbons were observed in the two-step process\textsuperscript{[21]}.

Regardless of all the considerable research efforts driven towards two-step CH₄ homologation, its low efficiency is the main limitation to further developing it as a commercial process\textsuperscript{[11]}. Nevertheless, these studies increased the knowledge of methane catalytic chemistry.

Thermodynamically, it is more favourable to convert methane into aromatics than it is olefins, as shown in Figure 1.1-2, reproduced from reference\textsuperscript{[11]}.

The preparation of a multi-functional catalyst in order to prevent the use of a two-step process has been proposed by several research groups. A patent filed by Mitchell and Waghorne indicated that if methane was passed over a M/M'On/M"O multi-component catalyst where M is a precious metal, M' is a VIB element, and M" is an IIA element, at 977 K for 30 min, benzene could be detected\textsuperscript{[22]}. More recently benzene has been seen to be produced by the dehydrogenative coupling of methane without the use of oxygen in the feed gas over a Pt-SO₄/ZrO₂ catalyst\textsuperscript{[23]}.

In the early nineties, Wang and co-workers reported on the dehydroaromatization of methane (MDA), for the formation of aromatics (mainly C₆H₆) under non-oxidising
conditions in a continuous flow reactor on Mo/H-ZSM-5 catalysts\cite{241} and this system is described in more detail below.

## 1.2 Dehydroaromatisation of methane under non-oxididative conditions

### 1.2.1 Introduction

The MDA reaction, which is generally run at ambient pressure and temperatures of ca. 973 K and above, is equilibrium limited with the limit of conversion being 11.5\% at atmospheric pressure and 973 K\cite{251}. As well as producing aromatics, MDA also produces a significant amount of hydrogen per benzene molecule produced, as shown in Equation 1-1.

\[
6\text{CH}_4 \rightarrow \text{C}_6\text{H}_6 + 9\text{H}_2 \quad \text{Equation 1-1}
\]

In certain niche applications, this reaction could be of interest as an alternative to the conventional route to hydrogen, methane steam reforming, Equation 1-2, which is highly endothermic and is usually operated at 1173 K:

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad \text{Equation 1-2}
\]

Since the initial reports of the MDA reaction by Wang et al. there have been many other research groups interested in this reaction and promising progress has been made, mainly by the groups of Lunsford\cite{26,27,28,29}, Ichikawa\cite{30,31}, Solymosi\cite{32}, and Iglesia\cite{33,34}.

The most important findings of the reaction to date are summarised below:

1. MoO\textsubscript{3}/H-ZSM-5 is a bi-functional catalyst, with both the Mo and zeolite components very necessary for the MDA active catalysts.
2. There is an induction period in the early stages of the reaction.
3. Carbonaceous deposits are formed during the reaction, which lead to catalyst deactivation.
4. Various strong interactions occur, such as, those between the framework Al of the zeolite and the Mo species.

In the early stages of research in MDA Xu et al.\cite{241} and Lin et al.\cite{35} used the GC analysis method to monitor the exit stream using flame ionisation and thermal conductivity
detectors. Both research groups ignored the carbonaceous products, which were formed during the reaction. However, at a later date, Lunsford et al. quantitatively corrected for coke formation using N\textsubscript{2} as an internal standard\textsuperscript{[29]}.

1.2.2 Catalyst choice and preparation

The catalysts employed in MDA are generally zeolite supported. Wang et al. reported that methane could be converted to benzene with a selectivity of 100% and a conversion of 1.4% over the zeolite H-ZSM-5. Furthermore, they demonstrated that by loading the zeolite with Mo or Zn cations that the methane conversion was greatly enhanced\textsuperscript{[24]}. Mo/H-ZSM-5 is a bi-functional catalyst since both the Mo species and the Brønsted acid sites of the zeolite are necessary components of an active catalyst. Although the zeolite H-ZSM-5 does show a little activity for MDA this activity is greatly enhanced with the incorporation of molybdenum. It has been shown by Ichikawa et al. that the SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio does have an effect on the formation rates of benzene. Maximum activity for MDA is observed for the H-ZSM-5 supports with SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios of ca. 40\textsuperscript{[36]}. Wang et al. were the first group to report the production of hydrocarbons other than benzene including naphthalene and toluene\textsuperscript{[29]}.

Generally all research groups have prepared the Mo/H-ZSM-5 catalyst by the impregnation method using (NH\textsubscript{4})\textsubscript{6}Mo\textsubscript{7}O\textsubscript{24}.4H\textsubscript{2}O as the precursor\textsuperscript{[11]}. It is believed that when the catalyst is calcined, the Mo containing ions, which are present on the external surface of the zeolite from the previous stage of impregnation decompose into MoO\textsubscript{3} crystallites. Some of these crystallites migrate into the channels of the zeolite and interact with the Brønsted acid sites. The appropriate temperature for the catalyst calcination is reported as 773 K to allow the migration of Mo ions and interaction with Brønsted acid sites\textsuperscript{[11]}.

Recently, a Mo/H-ZSM-5 catalyst for MDA was prepared by microwave heating\textsuperscript{[37]}. It was reported that catalysts prepared by microwave heating exhibited a greater selectivity towards benzene than catalysts prepared by conventional heating methods. They attributed the better catalytic performance for catalysts prepared by microwave heating to more Mo species being located on the outer surface of the catalyst. The findings of this study are contrary to the idea that shape selectivity is important\textsuperscript{[38]}; the shape selectivity of MDA catalysts is described in more detail later.

Since the MDA reaction was first reported there have been many transition metal ions that have been tested for methane activity, including, Mo, W, Fe, V, Cr, Re, Cu and Zn. The
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most effective metal ion precursor for the zeolite is molybdenum and the trend in activity in methane conversion is as follows: Mo > W > Fe > V > Cr. Mo/H-ZSM-5 has been the most well studied catalyst for MDA. It has been reported that the most favourable loading of MoO3 on ZSM-5 for MDA is in the range of 2-6 wt. % MoO3 loadings greater than 6% lead to blockage of channels and dealumination of the zeolite and therefore a loss in catalytic activity.

MDA catalysts are in general prepared by impregnating the transition metal ions onto the zeolite support. Weckhuysen et al. demonstrated from x-ray photoelectron spectroscopy (XPS) that transition metal suboxides are formed in all impregnated samples, except, Mo/H-ZSM-5. For this catalyst Mo2C was observed. The authors concluded that different transition metals will have different active phases that are responsible for the reaction.

From reviewing the literature, many research groups agree that H-ZSM-5 is the best support for MDA. However recently, Bao et al. have reported that Mo/H-MCM-22 catalysts prepared by the impregnation method showed better catalytic performance with higher benzene selectivity (ca. 80% in maximum) as well as a better tolerance to carbonaceous deposits, as compared with the Mo/H-ZSM-5 catalyst.

Zhang et al. have studied methane aromatisation over Mo-based catalysts supported on different types of zeolites, zeotypes and mesoporous materials. They found the activities of various Mo modified catalysts to be in the following order:


Zhang et al. linked the catalytic performance to the structure of the zeolites and came to the conclusion that silica-alumina zeolites with two-dimensional structures and a pore size near to the dynamic size of benzene (0.59 nm) are good supports for Mo-based catalysts in MDA. They report that materials with pore diameters smaller than that of benzene, such as SAPO-34, are not able to hold benzene in their channels. This results in the active phase for methane aromatisation only being supplied to the external surface, resulting in more ethylene being produced and the selectivity of benzene being lowered. Solymosi et al. have studied catalysts prepared from different molybdenum precursors (MoO3, Mo2C, K2MoO4 and MoO2) and supports (HZSM-5, Al2O3, SiO2, MgO and TiO2) . They found that a K2MoO4/HZSM-5 catalyst exhibited lower methane conversion than the MoO3/HZSM-5 catalyst. From studying the various supports they found the best support
was HZSM-5 and that the method of catalyst preparation affected the performance dramatically.

1.2.3 Induction period

It is well accepted that at the early stage of the MDA reaction that there is an induction period before the aromatisation occurs where molybdenum oxide species are reduced by methane into Mo$_2$C and/or MoO$_4$C$_x$\cite{1}. The research groups of Solymosi and Lunsford showed by XPS that it is Mo$^{VI}$ ions that are reduced by methane which lead to these new species and that they are accompanied by the deposition of carbonaceous cokes. They suggested that molybdenum carbide provides the active site for ethylene formation from methane, while the acid sites of the zeolite catalyse the subsequent conversion of ethylene to benzene. It was suggested that the molybdenum carbide species are most likely highly dispersed on the outer surface and that some of them reside in the channels of the zeolite. After the initial induction period, a benzene selectivity of 60-65% at a CH$_4$ conversion of 7-12% was achieved with the Mo/H-ZSM-5 catalyst$^{29,32,40}$.

It is thought that Mo$_2$C is the species responsible for the activation of methane. Ma et al. carried out temperature programme surface reaction studies on cobalt catalysts supported on H-MCM-22 and Mo catalysts supported on TiO$_2$. They were able to show that neither catalysts were capable for complete MDA since, Co/H-MCM-22 does not have the unique properties shown by Mo$_2$C to activate methane while Mo/TiO$_2$ cannot complete the aromatisation reaction as it does not contain any Bronsted acid sites, which are crucial in MDA reactions$^{39}$. Mo/H-MCM-22 was reported to have a longer catalytic lifetime than Mo/H-ZSM-5, which was attributed to its stronger ability to accommodate more carbonaceous deposits than Mo/H-ZSM-5. Mo/H-MCM-22 also undergoes an induction period where the Mo species are transformed into molybdenum carbide during the induction period. Therefore this group used Mo/H-MCM-22 as an alternative to Mo/H-ZSM-5 to investigate this activation study.

Using $^{1}$H MAS NMR spectroscopy to study proton species over Mo/H-ZSM-5, Bao et al. reported that when the temperature of the MDA reaction was at or below 873 K, only a small decrease in the Bronsted acid sites could be observed$^{41}$. However, after increasing the temperature to 973 K, the colour of the catalyst changed from blue-white to black, indicating the formation of molybdenum carbide (or coking). Along with this observation, the intensity of the signal of Bronsted acid sites at ca. 4.0 ppm decreased dramatically
instead of increasing. This was reported as confirmation that the Mo species keep in contact with the framework Al through two oxygen bridges.

Ichikawa and co-workers investigated the active structure of the Mo/H-ZSM-5 catalyst using molybdenum K-edge EXAFS\(^{361}\). Their studies indicated that the molybdenum oxide species are highly dispersed in the internal channels of H-ZSM-5. They also showed that the zeolite supported molybdenum oxide is converted with methane at ca. 955 K to molybdenum carbide (Mo\(_2\)C) clusters.

Iglesia et al\(^{42}\) prepared a Mo/H-ZSM-5 catalyst by the solid-state reaction method and studied the location and change of the Mo species during the preparation process in more detail. The catalyst was made by this method rather than the conventional method of impregnation for this study as it is reported to be easier to determine the location of the Mo species. They reported that MoO\(_x\) species migrated onto the external surface at ca. 623 K. Then at temperatures between 773 and 973 K, the Mo species migrated into the channels of the zeolite via surface movement and gas-phase transport, exchanged at the acid sites and reacted to form water. They assumed that each Mo atom replaced one H\(^+\) during the exchange, based on the amount of water that was evolved during the exchange process and the number of residual OH groups detected by isotopic equilibration. Using this stoichiometric measurement along with requirement of charge compensation, Iglesia proposed that the exchanged species consisted of a ditetrahedral structure of (Mo\(_2\)O\(_5\))\(^{2+}\), which interacts with two cationic exchangeable sites. It was reported that the (Mo\(_2\)O\(_5\))\(^{2+}\) species are reduced by methane at the initial stage of the reaction and form small MoC\(_x\) clusters. Iglesia and co-workers used near edge X-ray absorption to characterise the Mo species on Mo/H-ZSM-5 treated under various conditions. They estimated that the MoC\(_x\) clusters are ca. 0.6 nm in diameter and contain about 10 Mo atoms.

It is commonly agreed that there is an induction period in MDA, where Mo\(^{VI}\) species are reduced by methane to molybdenum carbide, mainly yielding H\(_2\)O, CO, CO\(_2\) and H\(_2\). After the induction period, CO and light hydrocarbons i.e. ethylene and ethane, along with benzene, toluene and naphthalene are formed.

### 1.2.4 Carbonaceous deposits and deactivation

Carbonaceous deposits are formed during the MDA reaction. These carbonaceous deposits are a major obstacle for further process development. Lunsford et al. observed surface carbon using XPS\(^{26}\). They saw three different types of surface carbon on an active Mo/H-
ZSM-5 catalyst; these are described in more detail in Chapter 4. The authors reported that the carbon species that gradually covers both the surface of the zeolite and the molybdenum carbide phase formed during methane activation is a hydrogen-poor sp hybridisation or pre-graphitic-type of carbon, and suggest that chains of the type \(-\text{C} = \text{C}_n\) may be precursors in the formation of graphite. This type of carbon is stated to be responsible for catalyst deactivation in MDA.

A $^{13}$C MAS NMR study carried out by Xu et al. details the carbonaceous deposits formed on Mo/H-ZSM-5 after the MDA reaction$^{[43]}$. They report that there are two kinds of carbonaceous deposits. The first kind is located on the acid sites of the zeolite and lowers their quantity. The acid sites are stated to be necessary for the transformation of ethylene into aromatics. The second kind is located on partially reduced molybdenum species, which are responsible for the activation of methane and the formation of ethylene$^{[43]}$.

Since the study by Xu et al. was reported, other similar studies have been reported. Temperature-programmed surface reaction (TPSR) of CH$_4$, temperature-programmed reduction with H$_2$ (TPR), temperature-programmed oxidation (TPO), temperature-programmed reaction of CO$_2$ (TPCO$_2$) and thermal gravimetric analysis (TGA) have all been used to characterise the carbonaceous deposits on Mo/H-ZSM-5 and Mo/H-MCM-22 after reaction$^{[44-46]}$. These studies conclude that there are at least three different types of coke: carbidic coke in molybdenum carbide, molybdenum-associated coke and aromatic-type coke on acid sites. Post-reaction treatment with H$_2$ and CO$_2$ demonstrated that H$_2$ may only react with coke which is burnt off at high temperatures in the TPO experiment, whereas CO$_2$ is able to remove both low and high temperature carbon deposits. It was also suggested that TPR followed by TPCO$_2$, or TPCO$_2$ followed by TPR can both only partially reduce the amount of coke on a Mo/H-ZSM-5 catalyst$^{[44]}$. Lunsford et al. reported that the pre-formation of Mo$_2$C on H-ZSM-5, without an associated coke deposit, did not fully eliminate the induction period. On this basis, they suggested that the clean surface of Mo$_2$C might be too reactive to form higher hydrocarbons and therefore that a coke modified Mo$_2$C surface may be the active species in the formation of ethylene$^{[29]}$.

Recently, Zhang et al.$^{[47]}$ carried out an investigation on the coke accumulation and deactivation of Mo$_2$C/H-ZSM-5 in MDA. This study was conducted using a physically separable Mo$_2$C/α-Al$_2$O$_3$ and H-ZSM-5 mixture. From TGA analysis of the post-reaction samples, they showed that the build-up of coke occurred mainly on H-ZSM-5. They
concluded that the coking which reduces the activity and selectivity of the Mo₂C/H-ZSM-5 catalyst in MDA is largely present on the Bronsted acid sites of the zeolite.

On the basis of the literature, it can be summarised that there are different types of carbon deposits formed in MDA and they affect the catalyst in different ways. These are, molybdenum carbide, which is formed during the induction period and is widely believed to be responsible for the activation of methane, CH₄, associated with Mo₂C, and finally the formation of coke, which leads to catalyst deactivation.

A recent publication by Lin and co-workers has shown that the coke formation on Mo/H-ZSM-5 can be effectively inhibited by hydrothermal post-synthesis of H-ZSM-5[18]. The hydrothermal post synthesis treatment was reported to develop mesopores in the parent H-ZSM-5 along with decreasing the acidity of H-ZSM-5.

Ichikawa et al.[49] have shown that Mo/H-ZSM-5 can be regenerated after the MDA reaction by treatment using NO in air (1/50 vol/vol). They demonstrated that this procedure increased the removal of coke compared to when NO/N₂ was used to regenerate the catalyst. They found that when using NO/air that all the coke could be removed from the catalyst 100 K lower than when NO/N₂ was used. They proposed the following mechanism for the regeneration:

\[
2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2
\]

\[
\text{NO}_2 + [\text{coke}] \rightarrow \text{NO} + \text{N}_2\text{O} + \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O}
\]

1.2.5 Interactions between the TMI component and the zeolite support

As both the calcination and reaction temperatures are high at ca. 773 and 973 K respectively, several interactions between the zeolite and the TMI components may occur during the preparation stages and during the reaction itself. These include interactions between Mo species and acid sites, between Mo species and framework Al of the zeolite, the reduction of molybdenum species by methane and the carbonaceous deposits which are formed during the reaction. The latter two were described previously.

The interaction between the Mo species and the zeolite can be split into two. Firstly there is the interaction between molybdenum and the acid sites of H-ZSM-5, and secondly there
is the interaction between molybdenum and the framework Al of H-ZSM-5. A study carried out by Xu et al. using XRD and BET measurements on the Mo/H-ZSM-5 catalyst revealed that the molybdenum species are highly dispersed in the channels of H-ZSM-5, resulting from the interaction between the molybdenum species and the zeolite [24]. They also reported that this interaction led to a decrease in the crystallinity of the zeolite component of the catalyst.

The same group also investigated the interaction at different stages of catalyst preparation using FTIR spectroscopy, differential thermal analysis (DTA) and NH₃-TPD [50, 51]. They reported that if Mo/H-ZSM-5 was calcined at an appropriate temperature such as ca. 773 K, the Mo species would interact with the Bronsted acid sites and some of them would move into the channel. If the calcination temperature is too high, such as ca. 973 K, then a strong interaction occurs between the Mo species and framework Al. This was reported to result in the formation of MoO₄²⁻ species, which are stated to be detrimental for methane activation. Xu et al. also studied the active molybdenum species by combining the aqueous ammonia extraction method with XRD, BET, NH₃-TPD and TPR. They reported that the specific surface area decreased with increasing Mo loading and that the Mo species prefer to deposit on the strong acid sites of H-ZSM-5 [51]. The aqueous ammonia extraction results indicated that there are several kinds of Mo species deposited on the surface i.e. octahedrally coordinated MoO₃ crystallites, Al₂(MoO₄)₃ and MoO₄²⁻ species.

Xu et al. went on to further study this interaction using ²⁷Al and ²⁹Si MAS NMR [50]. Their results revealed that there is a strong interaction between the framework Al of H-ZSM-5 and the Mo species. It was shown that the framework Al in the zeolite could easily be extracted by the introduction of molybdenum species, and that the extractability was seen to increase with increasing molybdenum loading and calcination temperature. If the calcination temperature and/or molybdenum loading were too high then the entire framework Al of the zeolite would be extracted so that the catalyst would deactivate.

NH₃-TPD studies have demonstrated that after the introduction of Mo species onto H-ZSM-5 that a new type of acid site develops [52]. Lin et al. studied the structure of Mo/H-ZSM-5 catalysts with various molybdenum loadings using XRD, IR, TPR and NH₃ uptake experiments [35]. They reported that both the BET surface areas and the acidity of the catalyst decreased with an increase in Mo loading.

Using FTIR, Lunsford and co-workers have reported that after the introduction of Mo species onto H-ZSM-5, the impregnated Mo species are located in the vicinity of the
hydroxyl groups\textsuperscript{[27, 29]}. Howe and co-workers conducted a study comparing Mo/H-ZSM-5 catalysts as prepared, calcined at 773 K and/or 973 K and after reaction using FTIR, \textsuperscript{27}Al and \textsuperscript{29}Si MAS NMR and Mo K-edge EXAFS experiments\textsuperscript{[53]}. They found evidence for migration of Mo species into the zeolite pores from comparing the infrared spectra in the $v$(OH) region. Impregnating their H-ZSM-5 sample with ammonium heptamolybdate caused some attenuation of the 3740 cm$^{-1}$ band, which confirmed the location of the initially adsorbed molybdenum on the external surface of the zeolite. EXAFS measurements at the Mo K-edge revealed that the Fourier transforms of the EXAFS from the three samples were all different.

It is clear from the findings mentioned above that there is a significant interaction between Mo species and the H-ZSM-5 zeolite and that these interactions have a crucial effect on the catalytic performance.

1.2.6 Pre-treatment and additives

As previously mentioned, during the MDA reaction coke deposition on the catalyst occurs. The conversion of methane rapidly reduces after a couple of hours due to the coke deposits on the catalyst. There have been several attempts to improve the catalytic activity either by modifying the catalyst itself or by altering the reaction conditions, i.e. by the inclusion of additives in the feed gas. These alterations made, are only briefly described in this section as they are described in the introductory sections in more detail in the subsequent chapters of this work.

To suppress the coke formation on Mo/H-ZSM-5, Ichikawa et al.\textsuperscript{[54]} have conducted experiments where 5.4% $H_2$ and 1.8% $H_2O$ have been added to the methane feed gas. They found that when $H_2$ and $H_2O$ were added together to the methane feed that there was a greater suppression of coke compared to when $H_2$ or $H_2O$ were added separately.

Ichikawa et al. showed that by incorporating an additional metal ion, for example, Fe or Co, into Mo/H-ZSM-5 that the catalytic activity can be enhanced. Another modification of MDA that optimises the reaction is addition of CO and/or CO$_2$ in the methane feed\textsuperscript{[55]}. TPO experiments were used to demonstrate that addition of CO or CO$_2$ in the methane feed reduces the amount of coke formed on the catalyst's surface\textsuperscript{[56]}. Recently, Iglesia and Lacheen\textsuperscript{[57]} have demonstrated that the stability of MoC$_n$/H-ZSM-5 catalysts can be improved by adding CO$_2$ to the methane feed gas in low concentrations.
They propose that CH₄ reacts with CO₂ exclusively at the beginning of the bed, this reaction occurs via scavenging of surface C* and inhibits C-C bond formation. After CO₂ is completely consumed, pyrolysis products are formed at lower yields as a result of H₂ formed in the CO₂-CH₄ section, H₂ was suggested to increase the rate of hydrogenation of surface species preventing formation of carbonaceous deposits.

### 1.2.7 Active sites and proposed reaction mechanisms

Currently, there is not a thorough understanding of the reaction mechanism of MDA. However, there have been several kinds of active sites and reaction mechanisms proposed. In the first report of MDA, by Wang and co-workers it was suggested that the activation of methane over H-ZSM-5 and Mo/H-ZSM-5 was initiated via the carbenium ion mechanism, with Mo⁶⁺ species or protonic sites acting as a hydride acceptor:

\[
\text{CH}_4 + \text{Mo}^{VI} \rightarrow \text{CH}_3^+ [\text{Mo-H}]^{V}
\]

\[
\text{CH}_4 + \text{H}^+ (s) \rightarrow \text{CH}_3^+ (s) + \text{H}_2
\]

Xu et al. suggested that ethylene was the intermediate of the reaction, which further oligomerised to form benzene²⁴, ²⁵. From XPS measurements they showed that molybdenum ions in the fresh catalyst were in the +⁶ valence and that during the MDA reaction, reduction of Mo⁶⁺ to Mo⁵⁺ to Mo⁴⁺ occurred. Xu et al. subsequently proposed the following reaction mechanism:

1. In the initial stage, methane conversion involving heterolytic dissociation of the C-H bond:

   \[
   \text{Mo}^{VI}(=\text{O})_3 + \text{H}^+ \rightarrow \text{CH}_3^+ \rightarrow \text{Mo}^{V}(=\text{O})_3 + \text{H}^+ + \text{CH}_3^+
   \]  

(1)

2. Ethylene formation involving Mo active sites in either +IV or +V oxidation state:

   \[
   2\text{H}^+ + \text{Mo}^{VI}(=\text{O})_3 \rightarrow \text{Mo}^{IV}(=\text{O})(-\text{O})_2 + \text{H}_2
   \]  

(2)

\[
\text{Mo}^{IV}(=\text{O})(-\text{O})_2 + \text{CH}_3^+ \rightarrow \text{Mo}^{IV}(=\text{O})(-\text{O})(-\text{OH})(=\text{CH}_2)
\]  

(3)

\[
\text{Mo}^{IV}(=\text{O})(-\text{O})(-\text{OH})(=\text{CH}_2) + \text{CH}_3^+ \rightarrow \text{Mo}^{V}(=\text{O})(-\text{OH})(-\text{C}_2\text{H}_5)
\]  

(4)

\[
\text{Mo}^{V}(=\text{O})(-\text{OH})(-\text{C}_2\text{H}_5) \rightarrow \text{Mo}^{IV}(=\text{O})(-\text{OH})_2 + \text{C}_2\text{H}_4
\]  

(5)
The initial induction period before the formation of benzene was also noticed by Wang and co-workers\cite{52}. They proposed that a Mo phase transformation took place at the early stage of the reaction and that the new Mo phase was perhaps molybdenum carbide. They subsequently proposed the following mechanism:

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{C} + 2\text{H}_2 \\
\text{MoO}_3 + \text{H}_2 & \rightarrow \text{MoO}_2 + \text{H}_2\text{O} \\
\text{MoO}_3 + 3\text{C} & \rightarrow \text{MoC} + \text{CO} + \text{CO}_2 \\
\text{MoO}_2 + 3\text{C} & \rightarrow \text{MoC} + 2\text{CO} \\
\end{align*}
\]

Lin and co-workers suggested that the conversion of methane was catalysed by the Mo species inside the channels of H-ZSM-5 together with the strong acid sites of the zeolite\cite{24}. It was reported that this process would form CH$_3^\cdot$ free radicals, which would dimerise to form C$_2$ hydrocarbons. Then ethylene could cyclise to form benzene with the aid of protons of H-ZSM-5:

\[
\begin{align*}
\text{CH}_4 \xrightarrow{\text{MoO}_x/ \text{H}^+} & \text{CH}_3^\cdot + \text{H}^+ \\
2\text{CH}_3^\cdot \xrightarrow{\text{MoO}_x} & \text{C}_2\text{H}_4 + \text{H}_2 \\
3\text{C}_2\text{H}_4 \xrightarrow{\text{H}^+} & \text{C}_6\text{H}_6 + 3\text{H}_2 \\
\end{align*}
\]

Solymosi et al.\cite{32, 58} examined a MoO$_x$/SiO$_2$ catalyst and deduced that in the first stage of the MDA reaction that CO, CO$_2$ and H$_2$O were produced from the reduction of MoO$_3$:

\[
\begin{align*}
3\text{MoO}_3 + \text{CH}_4 & = \text{CO} + 2\text{H}_2\text{O} + 3\text{MoO}_2 \\
4\text{MoO}_3 + \text{CH}_4 & = \text{CO}_2 + 2\text{H}_2\text{O} + 4\text{MoO}_2 \\
\end{align*}
\]

These reactions are then followed by the dehydrogenation of methane on the partially reduced catalyst:

\[
\begin{align*}
\text{CH}_4 + \text{O(s)} & = \text{CH}_3 + \text{OH(s)} \\
2\text{OH(s)} & = \text{H}_2\text{O} + \text{O(s)} \\
\end{align*}
\]
or decomposition of methane,

$$2\text{CH}_3 = \text{C}_2\text{H}_6 \quad (5)$$

$$2\text{CH}_2 = \text{C}_2\text{H}_4 \quad (6)$$

$$\text{C}_2\text{H}_4 + \text{CH}_3 = \text{C}_3\text{H}_7 \quad (7)$$

$$\text{C}_3\text{H}_7 + \text{H} = \text{C}_3\text{H}_8 \quad (8)$$

Solymosi and co-workers believed that ethane was the key intermediate for the formation of benzene, which was dehydrogenated to ethylene on the catalyst surface. In further studies, examining a $\text{K}_2\text{MoO}_4/\text{H-ZSM-5}$ catalyst, they suggested a similar mechanism. However, they proposed that the coupling of $\text{CH}_2$ species was the main reaction pathway in the ethylene production. Using XPS they showed that $\text{Mo}_2\text{C}$ was formed on the used catalyst and they regarded this as the active site. They also investigated the catalytic performance of unsupported and supported $\text{Mo}_2\text{C}$ and suggested that, as well as $\text{Mo}_2\text{C}$, the presence of some other Mo compounds i.e. $\text{MoO}_2$, were also required for methane activation and for the formation of ethylene from $\text{CH}_x$ fragments$^{[40]}$.

Pierella and co-workers carried out an investigation on the conversion of pure methane and natural gas with different purity of aromatic hydrocarbons$^{[59]}$. They proposed that pure methane was converted to aromatics over Mo containing catalysts via the following schemes:

$$\text{CH}_4 + \text{Mo/H-ZSM-5} \rightarrow \text{CH}_3^+ + [\text{Mo-H}]^{5+}/\text{H-ZSM-5} \quad (1)$$

$$\text{CH}_3^+ + \text{Mo/H-ZSM-5} \rightarrow \text{Mo=CH}_2/\text{H-ZSM-5} \quad (2)$$

$$\text{Mo=CH}_2 + \text{CH}_4 \rightarrow \text{C}_2\text{H}_6 \quad \rightarrow \text{aromatics} \quad (3)$$

$$\text{Mo=CH}_2 + \text{Mo=CH}_2 \rightarrow \text{C}_2\text{H}_4 \quad \rightarrow \text{aromatics} \quad (4)$$

$$\text{Mo=CH}_2 \rightarrow \text{coke} \quad (5)$$

$$\text{CH}_4 + \text{coke} + \text{Mo/H-ZSM-5} \rightarrow \text{aromatics} \quad (6)$$
They proposed that for natural gas containing some hydrocarbons that the main reaction mechanism could be as follows:

\[
\begin{align*}
\text{C}_2\text{H}_4 + \text{Mo/H-ZSM-5} & \rightarrow \text{C}_2\text{H}_4 \text{ carbenium ions} \\
\text{CH}_4 + \text{C}_2\text{H}_4 \text{ carbenium ions} & \rightarrow \text{aromatics} \\
\text{C}_2\text{H}_4 \text{ carbenium ions} & \rightarrow \text{coke} \\
\text{CH}_4 + \text{coke} & \rightarrow \text{aromatics}
\end{align*}
\]

Ichikawa et al. showed using Mo K-edge EXAFS and TG/DTA/Mass techniques that molybdenum oxide on H-ZSM-5 was converted by methane at 923 K to molybdenum carbide clusters with the evolution of \( \text{H}_2 \) and \( \text{CO} \), then \( \text{C}_6\text{H}_6, \text{C}_{10}\text{H}_8 \) and \( \text{C}_2\text{H}_4 \) were formed. These results suggested that molybdenum carbide on Mo/H-ZSM-5 is an active species for the catalytic methane aromatisation. Ichikawa and co-workers proposed that methane is activated on molybdenum carbide sites to form \( \text{CH}_4 \) and \( \text{C}_2 \) species, which may migrate at the interface of the ZSM-5 acidic support, followed by the aromatisation of the \( \text{C}_2 \) intermediates to form benzene, toluene and naphthalene.

To summarise, it has been shown that there have been several proposed mechanisms for MDA. From the suggested mechanisms it can be seen that, in particular, the elementary reaction pathways are speculative. Currently, there is not any direct experimental evidence for these proposed mechanisms.

### 1.3 Zeolites

The following section has been included in this chapter so as to give a general background on zeolites. H-ZSM-5 is one of the main components of the MDA reaction and is extensively investigated in this thesis. Therefore, it is appropriate to give some detailed information about zeolites in general.

Zeolites are microporous crystalline aluminosilicate solids with well-defined structures. In general they consist of silicon, aluminium and oxygen in their framework and cations, water and/or other molecules within their pores. Zeolites are complex, they comprise of an infinitely extending 3-dimensional four connected framework of \( \text{AlO}_4 \) and \( \text{SiO}_4 \) tetrahedra linked by the sharing of oxygen atoms. Each \( \text{AlO}_4 \) has a net negative charge and is
balanced by a cation. The primary structural units, AlO₄ and SiO₄, join together to form a wide variety of cages and rings known as secondary-building units, (SBU)⁶¹. SBUs found in zeolite structures are shown in Figure 1.3-1 taken from reference⁶².

The final zeolite structure comprises of grouping of the SBUs. It is the way in which these SBUs join together that give rise to the vast number of different zeolite frameworks that exist. The framework structure of zeolites with types ZON (ZAPO-M1), PAU (Paulingite) and VFI (VPI-5) framework are shown in Figure 1.3-2 taken from reference⁶³.

![Figure 1.3-1 Secondary-building units found in zeolites⁶².](image)

![Figure 1.3-2 ZON (ZAPO-M1), PAU (Paulingite) and VFI (VPI-5) framework structures⁶³.](image)
The framework of zeolites contains channels and pores with molecular dimensions. The pore sizes range from 0.3-0.8 nm and subsequently zeolites are classified according to their pore dimensions. The pore dimensions of a few well-known zeolites are shown in Table 1.3-1, taken from reference[64].

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Pore Dimensions, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Erionite</td>
<td>0.36 x 0.52</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>0.41</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>0.51 x 0.55</td>
</tr>
<tr>
<td>Faujasite</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Table 1.3-1 Selected zeolites and their pore dimensions[64].

These pore dimensions enable zeolites to be used for specific applications. The principal applications are ion exchange, desiccants, gas filtration, cracking for gasoline products and shape selective catalysis[64].

Although zeolites are classified according to their pore dimensions they can be further classified depending upon their Si/Al ratio. With increasing Si/Al ratio the stability of the crystal framework increases. Moreover, a zeolite is more stable in the presence of a concentrated acid when the Si/Al ratio is high compared to those with low Si/Al ratio and vice versa for basic solutions[64].

1.3.1 Zeolites – natural and synthetic

There are two classes of zeolites. The first class of zeolites occur naturally as minerals. Natural zeolites possess many applications ranging from gas adsorption, ion exchange to water treatment. For example, clinoptilolite, formed from the devitrification of volcanic ash in lake and marine water millions of years ago, has a channel size which enables it to act as a molecular gas sieve and selectively adsorb toxic gases such as ammonia. The second class are synthetic. These include, ZSM-5 which was developed by Mobil Oil in 1972[65] and has many applications ranging from a catalyst in organic reactions to petroleum refining[61].
1.3.2 H-ZSM-5

While there are many zeolites and zeotypes, one of the most well known is ZSM-5. The structure is referred to as pentasil based, this is because the tetrahedra combine to form a ring consisting of five oxygen atoms (pentasil units). These five ring-building units lead to the lattice structure arranged in a ten-ring way. The 3-dimensional structure of ZSM-5 is shown in Figure 1.3-3 taken from reference.

![Figure 1.3-3 3D structure of ZSM-5](image)

The pore structure of ZSM-5 is shown in Figure 1.3-4, taken from reference, there is a set of linear pores having diameters of 0.51 x 0.56 nm, which are perpendicular arranged to zigzag pores with a diameter of 0.54 x 0.56 nm.

![Figure 1.3-4 Schematic representation of the intracrystalline pore structure of ZSM-5](image)
1.3.3 Zeolites and catalysis

At present, one of the most important applications of zeolites is catalysis. Zeolites as catalysts are advantageous since they have a high density of catalytic sites and are stable to high temperatures, with decomposition temperatures ranging from 700 to 1300°C.

One of the beneficial properties of zeolites as catalysts is their acidic properties. The catalytic activity of decationised zeolites is attributed to the presence of acid sites arising from the AlO₄ tetrahedral units in the framework. These acid sites can be either of the Bronsted or Lewis type. The synthesis of zeolites is normally conducted using Na⁺ ions for balancing framework charges, but these can easily be exchanged for protons by reaction with an acid. This results in the formation of surface hydroxyl groups, i.e. the Bronsted sites. However, if the zeolite is not stable in an acid environment, it is common that NH₄⁺ forms, heat is supplied to drive off the ammonia, additional heating removes water from the Bronsted sites, which leads to the formation of the Lewis acid sites. A scheme for the formation of these sites is shown in Figure 1.3-5, taken from reference [64]. The surface of zeolites can therefore display either Bronsted or Lewis acid sites or both depending on how the zeolite has been prepared[64].

![Figure 1.3-5 Scheme for the generation of Bronsted and Lewis sites in zeolites](image)

[64] Reference number
Some of the most important reactions in which zeolites can act as catalysts are acid-catalysed cracking, isomerisation and hydrocarbon synthesis. They can support an extensive range of catalytic reactions including acid-base, metal induced, as well as oxidative and reductive reactions. Underpinning all these reactions is a zeolites' ability to act as a shape selective catalyst, which makes them so remarkable as catalysts. This type of reaction involves the unique microporous nature of the zeolite, where a steric influence is applied to the reaction by the shape and size of a particular pore system. These reactions take place within the internal cavities of the zeolite[61,64].

Zeolites can exhibit three different types of shape selective catalysis, reactant-selective, product-selective and transition-state-selective catalysis. Reactant selective catalysis is when only molecules with dimension less than a critical size can enter the pore of zeolites and reach the catalytic sites. Product-selective catalysis is when only products less than a certain dimension can leave the active sites and diffuse out through the channels. Transition-state-selective catalysis is when certain reactions are prevented because the transition-state requires more space than is available in the cavities[64]. The three types of shape selective catalysis that a zeolite can exhibit are shown schematically in Figure 1.3-6, reproduced from reference[64].
Shape selective xylene isomerisation can be carried out using the zeolite, ZSM-5\(^6\). ZSM-5 contains channels, which permits molecular diffusion if the size of the molecule is suitable. Figure 1.3-7 taken from reference\(^6\), illustrates the property of zeolites which leads to them commonly being called molecular sieves. For example, it can be seen from the figure that iso-paraffins are too large to enter the pores of zeolite A, whereas, straight chain paraffins fit.
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Figure 1.3-7 Pore dimensions of zeolites and critical dimensions of some hydrocarbons\textsuperscript{[64]}. 

---

\textit{Figure 1.3-7 Pore dimensions of zeolites and critical dimensions of some hydrocarbons\textsuperscript{[64]}.}
1.4 Summary

As previously mentioned, the conversion of methane into more desirable chemicals is an area of immense interest as a consequence of its high relative abundance. However, its stability makes any conversion process challenging. In the future it is most likely that the world will move away from a fossil fuel era and into a hydrogen economy. Thus in the meantime it is useful to build a link between the fossil fuels and hydrogen by producing hydrogen (which is a clean burning fuel) from methane (which is a greenhouse gas).

The direct conversion of methane under non-oxidising conditions can be seen as a pathway which bridges the fossil fuel energy era with the incoming hydrogen energy era since hydrogen is a product of methane conversion along with other basic chemicals such as, benzene. Therefore the development of MDA is a potentially important process for hydrogen production, together with aromatics.

Substantial effort has been undertaken in developing active and selective catalysts for MDA, although they have almost exclusively concentrated on aromatics production, as well as understanding the bi-functionality of Mo/H-ZSM-5 and the nature of the carbonaceous deposits formed during the reaction. It is generally agreed that during the reaction, methane is first activated and dehydrogenated into CH₄ species, which will oligomerise into C₂ species on Mo₂C and/or MoOₓCy species on the external surface and/or in the zeolite channels, these C₂ species then oligomerise further and cyclise into aromatics on the Brønsted acid sites of the zeolite. It is also well accepted that there is an induction period at the early stages of the reaction, which results in the transformation of molybdenum oxide to molybdenum carbide.

Catalysts have been observed to suffer relatively rapid deactivation, which has been attributed to coke formation. One of the major obstacles for a better understanding and for further development of MDA is the carbonaceous deposits, which are formed during the reaction.

It is hopeful that with the ongoing research in this area, along with the advancement of heterogeneous catalysis and materials science in general, that our understanding and knowledge of MDA will enhance and may lead to the development of an efficient, clean and commercially available process.
2 Experimental

2.1 Introduction

The experimental techniques employed in this work are presented in three discrete sections. These sections are as follows: catalyst preparation, catalytic testing and catalyst characterisation.

2.2 Catalyst preparation

Several catalysts were prepared for this work, they are predominantly molybdenum oxide loaded onto the zeolite H-ZSM-5. As mentioned in Chapter 1, the most active catalyst reported for the MDA reaction tested to date is MoO\textsubscript{3}/H-ZSM-5. The standard catalyst used throughout this project is 3wt%MoO\textsubscript{3}/H-ZSM-5.

Various modifications have been made to the MoO\textsubscript{3}/H-ZSM-5 catalyst in this project, such as varying the precursor of molybdenum oxide, altering the loading of molybdenum oxide, doping with additional metals and changing the support.

Other catalysts/materials that were prepared for this work were designed to be tested either independently and/or in conjunction with the standard catalyst.

2.2.1 H-ZSM-5 type catalysts prepared by impregnation

Most catalysts prepared for this work were made by impregnating H-ZSM-5 (Catal, Si/Al ratio = 40) to incipient wetness with an aqueous solution containing the required metal cation, precursor salt (for every 1 g of support ca. 1 ml of deionised water was used). The resultant slurry was slowly dried at 353 K for 24 h before being calcined in air at 773 K for 16 h. Catalysts that have been prepared in this way are listed in Table 2.2-1. The quantities of materials used in the preparation for ca. 1g of each catalyst are given in Table 2.2-1. These quantities were scaled up depending upon the quantity of catalyst required.

H-ZSM-5 based catalysts containing more than one metal were prepared by consecutive impregnation. The first stage involved incorporation of the molybdenum component onto H-ZSM-5 as described above, the next stage involved impregnation with the second metal precursor salt. After each stage, the resultant slurry was slowly dried at 353 K for 24 h.
before being calcined in air at 773 K for 16 h. Catalysts that have been prepared in this way are also listed in Table 2.2-1.

### Table 2.2-1 ZSM-5 (Si/Al ratio = 40) based catalysts prepared by impregnation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Precursors</th>
<th>Quantity (g)</th>
<th>ZSM-5 Quantity (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3%MoO₃/H-ZSM-5</td>
<td>(NH₄)₆Mo₇O₂₄·4H₂O</td>
<td>0.0368</td>
<td>0.9800</td>
</tr>
<tr>
<td>8.7%MoO₃/H-ZSM-5</td>
<td>(NH₄)₆Mo₇O₂₄·4H₂O</td>
<td>0.1104</td>
<td>0.9400</td>
</tr>
<tr>
<td>14.2%MoO₃/H-ZSM-5</td>
<td>(NH₄)₆Mo₇O₂₄·4H₂O</td>
<td>0.1840</td>
<td>0.9000</td>
</tr>
<tr>
<td>3%MoO₃-Co/H-ZSM-5</td>
<td>(NH₄)₆Mo₇O₂₄·4H₂O, Co(NO₃)₂·6H₂O</td>
<td>0.0368</td>
<td>0.9800</td>
</tr>
<tr>
<td>3%MoO₃-Ni/H-ZSM-5</td>
<td>(NH₄)₆Mo₇O₂₄·4H₂O, Ni(NO₃)₂·6H₂O</td>
<td>0.0368</td>
<td>0.9800</td>
</tr>
<tr>
<td>3%MoO₃-Al/H-ZSM-5</td>
<td>(NH₄)₆Mo₇O₂₄·4H₂O, Al(NO₃)₃·9H₂O</td>
<td>0.0368</td>
<td>0.9800</td>
</tr>
<tr>
<td>3%MoO₃-Fe/H-ZSM-5</td>
<td>(NH₄)₆Mo₇O₂₄·4H₂O, Fe(NO₃)₃·9H₂O</td>
<td>0.0368</td>
<td>0.9800</td>
</tr>
<tr>
<td>3%MoO₃-Ga/H-ZSM-5</td>
<td>(NH₄)₆Mo₇O₂₄·4H₂O, Ga(NO₃)₃·xH₂O</td>
<td>0.0368</td>
<td>0.9800</td>
</tr>
<tr>
<td>3%MoO₃-Ag/H-ZSM-5</td>
<td>(NH₄)₆Mo₇O₂₄·4H₂O, AgNO₃</td>
<td>0.0368</td>
<td>0.9800</td>
</tr>
<tr>
<td>3%Pd/H-ZSM-5</td>
<td>Pd(NO₃)₂·xH₂O</td>
<td>0.0649</td>
<td>0.9350</td>
</tr>
</tbody>
</table>

*a dopant metal ion/Mo molar ratio of 0.25

Table 2.2-1 ZSM-5 (Si/Al ratio = 40) based catalysts prepared by impregnation.

### 2.2.2 H-ZSM-5 type catalysts prepared by physical mixing

MoO₃/H-ZSM-5 based catalysts prepared from physical mixtures were also used in this work. The catalysts that were prepared from physical mixtures are listed in Table 2.2-2. These catalysts were prepared by making a mixture of the required amount of H-ZSM-5 (Catal) and molybdenum trioxide (Analar). The catalysts were calcined at 773 K for 16 h. The quantities of materials used in the preparation of ca. 1 g of each catalyst are given in Table 2.2-2.

### Table 2.2-2 ZSM-5 (Si/Al ratio = 40) supported catalysts prepared by dry mixing.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Precursors</th>
<th>Quantity (g)</th>
<th>ZSM-5 Quantity (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3%MoO₃/H-ZSM-5</td>
<td>MoO₃</td>
<td>0.0300</td>
<td>0.9800</td>
</tr>
<tr>
<td>8.7%MoO₃/H-ZSM-5</td>
<td>MoO₃</td>
<td>0.0890</td>
<td>0.9400</td>
</tr>
<tr>
<td>14.2%MoO₃/H-ZSM-5</td>
<td>MoO₃</td>
<td>0.1500</td>
<td>0.9000</td>
</tr>
</tbody>
</table>

Table 2.2-2 ZSM-5 (Si/Al ratio = 40) supported catalysts prepared by dry mixing.
2.2.3 Phosphorus containing catalysts prepared by impregnation

Table 2.2-3 lists phosphorus-containing catalysts that have been prepared for this work. All of the catalysts were prepared using the incipient wetness impregnation technique (for every 1 g of support ca. 1 ml of deionised water was used) and using the same drying and calcination conditions as those given in Section 2.2.1. The quantities of materials used in the preparation for ca. 1 g of each catalyst are given in the table below.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Precursors</th>
<th>Quantity (g)</th>
<th>ZSM-5 Quantity (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%P-5%MoO₃/ZSM-5ᵃ</td>
<td>(NH₄)₆Mo₇O₂₄·4H₂O, NH₄H₂PO₄</td>
<td>0.0613</td>
<td>0.9800</td>
</tr>
<tr>
<td>5%P-3%MoO₃/ZSM-5ᵇ</td>
<td>(NH₄)₆Mo₇O₂₄·4H₂O, NH₄H₂PO₄</td>
<td>0.0368</td>
<td>0.9800</td>
</tr>
<tr>
<td>5.8%P/MoO₃</td>
<td>(NH₄)₆Mo₇O₂₄·4H₂O, NH₄H₂PO₄</td>
<td>0.8143</td>
<td></td>
</tr>
<tr>
<td>5.8%P/ZSM-5ᵇ</td>
<td>NH₄H₂PO₄</td>
<td>0.1857</td>
<td>0.8143</td>
</tr>
</tbody>
</table>

ᵃ ZSM-5 (Si/Al ratio = 50) (Zeolyst)
ᵇ ZSM-5 (Si/Al ratio = 40) (Catal)

Table 2.2-3 Phosphorus containing catalysts prepared by impregnation.

2.2.4 Non-zeolite supported catalysts

The catalysts prepared for this work, which use supports other than a zeolite are listed in Table 2.2-4. Al₂O₃ (Aldrich), SiO₂ (Aldrich) and Zr(OH)₄ (MEL Chemicals) based catalysts were prepared using the incipient wetness impregnation technique (for every 1 g of support ca. 1 ml of deionised water was used) with the same drying and calcination conditions as those given in Section 2.2.1. The quantities of materials used in the preparation for ca. 1 g of each catalyst are given in the table below.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Precursors</th>
<th>Quantity (g)</th>
<th>Type</th>
<th>Support (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%MoO₃/Al₂O₃</td>
<td>(NH₄)₆Mo₇O₂₄·4H₂O</td>
<td>0.0610</td>
<td>δ-Al₂O₃</td>
<td>0.9390</td>
</tr>
<tr>
<td>5%P-5%MoO₃/Al₂O₃</td>
<td>(NH₄)₆Mo₇O₂₄·4H₂O, NH₄H₂PO₄</td>
<td>0.0610</td>
<td>δ-Al₂O₃</td>
<td>0.9390</td>
</tr>
<tr>
<td>3%Pd/Al₂O₃</td>
<td>Pd(NO₃)$_₂$·xH₂O</td>
<td>0.0650</td>
<td>δ-Al₂O₃</td>
<td>0.9350</td>
</tr>
<tr>
<td>5%MoO₃/ZrO₂</td>
<td>(NH₄)₆Mo₇O₂₄·4H₂O</td>
<td>0.0610</td>
<td>Zr(OH)$_₄$</td>
<td>0.9390</td>
</tr>
<tr>
<td>3%MoO₃/SiO₂</td>
<td>(NH₄)₆Mo₇O₂₄·4H₂O</td>
<td>0.0368</td>
<td>SiO₂</td>
<td>0.9632</td>
</tr>
</tbody>
</table>

Table 2.2-4 Non-zeolite supported catalysts.
2.2.5 Externally supplied catalysts

The catalysts listed in Table 2.2-5 were kindly prepared and supplied by Dr. Parida (Regional Research Laboratories, Bhubaneswar, India). These catalysts were prepared using the incipient wetness impregnation technique. The catalysts were dried overnight at 383 K and calcined at 773 K for 16 h.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal Ion Precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%Phosphomolybdic-acid/H-ZSM-5</td>
<td>H$<em>3$PMO$</em>{12}$O$_{40}$.xH$_2$O</td>
</tr>
<tr>
<td>5%Phosphomolybdic-acid/H-ZSM-5</td>
<td>H$<em>3$PMO$</em>{12}$O$_{40}$.xH$_2$O</td>
</tr>
<tr>
<td>10%Phosphomolybdic-acid/H-ZSM-5</td>
<td>H$<em>3$PMO$</em>{12}$O$_{40}$.xH$_2$O</td>
</tr>
<tr>
<td>15%Phosphomolybdic-acid/H-ZSM-5</td>
<td>H$<em>3$PMO$</em>{12}$O$_{40}$.xH$_2$O</td>
</tr>
<tr>
<td>5%Silicomolybdic-acid/H-ZSM-5</td>
<td>H$<em>2$SiMo$</em>{12}$O$_{40}$.xH$_2$O</td>
</tr>
<tr>
<td>5%Sodium-molybdate/H-ZSM-5</td>
<td>Na$_3$MoO$_4$.2H$_2$O</td>
</tr>
<tr>
<td>5%Ammonium-heptamolybdate/H-ZSM-5</td>
<td>(NH$_4$)$_6$Mo$<em>7$O$</em>{24}$.4H$_2$O</td>
</tr>
</tbody>
</table>

Table 2.2-5 Catalysts supplied by Dr. Parida, with Si:Al ratio of ZSM-5 = 50:1 (Zeolyst).

2.2.6 Preparation of ion-exchanged Ni(II) and Fe(III) LTA zeolites

Ni(II)/LTA and Fe(III)/LTA zeolites were prepared in conjunction with Dr Prem Pal (Indian Institute of Petroleum, Dehradun, India). The classical ion-exchange method was used. Initially LTA was protonated by NH$_4^+$ ion-exchange and then calcined at 773 K. Nickel and iron ion containing solutions were prepared by dissolving a known amount of the respective salt, i.e. Ni(NO$_3$)$_2$.6H$_2$O or Fe(NO$_3$)$_3$.9H$_2$O, in deionised water. A known amount of protonic zeolite A was then added to either the Ni or Fe ion containing solution (1:10 v/v), followed by stirring for 4-8 hours at 298 K. This step was repeated a number of times. The resultant slurry was filtered and dried at 383 K overnight, and then calcined at 773 K for 16 h. It should be noted that the metal content in the ion-exchanged zeolites was not measured.

2.2.7 Preparation of phosphide precursors

Binary and ternary transition metal phosphides catalysts were prepared in this work by reducing the corresponding phosphate doped oxide in methane. The details of which are given in section 2.3.
Binary and ternary phosphides that were prepared for this work are listed in Table 2.2-6. The materials employed in the preparation of each phosphide precursor material are also given. MoP and NiP precursor materials were prepared by using a 1:1 or 2:1 molar ratio of MoO₃ or NiO respectively to NH₄H₂PO₄ (Aldrich, 98+%). The required amount of NH₄H₂PO₄ was dissolved in ca. 15ml of deionised water and was impregnated onto MoO₃ or NiO for the preparation of the MoP or NiP precursors respectively, followed by drying at 373 K overnight and then calcined in air at 773 K for 5 hours.

<table>
<thead>
<tr>
<th>Phosphide</th>
<th>Materials used in preparation of phosphide precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoP</td>
<td>MoO₃, NH₄H₂PO₄</td>
</tr>
<tr>
<td>Ni₁₂P₅</td>
<td>NiO, NH₄H₂PO₄</td>
</tr>
<tr>
<td>CoMoP</td>
<td>MoO₃, NH₄H₂PO₄, Co(NO₃)₂.6H₂O</td>
</tr>
<tr>
<td>NiMoP</td>
<td>MoO₃, NH₄H₂PO₄, Ni(NO₃)₂.6H₂O</td>
</tr>
<tr>
<td>FeMoP</td>
<td>MoO₃, NH₄H₂PO₄, Fe(NO₃)₃.9H₂O</td>
</tr>
</tbody>
</table>

Table 2.2-6 Materials employed in preparation of phosphide precursors.

The first step in the preparation of the ternary phosphide precursor materials involves impregnating the 2nd metal nitrates i.e. cobalt, iron or nickel nitrate onto MoO₃. The precursor materials consist of a 1:1:1 molar ratio of Fe/Co/Ni:Mo:P. Essentially, the required amount of Co(NO₃)₂.6H₂O or Ni(NO₃)₂.6H₂O or Fe(NO₃)₃.9H₂O was dissolved in deionised water and impregnated onto MoO₃. This was followed by drying at 273 K overnight and then calcining in air at 773 K for 5 hours. The next step-involved impregnation with the required amount of NH₄H₂PO₄ to the material produced in the first step. This was followed by drying at 273 K overnight and then calcining in air at 773 K for 5 hours. Stuart Hunter (University of Glasgow, 4th year project student 2005-6) kindly assisted in the preparation of these phosphide precursor materials.
2.3 Catalytic testing

To evaluate the activity of the catalysts made for methane dehydroaromatisation for this study, a microreactor system was designed, built and commissioned, as shown in Figure 2-1.

2.3.1 Reactor design

The flow-micro quartz reactor was designed to be suitable to carry out methane conversion in the absence of a gas-phase oxidant.

![Figure 2-1 flow-micro reactor](image)

The catalyst samples were packed between plugs of silica wool in the quartz reactor vessel.

The reaction temperature was measured using a K-type thermocouple attached to the outside wall of the reactor vessel at the bed of the catalyst. Although ideally the temperature within the catalyst bed would be of most interest, the fact that the thermocouple would not be inert and the low levels of conversion make measurement of the reactor wall temperature an appropriate compromise.

The outlet line from the end of the quartz reactor was kept at 450 K using Thermolyne heating tape to prevent the condensation and strong adsorption of higher hydrocarbons produced during reaction. Product analysis was performed on a HP 5890 gas chromatograph (GC) using a combination of flame ionisation detection (FID) and thermal conductivity detection (TCD) with a Poraplot Q column (25 m) and a Molecular Sieve 13X column (12 feet) respectively. The GC carrier gas employed was argon (Puresshield, BOC). The GC set-up was not configured to detect carbon oxides. Therefore where applicable,
CO and CO₂ concentrations were monitored by off-line FTIR spectroscopy of the reactor effluent stream, which was continuously passed through a flow cell directly attached to the reactor exit. The spectra were obtained using an impact 410 Nicolet spectrometer and recorded over a range of 600 to 4000 cm⁻¹, using a total of 16 scans at a resolution of 4cm⁻¹ for each spectrum.

### 2.3.2 Gas calibrations

Calibrations were carried out for methane, ethane, ethylene, propane, benzene, hydrogen and nitrogen on the flow micro-reactor shown in Figure 2-1. Ethane, ethylene, propane and benzene detection was performed using the FID. Hydrogen and nitrogen calibrations were performed using the TCD. Methane detection was carried out using both detectors. The calibrations were carried out by varying the composition of gas mixtures and by taking the mean of six consistent measurements for each data point. In all cases, a line of correlation between the gc area counts and concentration was found. The calibrations were carried out in order to obtain the response factor for each gas. The response factor of each gas was used for the subsequent manipulation of GC data.

In order to calibrate for benzene, its vapour was injected into the FID inlet using a syringe, at 294 K and atmospheric pressure. This was repeated several times in order to obtain an average peak area for the GC effluent of benzene (the concentration of benzene was varied by dilution in the syringe with air). These conditions along with the Clausius-Clapeyron equation were used to obtain a response factor for benzene. Appendix 1 gives the calculations used for the benzene calibration.

To calibrate for CO and CO₂, an IR cell was flushed then filled with a known concentration of CO and CO₂, using a gas mixture which consisted of 10% H₂, 10% CH₄, 10% CO, 10% CO₂ and 60 % Argon (BOC). The IR spectra obtained was then used as a standard reference (since both the intensity of the bands and the concentration of CO and CO₂ are known). Thus the concentration of CO and CO₂ produced during the reaction could be calculated.
2.3.3 Catalytic testing procedure

For a typical catalytic test the experimental procedure was as follows:

0.5g of the catalyst was charged into the reactor between plugs of silica wool. The catalytic tests were performed at 973 K and atmospheric pressure. The feed gas mixture of 8 ml min\(^{-1}\) methane (99.9% CP grade, BOC) and 2 ml min\(^{-1}\) nitrogen (BOC, OFN) was introduced into the reactor through calibrated Brooks mass flow controllers. Typically a gas hourly space velocity (GHSV) of 840 hr\(^{-1}\) was employed. Nitrogen was used as an internal standard. The tail gas was sampled periodically and analysed by GC.

The same conditions as described above were also employed for the reduction of the doped metal phosphates by methane to the corresponding phosphide. However for these experiments a reaction temperature of 1023 K was used.

Throughout this work, wherever possible error bars have been employed in reaction data profiles. Error bars were calculated from multiple experiments and using the standard deviation method.

2.3.4 Manipulation of GC data

Reaction data is reported in terms of specific rates of formation of products rather than conversion and selectivity data. This approach has been adopted because, at the generally low levels of conversion which occur, the measurement of a small difference in the GC data may be subject to a relatively large degree of random error. This is a particular concern given that the reaction never attains steady state – it is either activating or deactivating. Within the literature, expressing data for this reaction as formation rates is fairly common practice, eg\(^{[30, 57]}\). Appendix 2 gives the equations used for the calculation of reaction data.

2.4 Catalyst Characterisation

2.4.1 X-ray powder diffraction

X-ray powder diffraction patterns were obtained on a Siemens D5000 diffractometer using Cu K\(\alpha\) radiation. Powder diffractograms were recorded over a range of 20 values from 5
to 75 ° using a step size of 0.02° and a counting rate of 1.5 s/step. Samples were prepared by compaction into silicon sample holders.

### 2.4.2 Laser Raman spectroscopy

Laser Raman spectroscopy was kindly performed by Dr Ann Robin, University of Strathclyde. The spectra were recorded on a Renishaw Ramascope 2000 spectrometer which consisted of an integral microscope, a notch filter, single grating and a cooled CCD detector was used. The spectral range examined was in the region of 400 to 1400 cm⁻¹. Excitation at 632.8 nm was delivered by a Spectra Physics 2020 helium-neon laser source (40mW). The samples investigated were in the fresh/calcined form.

### 2.4.3 Thermal gravimetric analysis

Thermal gravimetric profiles were recorded on a TA instrument TGA Q 500 series instrument. The catalyst charge was typically 0.02g, and the flow rate of air used was 90 ml min⁻¹. The catalysts were heated from room temperature to 1173 K in an air stream at a heating rate of 5 Kmin⁻¹.

### 2.4.4 Elemental analysis

CHN analysis by combustion was carried out on post reaction samples. This technique was kindly performed by Mrs. Kim Wilson, University of Glasgow. A CE-440 elemental analyser was used.

### 2.4.5 NH₃-TPD measurements

NH₃-TPD measurements were carried out using a TPD apparatus. Before adsorption, the samples (0.15g) were dried in flowing helium (30ml min⁻¹) at 873 K for 0.5 h. Pulses of ammonia gas of known volume (8.62cm³) and pressure (of ca. 150 Torr), were then introduced to the helium carrier gas, (30ml min⁻¹), from the sample loop at 323 K and passed over the catalyst until saturation was achieved. Then the catalyst was flushed with helium for 0.5 h before being ramped from 323 K to 873 K with a heating rate of 15 Kmin⁻¹, with He as the carrier gas. The amount of desorbed ammonia as a function of temperature was detected by a mass spectrometer.
2.4.6 BET

To calculate the surface area, pore size and pore volume of each catalyst a Flowprep 060 Micromeritics Gemini was used. For this technique a known mass of sample (typically ca. 0.04g), was placed in a tube of known volume and heated under vacuum to 383 K. The sample tube of each catalyst was then cooled in liquid nitrogen and a known amount of nitrogen gas was introduced into the cooled tube. The pressure was measured and the sequence was repeated with successive pulses of nitrogen. As the volume of the system, the temperature and the amount of gas added with each pulse was known, the expected pressure in the absence of any adsorption was able to be calculated. Due to the difference between the calculated pressure and the observed pressure at each point the amount of nitrogen adsorbed was determined.

2.4.7 $^{27}$Al and $^{29}$Si MAS NMR

$^{27}$Al and $^{29}$Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectra of the catalysts were recorded at ambient temperature on a Varian Infinity Plus 400 MHz spectrometer, operating at resonance frequencies of 104.2 and 79.4 MHz for $^{27}$Al and $^{29}$Si respectively. Spectra were measured at a spinning rate of 6 and 5 kHz using a pulse width of 2.5 and 4.5 μs for $^{27}$Al and $^{29}$Si respectively. Kaolin and TMS (tetramethylsilane) were used as the external standard references for the aluminium and silicon chemical shifts respectively. Samples were allowed to hydrate in ambient conditions.

2.4.8 Transmission Electron Microscopy

Transmission electron microscopy (TEM) was performed on samples at either the University of Glasgow or the University of Reading. At the University of Glasgow TEM was performed with an FEI Tecnai G20 T20 and samples were prepared for TEM by gently grinding the sample using an agate mortar and pestle before adding a few drops of ethanol. Using a drawn pipette, the suspension was deposited onto a 3mm, 300 mesh holey carbon copper grid and allowed to dry. Mr. Jim Gallagher, University of Glasgow, kindly performed these measurements.

At the University of Reading, TEM was performed with a JOEL 2010FX instrument. The samples were prepared for TEM by gently grinding the sample using an agate mortar and pestle under iso-propyl alcohol, the suspension was deposited onto ‘lacey’ carbon support
film and allowed to dry. Dr Peter Harris, University of Reading, kindly performed these measurements.

2.4.9 EXAFS

Al K-edge EXAFS experiments were performed at Station 3.4, Daresbury Laboratory jointly in conjunction with Dr Michael Stockenhuber, Nottingham Trent University. Thin disc samples were held in a cell, which achieved a vacuum of ca. 10^{-5} \text{ mbar}. Samples were degassed for one hour at room temperature under dynamic pumping, heated to the activation temperature with a ramp rate of 5 K/min and then cooled to 383 K. EXAFS data analysis, predominantly performed by Dr Michael Stockenhuber, used the standard suite of Daresbury programs, including EXCURV98.

2.4.10 In-situ FTIR studies

Dr Michael Stockenhuber, Nottingham Trent University, kindly performed in-situ FTIR studies. The in-situ FTIR studies were performed using an ATI Research Series FTIR spectrometer operating in transmission mode. The spectrometer was equipped with an in-situ stainless steel cell with calcium fluoride windows, capable of a base pressure <10^{-7}\text{ mbar}. The IR cells containing the samples were degassed for one hour at room temperature, heated to the activation temperature with a ramp rate of 5 K/min and then cooled to 423 K.
3 Catalytic activity of MoO$_3$/H-ZSM-5

3.1 General introduction

In recent years the production of benzene by the dehydroaromatisation of methane has attracted a lot of interest, for example[11]. Within the literature most attention has been focused towards the production of aromatics. It should be noted that despite the fact that hydrogen is expected to be the major product of the reaction, very few studies in the literature have reported its quantification. This is very surprising in view of the fact that the production of hydrogen is at least comparable, and probably greater, interest to that of benzene by this pathway. The MDA reaction could be viewed as a potential alternative route to hydrogen production from methane. Direct decomposition of methane to produce CO-free sources of hydrogen for use of chemical feedstocks in reactions such as ammonia synthesis and/or for fuel cell applications has been the subject of some interest[68, 69] and the MDA reaction may represent one such CO-free route.

3.2 Results and discussion

3.2.1 Influence of reactor material

Ideally, the material of construction of the reactor employed in MDA should play no role in the chemistry/catalysis of the reaction. Experiments employing an empty stainless steel reactor demonstrated that stainless steel was not inert under the reaction conditions of interest. As well as reacting with methane, it is also expected that benzene would undergo secondary reactions on the stainless steel reactor walls. Therefore, quartz, which is known to be more inert, was employed as the reactor material in the rest of the work carried out for this study.

On comparing the catalytic activity of the standard catalyst used throughout this work, 3%MoO$_3$/H-ZSM-5, it was seen that the use of a stainless steel reactor leads to lower product formation rates than with a quartz reactor. Figure 3.2-1 and Figure 3.2-2 give the hydrogen and benzene formation rates against time on stream for 3%MoO$_3$/H-ZSM-5 when both a quartz and stainless steel reactor have been employed.
It is interesting to note that some research groups, for example, Ichikawa and co-workers have reported some of their reaction data for MDA when they have employed a stainless steel reactor vessel\cite{54, 70}, consequently, they cannot be measuring the intrinsic catalytic activity over the catalyst in these cases.
3.2.2 Reaction data of 3%MoO$_3$/H-ZSM-5

Figure 3.2-3 reports the hydrogen and benzene formation rates (the two major products of the reaction) for the standard catalyst, 3%MoO$_3$/H-ZSM-5, which was run at 973 K for 6.5 h. The profiles shown are generally similar to those reported in the literature for comparable catalysts tested under similar conditions, in that there is an initial induction period, after which the rate of formation of products decline with time on stream. The gradual deactivation of the catalyst has been attributed to coke formation$^{[29]}$. As is shown in Figure 3.2-3 hydrogen production has been determined in this study. As already mentioned, within the literature most groups studying this reaction direct the attention towards the production of benzene, and it is surprising that apart from a few exceptions, e.g. $^{[55, 57]}$, so little attention has been given towards the production of hydrogen.

If hydrogen and benzene were the sole products produced, the ratio of their rates would be expected to be 9, i.e. Equation 2-3. However, as shown in Figure 3.2-4, the ratio is closer to 21, which is indicative of side reactions occurring. There are a number of possible processes, which can occur to produce hydrogen, including methane cracking, Equation 2-1, the production of ethylene, Equation 2-2 (believed to be the reaction intermediate), and the production of benzene, Equation 2-3.

\[
\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \quad \text{Equation 2-1}
\]
When the production of C₂ hydrocarbons is taken into consideration, the H₂: C₆H₆ ratio would be expected to be in the region of 13. The ratio of 21 is indicative of the formation of heavier aromatics, as reported by others, e.g. [34] and coke deposition. Since heavier aromatics, e.g. naphthalene are generally produced in much lower selectivity than benzene, it is likely that the major contribution to the higher ratio is from coke formation. This is in agreement with carbon analysis on post-reaction samples where it was observed that, 4.21 wt.% carbon is deposited on 3%MoO₃/H-ZSM-5 after 390 min on stream. If the stoichiometry of the Mo containing phase is assumed as Mo₂C, as it is most commonly reported in the literature, then this means that ca.4.08 wt.% C is deposited on the catalyst as coke. It can also be seen from Figure 3.2-4, that there is a relative constancy of the hydrogen to benzene formation rate ratio, which implies that the benzene formation and hydrogen producing side reactions decline at similar rates.

![Image](image_url)  
*Figure 3.2-4 The ratio of hydrogen to benzene as a function of time on stream for 3%MoO₃/H-ZSM-5.*

### 3.2.3 Isothermal carburisation of MoO₃

It has been well documented in the literature that there is an induction period at the beginning of the MDA reaction [39, 43], this can be seen from Figure 3.2-3, where there is a short delay before the maximum in product formation is achieved. During this process
Mo^{VI} species are reported to be reduced to Mo^{V} and Mo^{IV} species, attributed to the conversion of molybdenum oxide into molybdenum carbide. The products of the induction period are CO$_2$, H$_2$O, CO and H$_2$.[29]

Recently Iglesia et al.[71] have investigated the isothermal activation pathways of oxomolybdenum species in ZSM-5 using pure methane at a temperature of ca. 953 K. In the current study, the isothermal activation of bulk MoO$_3$ has been investigated. The formation rates of the products formed during this study on the isothermal carburisation of bulk MoO$_3$ are presented in Figure 3.2-5. It should be noted that the analysis set-up is not equipped to detect water, however, this is also an expected product of the reaction.

![Figure 3.2-5 Products formed during the isothermal carburisation of MoO$_3$.](image)

It can be seen from Figure 3.2-5 that the burst in H$_2$ formation is associated with a simultaneous burst of CO (although this product is slightly delayed compared to that of hydrogen). The maximum in hydrogen formation is achieved at ca. 320 min on stream. The evolution of these products is associated with the carbiding of MoO$_3$. The resultant XRD pattern following the carburisation of MoO$_3$ is shown in Figure 3.2-6. The pattern was checked using the database of the Joint Committee on Powder Diffraction Standards (JCPDS). The pattern shows reflections at 34.3, 37.3 and 39.4°2θ, these reflections are indicative of a β-Mo$_2$C phase. This pattern agrees well with the reference pattern of β-Mo$_2$C (PDF 35-787).
From reviewing the literature, there does not appear to be many studies regarding the isothermal carbiding of MoO3 with methane. Most studied have followed the process using temperature programmed routes with H2/CH4 mixtures\cite{72-74}. However, as previously mentioned, Iglesia et al. have investigated the isothermal activation pathways of oxomolybdenum species in ZSM-5 using pure methane. In general terms, relative concentrations and evolution times of H2, CO and CO2 are markedly comparable to those evident in Figure 3.2-5. However, in their work the maxima were obtained after ca. 10 min on stream, in contrast to the ca 320 min observed in Figure 3.2-5. This shows that there is a massive enhancement of the carbiding rate on dispersion of MoO3 on the ZSM-5 matrix. The nature of the phase transition with time on stream reported in Figure 3.2-5 is consistent with reports that the isothermal reduction of bulk MoO3 involves an induction period which has been ascribed to rate determining nucleation or autocatalytic effects\cite{75}.

### 3.3 Introduction - influence of zeolite support

In recent years, there has been immense interest in zeolite-supported catalysts e.g.\cite{76}, since their frameworks can stabilise TMI (transition metal ions), especially when TMI migrate into intra-crystalline zeolite cavities and/or channels. Moreover, by combining acid sites with TMI, bi and/or multi-functional catalysts with unique catalytic properties can be produced. The direct conversion of methane into aromatics and hydrogen over MoO3/H-ZSM-5 based catalysts is a typical example of these bi-functional catalytic properties. Mo/H-ZSM-5 is a bi-functional catalyst since both the molybdenum species and the Bronsted acid sites are necessary components of an active catalyst.
In this work, a short study on supporting MoO$_3$ onto Al$_2$O$_3$ and ZrO$_2$ supports has been investigated. From reviewing the literature, it does not appear that MoO$_3$ supported on ZrO$_2$ has been previously tested for MDA.

Recently, zirconia has received much interest because of its potential use as a catalyst support. Some important properties of zirconia include its high thermal stability and both acid and base functions. Zirconia has been employed as a support in reactions such as hydroprocessing and oxidation of alcohols\textsuperscript{[77]}\textsuperscript{[78]}. Brown et al.\textsuperscript{[78]} reported work where zirconia-supported molybdenum oxide catalysts were prepared using conditions reported to generate "superacidity". This MoO$_3$/ZrO$_2$ superacidic system could possibly have some similarities in behaviour with the acidic MoO$_3$/H-ZSM-5 catalyst employed in MDA. Therefore, the use of zirconia as a support for MoO$_3$ in MDA appears to be a suitable choice. Alumina has also been chosen as an alternative support, as it has previously been examined in the literature as a catalyst for MDA.

### 3.4 Results and discussion - influence of zeolite support

#### 3.4.1 Reaction data

The hydrogen formation rates as function of time on stream for 3%MoO$_3$/H-ZSM-5, 5%MoO$_3$/\textdelta-\textalpha-Al$_2$O$_3$ and "superacidic" 5%MoO$_3$/ZrO$_2$ (where ZrO$_2$ is a mixed phase of monoclinic and tetragonal) are given in Figure 3.4-1. It should be noted that it would be best if the loading of molybdenum oxide on the Al$_2$O$_3$ and ZrO$_2$ materials were exactly the same as the loading of molybdenum oxide on the ZSM-5 supported catalyst. However, general comparisons between the materials can still be made.
Figure 3.4-1 Hydrogen formation rate as a function of time on stream for 3%MoO$_3$/H-ZSM-5, 5%MoO$_3$/ZrO$_2$ and 5%MoO$_3$/Al$_2$O$_3$.

Similar to the standard methane aromatisation catalyst, MoO$_3$/H-ZSM-5, hydrogen is continuously obtained for the 5%MoO$_3$/Al$_2$O$_3$ catalyst. There is an initial induction period in the formation of products and the catalytic performance slowly deteriorates with time on stream. It is clear to see that at longer times on stream i.e. after 100 min, that 5%MoO$_3$/Al$_2$O$_3$ exhibits a lower activity for hydrogen formation than the standard methane aromatisation catalyst.

There does not appear to be an induction period before the maximum in the hydrogen formation for the ZrO$_2$ supported catalyst, initially, the hydrogen formation rate is at its maximum and declines throughout the remaining time on stream. Apart from at its maximum, the H$_2$ produced for the ZrO$_2$ supported catalyst is lower than that of the standard catalyst.

The benzene formation rate against time on stream for the 5%MoO$_3$/Al$_2$O$_3$ catalyst is given in Figure 3.4-2 and the profile for the standard catalyst, 3%MoO$_3$/H-ZSM-5 is also given for comparison. The alumina supported sample, which although produces benzene to a much lesser extent than the standard sample, does follow the same general benzene formation profile over the first 200 minutes of the reaction. However, beyond this length of time on stream benzene is no longer produced. Xu et al.\textsuperscript{[24]} report a benzene selectivity of 61\% for their MoO$_3$/Al$_2$O$_3$ catalyst, hydrogen production was not mentioned or discussed in their work. No benzene was detected for the 5%MoO$_3$/ZrO$_2$ catalyst.
Therefore, it has been shown that alumina supported molybdenum oxide is active for MDA, in that both hydrogen and benzene are produced, although to a lesser extent than the standard catalyst, 3%MoO₃/H-ZSM-5 and with a limited lifetime. Hydrogen production for zirconia supported molybdenum oxide is less than that of the standard catalyst. No benzene was produced for the zirconia supported sample.

From reviewing the literature and the work presented here on comparing supports for MoO₃ in MDA, it is evident that the zeolite support in particular, H-ZSM-5, is an important component of an active MDA catalyst. Hence, the best catalytic activity of MDA is observed when a MoO₃/H-ZSM-5 based catalyst is employed.

### 3.4.2 XRD patterns

The XRD pattern of 5%MoO₃/ZrO₂ in the calcined and post reaction form is given in Figure 3.4-3. Both fresh and post reaction patterns show no evidence of discrete molybdenum-containing phases, this reveals that the molybdenum species in the catalyst must be highly dispersed. The reflections at 28 and 31.5 °2θ are characteristic of the monoclinic phase of ZrO₂ and the reflection at 30 °2θ is characteristic of the tetragonal phase. It is clear to see from the patterns that the monoclinic phase increases by about 10% and the tetragonal phase decreases by about 10% on the post reaction catalyst compared to the fresh/calcined catalyst, this was confirmed by quantitatively calculating the phase compositions in the fresh and post reaction samples, using Toraya’s method[79]. Therefore,
it is apparent from these patterns that reaction of MoO$_3$/ZrO$_2$ with methane under non-oxidative conditions adjusts the proportion of monoclinic to tetragonal phases in zirconia.

![Figure 3.4-3 XRD pattern of 5%MoO$_3$/ZrO$_2$ in the calcined and post reaction form.](image)

### 3.5 Introduction – Pd/H-ZSM-5 as a catalyst for MDA

It has been reported in the literature as early as the 1970’s, that transition metal carbides display some catalytic properties characteristic of the noble metals. In particular, Levy and Boudart$^{80}$ demonstrated that tungsten carbide exhibits catalytic behaviour which is typical of platinum. For example, they showed that tungsten carbide catalyses the formation of water from hydrogen and oxygen at room temperature. They suggested that the surface electronic properties of tungsten are modified by carbon in such a way that it resembles those of platinum.

The noble metals are expensive, so in some reactions where they are employed as a component of a catalyst there is a possibility for them to be replaced by the relatively abundant Group 6 metals. For example, Lee et al.$^{81}$ have reported that unsupported and alumina supported Mo$_2$C have similar turnover rates for n-butane hydrogenolysis to Ru/$\gamma$-Al$_2$O$_3$.

Since it is believed that during reaction conditions in MDA the active phase of molybdenum is the carbide$^{36, 40}$, it appears to be appropriate to compare the catalytic activity of MoO$_3$/H-ZSM-5 with Pd/H-ZSM-5 in MDA. By analogy with the situation...
described above for tungsten carbide, it could be anticipated that the electronic properties of molybdenum carbide may resemble those of palladium.

From reviewing the literature, it does not appear that there have been any reports on Pd/H-ZSM-5 as a comparison of MoO$_3$/H-ZSM-5 for MDA. However, Pt/H-ZSM-5 has been tested for MDA by Xu et al.$^{[24]}$. Xu and co-workers reported that under the conditions they employed, no benzene was produced over the Pt/H-ZSM-5 catalyst and that methane conversion was 0.03% at a loading of 2wt.%Pt. Hydrogen production was not reported or even mentioned in their work.

At this point it should be noted that throughout the literature it is commonly stated that the formation of metal carbides is extensive throughout the periodic table, with the exception of Pd (along with Rh, Ir and Pt) which does not form a carbide, for example.$^{[73]}$. However, there are also reports in the literature, which states that Pd does form a carbide, it was reported in 1978 that during ethylene hydrogenation at moderate temperature (373 K) that carbon atoms penetrated into the palladium lattice, and that a solid solution of carbon in palladium was formed (PdC$_x$ where 0 < x ≤ 0.13) $^{[82]}$.

3.6 Results and discussion – Pd/H-ZSM-5

3.6.1 Reaction data

The hydrogen formation rate against time on stream for 3%Pd/H-ZSM-5 is given in Figure 3.6-1, the data for the standard catalyst, 3%MoO$_3$/H-ZSM-5 is also given for comparison. It is very clear to see from the profiles that Pd/H-ZSM-5 does not behave like MoO$_3$/H-ZSM-5. The Pd catalyst after 50 minutes on stream produces approximately 5 times more hydrogen than the standard catalyst. The palladium catalyst produced its maximum amount of hydrogen initially then slowly declined for the rest of the run. This is most likely due to catalyst deactivation due to carbon deposition. However, the standard catalyst has an induction period before the maximum in hydrogen formation is obtained. The Pd/H-ZSM-5 catalyst under the conditions employed is much more active for hydrogen production than the standard catalyst.
No benzene was produced for the Pd loaded H-ZSM-5 catalyst. Periodic off-line gas-phase FTIR analysis of the effluent revealed that no carbon oxides were produced during the reaction. So it appears, that Pd/H-ZSM-5 is an active catalyst for producing pure hydrogen i.e with no carbon oxides produced as by-products. However, a lot of carbon was deposited on the catalyst. Post reaction CHN analysis given in Table 3.6-1 shows that 30%wt of the Pd/H-ZSM-5 catalyst after reaction was coke compared to only 4.08%wt coke for the standard catalyst. In view of the earlier contrasting comments on palladium being able to form a carbide, it has not been possible to elucidate if it does or does not in this study, the XRD pattern of the post reaction Pd/H-ZSM-5 catalyst, given in Section 3.6.2, shows no reflections indicative of any palladium phases. The wt% of coke based carbon given for the standard catalyst is the weight after the subtraction of the carbon which is carbidic.

The current study shows that there is little similarity in the behaviour of MoO₃/H-ZSM-5 compared to Pd/H-ZSM-5 despite the fact that molybdenum carbide is proposed as an active phase in the former. This observation puts uncertainties to the comparisons that can be drawn between Mo₂C and Pd within this system. Whether this is due to the possibility that Mo₂C is not in fact formed in MoO₃/H-ZSM-5, requires further investigation.

It should be noted that if molybdenum carbide, in particular, β-Mo₂C is indeed the active phase of the molybdenum species in MDA, then when taking into consideration the unit cell parameters of β-Mo₂C, which are, \(a=3.0124\text{Å} \quad b=3.0124\text{Å} \quad c=4.7352\text{Å}\) (these
parameters have been taken from the reference pattern of β-Mo2C from the JCPDS (reference file PDF- 35-787)) then it is apparent that only a single unit cell of β-Mo2C can form in the channels of the zeolite (providing the ZSM-5 structure stays intact). As stated in Chapter 1, the linear pores of ZSM-5 have dimensions of 5.1 x 5.6Å and the zigzag pores have dimensions of 5.4 x 5.6Å. If only a single unit cell were formed it would be electronically very different from the bulk phase. In addition, the spacings of the channel intersections are longer at ca. 13Å but this still only equates to a couple of unit cells. Therefore it is unlikely that any comparison can be made with the bulk electronic structure.

Due to the superior H2 production that the Pd/H-ZSM-5 catalyst exhibits compared to the standard MDA catalyst another supported palladium catalyst was prepared and tested for hydrogen production. The hydrogen formation rate against time on stream for 3%Pd/δ-Al2O3 is given in Figure 3.6-2. The profile for 3%Pd/H-ZSM-5 is also given for comparison. It can be seen that the hydrogen formation for the alumina supported Pd catalyst is greater than that for the zeolite supported Pd catalyst. From this comparison it can be seen that the support of the catalyst does effect the hydrogen production, i.e. alumina is a better support for hydrogen production than the zeolite, under the conditions employed. Again no benzene was produced for the 3%Pd/δ-Al2O3 catalyst.

![Figure 3.6-2 Hydrogen formation rates as a function of time on stream for 3%Pd/H-ZSM-5 and 3%Pd/δ-Al2O3.](image-url)
3.6.2 XRD patterns of Pd/H-ZSM-5

The XRD patterns of 3%Pd/H-ZSM-5 in both the calcined and post reaction form are presented in Figure 3.6-3. The pattern of the calcined 3%Pd/H-ZSM-5 shows the characteristic reflections of H-ZSM-5 with the main 2θ values of ca. 8, 9 and 23-25°. No palladium containing crystallites could be detected (reflections indicative of palladium would be visible at 41, 46.5 and 68°). This suggests that Pd crystallites are highly dispersed on the surface or in the channels of the H-ZSM-5 zeolite and have a particle size too small as to be detected by the XRD technique.

![XRD pattern of 3%Pd/H-ZSM-5 in the calcined and post reaction form.](image)

Only reflections indicative of H-ZSM-5 are visible in the XRD pattern of the post reaction catalyst. The only apparent visible change between the two patterns is that the post reaction catalyst appears less crystalline as the peaks are slightly less intense.

3.6.3 Post reaction TGA, CHN and TEM analysis

TGA studies of the oxidation of post-reaction carbon species have been undertaken. The TGA profiles recorded for the Pd/H-ZSM-5 and standard catalyst, 3%MoO3/H-ZSM-5 are shown in Figure 3.6-4. The first derivative weight changes for the standard catalyst are also given, Figure 3.6-5.
The profile for the standard catalyst has been assigned on the basis of the study by Liu at all. Any weight loss before ca. 250°C is attributed to desorption of adsorbed water. A weight increase around about 450°C results from the reaction between Mo₂C and/or Mo₂CₓOᵧ with oxygen in the air stream. Burning off coke causes the decrease in the weight from 450°C to 750°C. So, the total amount of carbon on the post reaction catalysts consists of two parts, the first is carbon in molybdenum carbide and the second is coke, which, as detailed in the introduction, can be further subdivided. Any weight loss between 750°C to 900°C may be due to the sublimation of molybdenum oxide, as MoO₃ melts at 795°C and MoO₃ is known to sublime and the sublimation process should occur around this temperature. The vapour pressure of MoO₃ at 800°C is 1.7 Pa.

As can be seen from Figure 3.6-4 for the standard catalyst, there is no obvious weight increase in the region where molybdenum carbide, would be expected to be oxidised to molybdenum oxide, i.e. ca. 450°C. If the stoichiometry of the Mo containing phase is assumed as Mo₂C, then using the post reaction carbon analysis of the 3%MoO₃/H-ZSM-5 catalyst, the carbon content associated with the carbide can be calculated. This means that 4.08%C is deposited on the catalyst as coke, while 0.13%C is carbidic carbon. At higher loadings of molybdenum oxide catalysts, the weight increase in this region should become apparent. This is shown in Chapter 4, where higher loadings of molybdenum oxide post reaction catalysts have been analysed by TGA.

The first derivative weight changes for the standard catalyst, Figure 3.6-5, show that there are two peaks in the burning off coke region, at ca. 460 and 590°C, these can be attributed to low and high temperature coke combustion respectively.

As can be seen from Figure 3.6-4 the post reaction Pd/H-ZSM-5 catalyst has undergone a weight loss of ca. 32% upon being heated up to 900°C. The weight loss from room temperature to ca. 100°C can be attributed to water elimination. From Figure 3.6-4 it can be seen that the Pd/H-ZSM-5 catalyst contains significantly less water than the MoO₃/H-ZSM-5 catalyst as the weight change for the standard catalyst is noticeably far greater than that of the Pd/H-ZSM-5 catalyst in the region of room temperature to 100°C.

It should be noted that the anomaly in the profile of Pd/H-ZSM-5 at ca. 600°C in Figure 3.6-4 is due to sensitivity effects in the experimental apparatus. This feature does not represent true changes in the weight of the sample. The weight loss between 500 and 700°C is due to burning off coke that has been deposited on the catalyst, this weight loss of about 30% agrees very well with the CHN analysis results which show that 30.24% of the
sample after the MDA reaction was carbon, Table 3.6-1. The post reaction 3%Pd/H-ZSM-5 carbon content is not a surprising finding as Pd is an active catalyst for methane decomposition, (where the products are essentially hydrogen and carbon)[85].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>wt%C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3%MoO\textsubscript{3}/H-ZSM-5</td>
<td>4.21</td>
</tr>
<tr>
<td>3%Pd/H-ZSM-5</td>
<td>30.24</td>
</tr>
</tbody>
</table>

Table 3.6-1 Post reaction C analysis of catalysts after 390 min on stream.

Figure 3.6-4 TGA profiles for the post reaction 3%Pd/H-ZSM-5 and 3%MoO\textsubscript{3}/H-ZSM-5.

Figure 3.6-5 TGA profile for the post reaction 3%MoO\textsubscript{3}/H-ZSM-5.
Post reaction TEM images of Pd/H-ZSM-5 are given in Figure 3.6-6. From the images it is clear that carbon nanotube (CNT) formation has occurred over the catalyst during the conditions employed in MDA. Several groups have reported on the synthesis of CNTs through decomposition of hydrocarbons over metal catalysts (often termed chemical vapour deposition or CVD), though other routes of synthesising carbon nanotubes are available, such as, arc-discharge and laser vapourisation.

Zhao et al. have reported that CNT formation occurs over a plasma reduced Pd/H-ZSM-5 catalyst, they conducted methane decomposition over the plasma reduced Pd/H-ZSM-5 catalyst at 700°C. Many authors propose the ‘tip growth’ and ‘base growth’ mechanisms for the formation of CNTs through decomposition of hydrocarbons over metal catalysts. Zhao et al report that the CNTs produced over their Pd/H-ZSM-5 catalyst are of the tip growth kind, i.e. a dense dark region (metal particle) at the tip of the CNT is observed.

From the TEM images presented in Figure 3.6-6, it is difficult to say if the nanotubes were synthesised by the ‘tip growth’ or ‘base growth’ mechanism. However due to the visible ends being free from any metal particles it is likely that the CNTs were grown via a ‘base growth’ mechanism. It can be seen that the nanotubes are closed and not open-ended, this differs to nanotubes of the standard catalyst, 3%MoO3/H-ZSM-5, which are open-ended (although the standard catalyst has been doped with small quantities of additional metals in this case) TEM images of these post reaction materials are given in Chapter 4.

The nanotube in the TEM image on the left hand side of Figure 3.6-6 is ca. 40 nm in diameter. This CNT has a ‘stacked-cup’ or ‘herring bone’ like structure. In the literature it
has been proposed that for CNTs with a ‘herring-bone’ structure, graphene sheets do not connect but surround a hollow core.

This short investigation on examining the activity of Pd/H-ZSM-5 in MDA was carried out due to the apparent analogous behaviour reported between transition metal carbides and noble metals. It has clearly been shown that the catalytic behaviour of Pd/H-ZSM-5 is very different to that of the standard MDA catalyst. Firstly the H₂ formation rate for the Pd/H-ZSM-5 catalyst is noticeably greater than that of the standard catalyst, and secondly no benzene was produced for the Pd based catalyst. The absence of benzene production for the Pd based catalysts may be due to the reaction intermediate ethylene not being created by these systems. These results show that either there are uncertainties in the analogous behaviour of palladium and molybdenum carbide or that molybdenum carbide is not in fact the active phase that it is thought to be in the MDA reaction.

Along with the interesting catalytic activity of Pd/H-ZSM-5 that was observed in this study, it has also been shown that CNTs are produced by the decomposition of methane over the Pd/H-ZSM-5 catalyst at 700°C.

### 3.7 Introduction – H₂ additive in Feed gas

In the literature it has been reported that co-reactants such as O₂, CO, CO₂ and H₂ can suppress deactivation processes and improve catalytic activity. The findings based on literature reports for O₂, CO and CO₂ co-reactants are discussed in following chapters.

Iglesia and co-workers reported that when 3 kPa of H₂ was added into 85 kPa of CH₄, both methane conversion and benzene formation rate decreased. Overall, they reported that the selectivity of products was not strongly influenced by H₂ being added into the feed gas. Osawa et al. report that H₂ addition (10%) barely affects the conversion of methane, but prevents deactivation of the catalyst i.e., benzene formation remained constant during a 6 h test. They suggested that, in view of equilibrium of the aromatisation of methane, the addition of hydrogen is unfavourable for the formation of aromatic compounds. They also suggested that H₂ addition may decrease catalyst deactivation by reducing the surface carbon deposits. Consequently, adding hydrogen into the feed gas may contribute to increasing the total amount of aromatic compounds.

In this study addition of H₂ into the methane feed gas has been re-examined.
3.8 Results and discussion - H₂ additive in Feed gas

3.8.1 Reaction data

The hydrogen and benzene formation rates against time on stream for 3%MoO₃/H-ZSM-5 where the feed gas comprises of 82% CH₄ and 1.8% H₂ with the balance being Ar is given in Figure 3.8-1 and Figure 3.8-2 respectively, the profiles for 3%MoO₃/H-ZSM-5 under the normal reaction conditions i.e. where no hydrogen is added to the feed gas are also given for comparison. It can be seen from Figure 3.8-1, that the shape of the profiles for hydrogen formation for 3%MoO₃/H-ZSM-5 with H₂ added to the feed and under standard reaction conditions are identical. The hydrogen formation is greater for the catalyst where hydrogen was added into the feed.

Figure 3.8-1 Hydrogen formation rate as a function of time on stream for 3%MoO₃/H-ZSM-5 with H₂ added into feed gas and under standard reaction conditions.
Again, the profiles for the benzene formation rate for the standard catalyst under standard reaction conditions and where H$_2$ has been added into the feed are similar in shape, Figure 3.8-2. It appears that benzene formation has been slightly suppressed upon addition of hydrogen, more noticeable at the first point in the profile. Therefore, H$_2$ as a co-reactant is unfavourable for the production of benzene compared to the standard reaction conditions. To access whether hydrogen addition reduces the overall amount of coke deposited on the catalyst, post reaction carbon analysis was conducted and the results are given in the following section.

### 3.8.2 Post reaction carbon analysis

The post reaction carbon analysis of 3%MoO$_3$/H-ZSM-5 under standard reaction conditions and where H$_2$ has been added into the feed is given in Table 3.8-1. The post reaction carbon analysis confirms that H$_2$ addition into the feed does in fact reduce the carbon that is deposited on the catalyst compared to when no H$_2$ is added i.e., 3.49%C with H$_2$ in feed and 4.21%C with no H$_2$ in feed.
Addition of H₂ to the methane feed gas has been shown to result in a slight decrease in the benzene formation rate. The carbon content in the post reaction catalyst has also decreased compared to when no H₂ is added into the feed gas. Although coke formation has decreased it does not appear to have a promotional effect on the production of benzene.

### 3.9 Introduction - \(^{27}\)Al and \(^{29}\)Si MAS NMR study of MoO₃/H-ZSM-5

\(^{27}\)Al and \(^{29}\)Si MAS NMR are both very useful techniques in giving information about the structure of aluminium and silicon atoms in zeolites. In particular, \(^{27}\)Al MAS NMR gives direct information relating to the local environment of aluminium nuclei in zeolite structures\[^{95, 96}\], whereas \(^{29}\)Si MAS NMR provides a direct measurement of the way in which aluminium atoms are coordinated to silicon atoms in the framework of zeolites\[^{97}\]. Moreover \(^{29}\)Si MAS NMR can be used to determine the framework Si/Al in a zeolite using the following equation, as reported by Liu et al.\[^{50}\]:

\[
\text{Si/Al} = \frac{\sum_{N=0}^{4} I_{\text{Si}(n\text{Al})}}{\sum_{N=0}^{4} \frac{1}{4n} I_{\text{Si}(n\text{Al})}}
\]

In this study \(^{27}\)Al and \(^{29}\)Si MAS NMR measurements of MoO₃/H-ZSM-5 catalysts with different molybdenum loadings and starting materials of molybdenum are examined.

### 3.10 Results and discussion - \(^{27}\)Al and \(^{29}\)Si MAS NMR study of MoO₃/H-ZSM-5

\(^{27}\)Al MAS NMR spectra of 3, 8.7 and 14.2% wt. MoO₃/H-ZSM-5 catalysts, where ammonium heptamolybdate was used as the starting material of the molybdenum component, together with H-ZSM-5 are given in Figure 3.10-1. As expected there are two main peaks. The peak at ca. 53 ppm, is typical of tetrahedrally coordinated framework
aluminium in ZSM-5 and the peak at ca. -2 ppm can be attributed to octahedral non-framework aluminium.\textsuperscript{[50, 53, 98, 99]} Quantification of the NMR spectra was not attempted because of uncertainty about the NMR visibility of aluminium species in distorted coordination.

The $^{27}\text{Al}$ MAS NMR spectra of $\text{H-ZSM-5}$ and $3\%\text{MoO}_3/\text{H-ZSM-5}$ are comparatively similar. This shows the high stability of the ZSM-5 framework upon incorporation of molybdenum species into H-ZSM-5. Although, it can be seen that there is an increase in the peak associated with non-framework Al (i.e. -2 ppm peak) in the spectrum of $3\%\text{MoO}_3/\text{H-ZSM-5}$ compared to the spectrum of H-ZSM-5. This indicates that extraction of framework Al occurs upon incorporation of molybdenum species into H-ZSM-5, however, it should be noted that upon hydration for some zeolites it is possible to make tetrahedral framework Al octahedral Al. The interaction between molybdenum species and framework aluminium in this system has been extensively reported in the literature\textsuperscript{[53, 99, 100].

Figure 3.10-1 $^{27}\text{Al}$ MAS NMR spectra of calcined (a) $\text{H-ZSM-5}$ (b) $3\%\text{MoO}_3/\text{H-ZSM-5}$ (c) $8.7\%\text{MoO}_3/\text{H-ZSM-5}$ (d) $14.2\%\text{MoO}_3/\text{H-ZSM-5}$ (with ammonium heptamolybdate as the source of Mo).
On comparing the relative intensity of the peak at -2 ppm with that of the 53 ppm peak of the 3wt% MoO$_3$ sample, with the higher loaded samples of MoO$_3$ i.e. 8.7 and 14.2% MoO$_3$, it can be seen that it has decreased. This may be due to the evolution of an aluminium molybdate phase for the higher loaded MoO$_3$ samples. The signal at ca. -15 ppm in the spectra of 8.7 and 14.2% MoO$_3$/H-ZSM-5 has been assigned to octahedral aluminium in crystalline Al$_2$(MoO$_4$)$_3$ on the basis of the study by Liu et al. They reported that Mo species interact with the framework Al of H-ZSM-5 and that this interaction increases with increasing Mo loading and calcination temperature. The strong interaction finally leads to the extraction of framework aluminium and the formation of a new Al$_2$(MoO$_4$)$_3$ phase. If the Mo loading and calcination temperature are high enough, then all of the framework aluminium in the zeolite can be extracted and the framework of ZSM-5 collapses. Liu and co-workers reported that the formation of Al$_2$(MoO$_4$)$_3$ is a detrimental feature for MDA.

It should be noted that the signal at ca. -2 ppm for the 3% MoO$_3$/H-ZSM-5 catalyst in Figure 3.10-1 has a "liquid-like" NMR appearance. This signal rather than being due to the conventional octahedral non-framework aluminium may be due to some form of "disordered" octahedral aluminium. For example, it would be consistent with [Al(H$_2$O)$_6$]$^3+$ wherein deprotonation was suppressed by the inherit acidity of the zeolite host. However, further $^{27}$Al MAS NMR studies would be required to elucidate this further. This "liquid-like" signal occurs again in Figure 3.10-2 and again in more MoO$_3$/H-ZSM-5 based catalysts which are presented and discussed in Chapter 4.

An $^{27}$Al MAS NMR study on MoO$_3$/H-ZSM-5 based catalysts carried out by Zhang et al. reports the presence of a peak at ca. 30 ppm, which was assigned to penta-coordinated non-framework aluminium. The absence of this peak in this work implies that either no penta-coordinated non-framework aluminium species are present in these samples or that these species are "invisible". In the latter regard, it has been reported that second-order quadrupole interactions are not completely removed by MAS. Moreover, it has been reported that the second-order quadrupole interaction, which is only partially averaged by MAS, can lead to sufficient broadening that makes some $^{27}$Al signals "invisible" in a normal single-pulse MAS NMR experiment.

In Figure 3.10-1 there appears to be a slight increase in the line width of the octahedral non-framework aluminium peak with increasing loading of Mo. This implies an increase in the quadrupolar interaction between the octahedral coordinated aluminium and water molecules, as magic angle spinning cannot eliminate the quadrupole interaction. Overall for these samples the interaction between Mo species and H-ZSM-5 is not strong.
enough to structurally damage the zeolite as it can be seen that a large proportion of the framework aluminium of ZSM-5 has remained.

$^{27}$Al MAS NMR spectra of 3, 8.7 and 14.2% wt. MoO$_3$/H-ZSM-5 catalysts, where molybdenum trioxide was used as the starting material of the molybdenum component are given in Figure 3.10-2. On comparing these spectra with that of the parent zeolite, ZSM-5, shown in Figure 3.10-1, it can be seen that there is an increase in the non-framework aluminium peak upon incorporation of Mo species into H-ZSM-5.

It is interesting to note that for the catalysts prepared using molybdenum trioxide as the starting material of the molybdenum component there does not appear to be a signal at ca. –15 ppm in the spectra, Figure 3.10-2, which was present in the $^{27}$Al NMR spectra of the samples prepared by ammonium heptamolybdate, Figure 3.10-1. Therefore, it appears that the appearance of a Al$_2$(MoO$_4$)$_3$ phase depends on the starting material of the molybdenum component.

![Figure 3.10-2 $^{27}$Al MAS NMR spectra of calcined (a) 3%MoO$_3$/H-ZSM-5 (b) 8.7%MoO$_3$/H-ZSM-5 (c) 14.2%MoO$_3$/H-ZSM-5 (with molybdenum trioxide as the source of Mo).](image-url)
On closer analysis of the $^{27}$Al MAS NMR spectra in Figure 3.10-1 and Figure 3.10-2, it can be seen that there is a very small peak at ca. 12 ppm. This signal occurs in all of the spectra apart from that of the parent zeolite, H-ZSM-5. Zhang et al.\cite{100} report a signal at 13 ppm in their $^{27}$Al MAS NMR spectra of Mo/H-ZSM-5 based catalysts. They attribute the signal to octahedral non-framework Al in MoO$_3$.Al$_2$O$_3$.nH$_2$O (where n is the coordination number of H$_2$O, n>1).

The $^{29}$Si MAS NMR spectra of 3, 8.7 and 14.2% wt.MoO$_3$/H-ZSM-5 catalysts, where ammonium heptamolybdate was used as the starting material of the molybdenum component, together with H-ZSM-5 are given in Figure 3.10-3, the corresponding chemical shifts and Si/Al ratio for each sample are given in Table 3.10-1. It should be noted that according to Loewenstein's rule, Al-O-Al linkage cannot exist in zeolites. H-ZSM-5 generally only exhibits Si(0Al) and Si(1Al) configurations due to its high Si/Al ratio.

Figure 3.10-3 $^{29}$Si MAS NMR spectra of calcined (a) H-ZSM-5 (b) 3%MoO$_3$/H-ZSM-5(c) 8.7%MoO$_3$/H-ZSM-5 (d) 14.2%MoO$_3$/H-ZSM-5 (with ammonium heptamolybdate as the source of Mo).
Table 3.10-1 The results of $^{29}\text{Si}$ MAS NMR.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mo precursor</th>
<th>Si($\text{Al}$)</th>
<th>$\delta$(ppm)</th>
<th>Si/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-5</td>
<td>-</td>
<td>Si($\text{Al}$)</td>
<td>-108</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si(0$\text{Al}$)</td>
<td>-115</td>
<td>39</td>
</tr>
<tr>
<td>3%MoO$_3$/H-ZSM-5</td>
<td>AHM*</td>
<td>Si(1$\text{Al}$)</td>
<td>-108</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si(0$\text{Al}$)</td>
<td>-115</td>
<td>50</td>
</tr>
<tr>
<td>8.7%MoO$_3$/H-ZSM-5</td>
<td>AHM*</td>
<td>Si(1$\text{Al}$)</td>
<td>-108</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si(0$\text{Al}$)</td>
<td>-115</td>
<td>60</td>
</tr>
<tr>
<td>14.2%MoO$_3$/H-ZSM-5</td>
<td>AHM*</td>
<td>Si(1$\text{Al}$)</td>
<td>-108</td>
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<td></td>
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<tr>
<td>3%MoO$_3$/H-ZSM-5</td>
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<td>Si(1$\text{Al}$)</td>
<td>-108</td>
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</tr>
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<td></td>
<td></td>
<td>Si(0$\text{Al}$)</td>
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<td>8.7%MoO$_3$/H-ZSM-5</td>
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<td>Si(1$\text{Al}$)</td>
<td>-108</td>
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<td>Si(0$\text{Al}$)</td>
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<td>14.2%MoO$_3$/H-ZSM-5</td>
<td>MoO$_3$</td>
<td>Si(1$\text{Al}$)</td>
<td>-108</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si(0$\text{Al}$)</td>
<td>-115</td>
<td>67</td>
</tr>
</tbody>
</table>

*a ammonium heptamolybdate

It can be seen from Figure 3.10-3 that there are two peaks in the $^{29}\text{Si}$ MAS NMR spectra with chemical shifts at ca. $-108$ ppm and $-115$ ppm. The first peak can be attributed to Si($\text{Al}$) and the second peak can be attributed to Si(0$\text{Al}$). These peaks have been assigned based on NMR studies of these types on materials reported in the literature[^3, 98, 99, 102]. The shoulder peak at ca $-117$ ppm is commonly attributed to the crystallographically inequivalent sites of Si(0$\text{Al}$)[^103]. The Si/Al ratios were calculated using the intensities of the Si(0$\text{Al}$) and Si($\text{Al}$) peaks.

It can be seen from Table 3.10-1, that upon addition of molybdenum species to H-ZSM-5 that the Si/Al ratio increases, this ratio increases with increasing molybdenum loading. The increase in the ratio reveals that dealumination increases with increasing Mo content.

The $^{29}\text{Si}$ MAS NMR spectra of 3, 8.7 and 14.2% wt. MoO$_3$/H-ZSM-5 catalysts, where molybdenum trioxide was used to prepare the catalysts are given in Figure 3.10-4, the corresponding chemical shifts and Si/Al ratio for each sample are given in Table 3.10-1. Again the peaks at ca. $-108$ ppm and $-115$ ppm can be assigned to Si($\text{Al}$) and Si(0$\text{Al}$) respectively. Similar to the catalysts prepared by AHM, the catalysts prepared by molybdenum trioxide also show an increase in Si/Al ratio with increasing molybdenum loading. It can be seen from Table 3.10-1, that the ratios of the 3, 8.7 and 14.2%MoO$_3$/H-ZSM-5 catalysts are almost identical when prepared by both AHM and MoO$_3$. 

[^3]: Reference 3
[^98]: Reference 98
[^99]: Reference 99
[^102]: Reference 102
[^103]: Reference 103
3.11 N$_2$ adsorption isotherms

The N$_2$ adsorption isotherms of the parent zeolite, H-ZSM-5 and the standard catalyst, 3%MoO$_3$/H-ZSM-5 are given in Figure 3.11-1 and Figure 3.11-2 respectively. It can be seen that the N$_2$ adsorption isotherm of H-ZSM-5 represents a combination of Type I and IV isotherms, with a slight hysteresis loop. This is typical for microporous materials with a very small degree of mesoporosity. It can also be observed for the standard catalyst, 3%MoO$_3$/H-ZSM-5, which is also a combination of Type I and IV isotherms, that although the hysteresis loop, resulting from capillary condensation in mesopores$^{[104]}$, is still small it is more prominent than that of the parent zeolite. The difference in the hysteresis indicates that mesopores were developed during the incorporation of molybdenum species into H-ZSM-5.
Figure 3.11-1 N\textsubscript{2} adsorption isotherm of H-ZSM-5.

Figure 3.11-2 N\textsubscript{2} adsorption isotherm of 3\%MoO\textsubscript{3}/H-ZSM-5.
3.12 Al EXAFS study of MoO$_3$/H-ZSM-5

As previously mentioned in the introduction chapter and shown in Section 3.10 of this chapter, there is an interaction between Mo species and the framework Al of ZSM-5. The powder XRD pattern of Mo/H-ZSM-5 in the calcined form, shown in Chapter 4, only shows reflections, which are indicative of ZSM-5. This agrees well with the literature. The XRD pattern does not show any evidence of destruction of the zeolite framework upon activation. However, it is of interest to investigate the effect of activation on the local structure of the zeolite framework. Therefore Al K-edge EXAFS studies have been conducted.

The experimental and best fit calculated EXAFS spectra for activated MoO$_3$/H-ZSM-5 is shown in Figure 3.12-1. Ten spectra were recorded over ca. 8 hours following the pre-treatment outlined in the experimental section. The quality of the fit, which was performed by Dr. M. Stockenhuber is good with the R factor being 21.9. The structural parameters of the average local Al environment, which have been extracted from the spectra, are given in Table 3.12-1.

It was found that during fitting, the inclusion of a molybdenum scatterer significantly improved the fit. However, as can be seen from the data in Table 3.12-1 the Al-Mo interatomic distance is comparatively long, at 4.97 Å. This displays the absence of a direct Mo-Al binding interaction and is consistent with the presence of a light scattering element, for example oxygen, lying between the two atomic centres. This proposal, which requires further confirmation, is consistent with the literature describing the presence of molybdenum oxo clusters within the zeolite channels$^{[42,105-109]}$. 
Figure 3.12-1 Experimental and calculated best fit Al K-edge EXAFS spectra for the activated MoO$_3$/H-ZSM-5 catalyst precursor.

Table 3.12-1 Structural parameters for the activated MoO$_3$/ZSM-5 zeolite (r corresponds to interatomic distances and DW to the Debye-Waller factors). The data was calculated from EXAFS multiple scattering calculations. For these calculations four oxygen next nearest and four silicon neighbours were used.

<table>
<thead>
<tr>
<th>Mo/H-ZSM-5</th>
<th>r/ Å</th>
<th>DW/ Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-O</td>
<td>1.77</td>
<td>0.001</td>
</tr>
<tr>
<td>Al-O</td>
<td>1.64</td>
<td>0.001</td>
</tr>
<tr>
<td>Al-O</td>
<td>1.77</td>
<td>0.001</td>
</tr>
<tr>
<td>Al-O</td>
<td>1.88</td>
<td>0.006</td>
</tr>
<tr>
<td>Al-Mo</td>
<td>4.97</td>
<td>0.012</td>
</tr>
<tr>
<td>Al-Si average</td>
<td>3.09</td>
<td>0.006</td>
</tr>
</tbody>
</table>
A schematic of the local Al environment, including the presence of Mo is given in Figure 3.12-2, for comparison an idealised tetrahedral framework Al species for NH$_4$-ZSM-5 is also given.

From this schematic, it appears like the average framework structure of the zeolite is strongly perturbed by the presence of Mo species, with the Al species being drawn out towards them. This is in agreement with observations, which suggest that aluminium can be directly extracted from the ZSM-5 framework either by increasing the Mo loading and/or the severity of thermal pre-treatment, for example [42, 50]. This phenomenon was also observed in the $^{27}$Al MAS NMR spectra of MoO$_3$/H-ZSM-5 catalysts shown in Section 3.10. It is interesting to note that the degree of perturbation of the framework Al in the catalysts activated under standard conditions has not been widely discussed, although Figure 3.12-2 shows it to be potentially significant. However, it should be noted that the information extracted from the Al EXAFS is a weighted average.

The $^{27}$Al MAS NMR spectra of the MoO$_3$/H-ZSM-5 catalysts given in Section 3.10 were activated under the conditions employed in the MDA catalysis experiments. Whilst this activation is conducted at a similar temperature to that employed in the EXAFS study, the duration of calcination (16 hours) is much longer. Consequently, the NMR studies can be seen as giving an upper limit on the fraction of non-tetrahedral Al. It was seen in Section 3.10 that the tetrahedral framework Al in the $^{27}$Al MAS NMR spectra of 3%MoO$_3$/H-ZSM-5 constitutes the vast majority of the Al species observed, which gives confidence that the contribution to the EXAFS is dominated by the framework species. As previously mentioned, there is a sharp resonance at 0 ppm in the $^{27}$Al MAS NMR spectra of...
3%MoO₃/H-ZSM-5, suggesting that the species are "liquid-like" in nature and may be present either as highly disordered species or possibly hydrated cations. Even though this resonance is really strong, it is narrow resulting in a comparatively low relative area and therefore a small contribution to the average Al environment.

Given that MoO₃ is known to reduce under relatively mild conditions via the formation of shear planes, it is important to show that pre-treatment at elevated temperature in vacuo, which is required in these EXAFS experiments, does not result in any reduction in the molybdenum oxidation state. Such changes would be expected to lead to modifications in the interactions between the zeolite framework and extra-lattice molybdenum oxo clusters. Consequently, FTIR studies were undertaken in collaboration with Dr. M. Stockenhuber and the results are given in the following section.

3.13 IR activation study of MoO₃/H-ZSM-5

Figure 3.13-1 shows the effect of activation on the MoO₃/H-ZSM-5 precursor. In both spectra, stretches of 3610 and 3745 cm⁻¹ can be seen in the hydroxyl region, which corresponds to the presence of bridging Si-OH-Al and terminal Si-OH groups respectively [110]. The intensity of the background within the ca. 3000 to 3800 cm⁻¹ region is also noteworthy and is consistent with the presence of hydroxyl nests of hydrogen bonded bridging groups.

![Figure 3.13-1 In-situ FTIR spectra of 3%MoO₃/H-ZSM-5(a) before and (b) after activation in vacuo at 450°C.](image)
Upon activation, it can be seen that there are significant changes to the hydroxyl region. The intensity of the background is considerably lowered and the bridging Si-OH-Al intensity is increased while the terminal Si-OH group intensity remains unchanged. This reveals, that there is no, or little, interaction between molybdenum oxo species with terminal Si-OH groups, while the apparent increase in intensity of the bridging Si-OH-Al is contrary to work reported in the literature\textsuperscript{42, 105}. However, it is possible to reconcile this difference by taking the difference in the general background in the OH stretching region into account. Taking this into account, it suggests that activation leads to a disruption of hydrogen bonded bridging groups, which leads to the apparent small increase in intensity of the 3745 cm\textsuperscript{-1} feature.

In \textit{in-situ} FTIR studies by Dr. M. Stockenhuber, no adsorption of NO, a useful probe molecule for the determination of molybdenum oxidation state\textsuperscript{111}, was observed. This is consistent with the Mo(VI) oxidation state, revealing that activation \textit{in-vacuo} does not lead to reduction of molybdenum oxo species. Therefore, it is most likely that the EXAFS experiments shown in this work reflect the activated form of the catalyst.

The modification of the average framework Al local structure has interesting implications, since it would be anticipated that any changes to the Al-OH-Si bond angles would influence the acidity\textsuperscript{112}. In view of this, it is of interest to probe the acid characteristics of the system. Using NH\textsubscript{3} adsorption, the acidity of the activated samples has been probed by \textit{in-situ} FTIR and the resultant spectra are shown in Figure 3.13-2.
From this figure, it can be seen that there is a progressive loss of the hydroxyl features at 3610 and 3745 cm$^{-1}$ together with the development of N-H stretching modes and the associated development of the band at 1500 cm$^{-1}$ which can be attributed to NH$_4^+$ species. It is important to note the absence of any feature at 1620 cm$^{-1}$, which demonstrates the absence of Lewis acid sites in this system. This is especially important considering the presence of the octahedral feature in the $^{27}$Al MAS NMR spectrum presented in Section 3.10. As a result, NH$_3$-TPD experiments on the precursors activated by heating in air for 16 hours were carried out, these results are presented and will be discussed in greater detail, in Chapter 4. The NH$_3$-TPD experiments show that, as expected, ammonia interacts with the Brønsted acid sites of the zeolite. In this study it is noticeable that the inclusion of molybdenum species into HZSM-5 results in the temperature of the high temperature peak, which has been ascribed to ammonia adsorbed on the bridging hydroxyl group Si-OH-Al, exhibiting a lower temperature maxima for the MoO$_3$/H-ZSM-5 material compared to H-ZSM-5, which demonstrates that upon loading Mo species into HZSM-5 that the strength of the Brønsted acid sites decreases.
3.14 Summary

In this study the influence of the material of the reactor employed in MDA has been investigated. It has been shown that stainless steel reactors are not inert to reaction with methane, however quartz reactors play no role in the catalysis of the reaction. It is surprising that some catalytic data reported in the literature for this reaction has been reported when a stainless steel reactor has been employed.

From preliminary studies on MDA using a MoO3/H-ZSM-5 catalyst, hydrogen production has been quantified and it has been shown to be the dominant product of the reaction. The actual ratio of H2: C6H6 produced when using MoO3/H-ZSM-5 in MDA was shown to be ca. 21, indicating that significant side reactions occur in MDA.

A short study on the importance of the zeolite support in MDA demonstrated that H-ZSM-5 is a substantially superior support for MoO3 in MDA compared to mixed phase ZrO2 or 8-Al2O3.

On comparing the catalytic activity of MoO3/H-ZSM-5 with Pd/H-ZSM-5, it was seen that these two catalysts exhibited little similarity in behaviour. This implies that either Mo2C is not the active phase of molybdenum in MoO3/H-ZSM-5 or that there are uncertainties in the comparisons that can be drawn between Mo2C and Pd within this system. Pd/H-ZSM-5 was found to be an active methane decomposition catalyst, where the hydrogen produced was free from any COx co-products. The carbon deposited on the catalyst during the reaction was shown to be in the form of carbon nanotubes with a “herring-bone” structure.

27Al and 29Si MAS NMR experiments conducted on H-ZSM-5 and MoO3/H-ZSM-5 catalysts revealed that there is an extraction of framework Al upon incorporation of Mo species into H-ZSM-5. The appearance of a sharp signal in the 27Al MAS NMR spectra of MoO3/H-ZSM-5 catalysts is noteworthy. This suggests that such species are “liquid-like” in nature and may be present as either highly disordered species or possibly as hydrated cations. The interaction between Mo species and HZSM-5 was also demonstrated through the N2 adsorption isotherms of the parent zeolite, H-ZSM-5 and the standard catalyst, 3%MoO3/H-ZSM-5, it was shown that mesopores were developed during the incorporation of molybdenum species into H-ZSM-5.

A study on the activation of MoO3/H-ZSM-5 catalyst precursors for MDA using Al K-edge EXAFS has shown that there is a significant distortion of the tetrahedral framework
Al environment, with Al species being drawn towards molybdenum centres. In-situ FTIR studies demonstrated that molybdenum remains in the +VI oxidation state under the conditions employed in the EXAFS experiments, and that the acidity displayed by such precursors is exclusively of Brønsted type.
4 The effect of dopants and molybdenum precursors on the activity of MoO\textsubscript{3}/H-ZSM-5 catalysts

4.1 Introduction

4.1.1 Dopants

As shown in Chapter 3 and reported in the literature \cite{26,43,44} carbonaceous deposits are formed during MDA. Lunsford and co-workers observed three different types of surface carbon using XPS. They reported that the first type was mainly present in the zeolite channels and was due to graphite-like carbon. The second type was observed on the outer surface of the zeolite and was carbide like carbon in Mo\textsubscript{2}C. However, alternative locations for molybdenum carbide species have been reported, studies carried out by Zhang et al. \cite{53} have reported the migration of molybdenum species into the zeolite pores. They showed using Mo EXAFS experiments, that calcination causes re-dispersion of molybdenum into the zeolite pores. The last type of surface carbon reported by Lunsford and co-workers is also present on the outer surface of the zeolite and is hydrogen poor. They suggested that this last type of carbon is responsible for gradual deactivation of the catalyst and a greater amount is seen as the length of time of stream increases \cite{26}. Consequently, the conversion of methane rapidly reduces after a couple of hours due to the coke deposits on the catalyst.

To suppress this deactivation process modifications of the reaction conditions and/or the catalyst have been tested. Optimisation of reaction conditions has been extensively studied. Addition of other gases, such as CO, CO\textsubscript{2} and H\textsubscript{2} into the methane feedstock have been tested \cite{34,56,91,92,113}. These additives have been shown to increase the stability of the catalyst. There have been many suggested mechanisms relating to CO addition. For example, Ohnishi et al. \cite{34} reported that the improvement in aromatisation by CO addition is due to the formation of minute amounts of CO\textsubscript{2} formed via the Bouduard reaction (Equation 4-1). These CO\textsubscript{2} species are proposed to remove surface carbon species on Mo/H-ZSM-5 and regenerate CO.

\[
2\text{CO} \rightarrow \text{CO}_2 + \text{C} \quad \text{Equation 4-1}
\]
They also suggested that the active oxygen species derived from CO reacts with the surface carbon, which otherwise forms inactive coke, (Equations 4-2 and 4-3).

\[
\text{CO} \rightleftharpoons [\text{C}] + [\text{O}] \quad \text{Equation 4-2}
\]

\[
[\text{O}] + \text{Coke} \rightleftharpoons \text{CO or CO}_2 \quad \text{Equation 4-3}
\]

On the other hand, the results reported by Liu et al.\cite{921} showed that CO addition did not display any beneficial effects. Ohnishi et al.\cite{34} reported that adding a few percent of CO\(_2\) to the methane feed results in improving the stability of the catalyst via the formation of CO by the reforming reaction, and/or the reverse Bouduard reaction at 973 K on the catalysts, (Equations 4-4 and 4-5 respectively).

\[
\text{CO}_2 + \text{CH}_4 \rightleftharpoons 2\text{CO} + 2\text{H}_2 \quad \text{Equation 4-4}
\]

\[
\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO} \quad \text{Equation 4-5}
\]

However, it was reported that excess addition of CO\(_2\) (>10\%) inhibits the formation of benzene. Au and co-workers also attributed the beneficial effect of CO\(_2\) addition to the reforming of methane\cite{94}.

Studies carried out on experimental conditions such as temperature\cite{25}, pressure and methane space velocity\cite{24} have also shown that experimental parameters exert influence on the catalytic performance.

Ichikawa et al. have shown that the reaction can be optimised by the addition of a second metal component to the MoO\(_3\)/H-ZSM-5 based catalyst. They reported that doping with cobalt or iron\cite{34,55} retards deactivation and enhances catalytic activity. They found that the maximum yield of aromatics was attained in low concentrations of Fe and Co in Mo/H-ZSM-5. 1\% Co loaded into Mo/H-ZSM-5 resulted in an increase in benzene, which was attributed to an increase in conversion compared to Mo/H-ZSM-5, whereas they reported the enhancement in benzene upon Fe addition to Mo/H-ZSM-5 was due to suppressed coking. They suggested that the binary FeMo and CoMo oxide/carbides formed on the ZSM-5 support are active for methane dehydroaromatisation.

The loading of other metal ions into the MoO\(_3\)/H-ZSM-5 catalyst has also been reported to improve catalytic activity. Incorporation of Ru, W and Zr was found to improve the reactivity and/or stability of the MoO\(_3\)/H-ZSM-5 catalysts\cite{25,52}. However, the loading of
Li and P has an negative effect on the catalytic activity \[^{[35]}\]. It has been reported that when introducing a second metal component, the molybdenum species should be impregnated first \[^{[10]}\].

In this study, the effect of Co\(^{2+}\) and Fe\(^{3+}\) dopants have been re-examined and the range has been extended to include Al\(^{3+}\), Ga\(^{3+}\) and Ni\(^{2+}\). The use of metal ion dopants as a means of obtaining promotional effects was chosen over that of employing gas phase oxidants, such as, CO\(_x\), due to the potential application of systems to the production of CO-free hydrogen.

The varying performance of methane dehydroaromatisation catalysts prepared via the impregnation of H-ZSM-5 with ammonium heptamolybdate, phosphomolybdic acid, silicomolybdic-acid and sodium-molybdate as the molybdenum oxide precursor has also been investigated.

### 4.2 Results and discussion – dopant study

#### 4.2.1 Reaction data

Continuing on from work reported by Ichikawa and co-workers \[^{[34, 55]}\], the effect of the addition of Co and Fe dopants have been re-investigated. The level of dopant added corresponds to that reported to have the maximum effect. In the case of cobalt, no significant promotional effect has been observed aside from an initial burst of activity where hydrogen was observed, as shown in Figure 4.2-1. This feature is due to the reduction and/or carbiding of the molybdenum and cobalt components. A similar high initial, and rapidly declining, hydrogen profile has been observed for a Ni\(^{2+}\) doped 3%MoO\(_3\)/H-ZSM-5 catalyst also shown in Figure 4.2-1. The presence of cobalt or nickel in the current study appears to have little effect on benzene formation, as shown in Figure 4.2-2.
Figure 4.2-1 Hydrogen formation rates as a function of time on stream for the parent 3%MoO$_3$/H-ZSM-5 catalyst, and those doped with Co$^{2+}$ and Ni$^{2+}$ (dopant metal ion/Mo atomic ratio of 0.25).

Figure 4.2-2 Benzene formation rates as a function of time on stream for the parent 3%MoO$_3$/H-ZSM-5 catalyst, and those doped with Co$^{2+}$ and Ni$^{2+}$ (dopant metal ion/Mo atomic ratio of 0.25).

This study has shown that upon doping with cobalt or nickel, apart from the initial enhancement in benzene production at earlier times on stream, no pronounced promotional effect can be observed, although the induction period has been removed by the addition of cobalt and nickel. These results conflict with the findings by Ichikawa and co-workers, who reported that a Co-modified Mo/H-ZSM-5 catalyst results in a remarkably enhanced production of benzene.
In order to investigate the lack of promotional effect of cobalt addition on catalyst behaviour at longer times on stream, a number of variables such as calcination procedure have been investigated, but have not been found to produce significant differences.

Figure 4.2-3 shows that both Co and Ni doped MoO\textsubscript{3}/H-ZSM-5 catalysts have a slightly larger H\textsubscript{2}:C\textsubscript{6}H\textsubscript{6} formation rate ratio than the undoped catalyst. The higher ratio is an indication that upon addition of cobalt or nickel the relative coke formation increases compared to that of the standard catalyst. This is consistent with the CHN analysis given in section 4.2.6.

Unlike cobalt and nickel, the use of an iron dopant does enhance activity at longer times on stream. At the start, the benzene formation rate profile for the iron doped catalyst is similar to the parent 3\%MoO\textsubscript{3}/H-ZSM-5 catalyst as shown in Figure 4.2-5. However, as can be seen, the addition of iron displays beneficial effects in terms of benzene formation at longer times on stream. This may be due to delayed deactivation or the slow evolution of additional active phases with time on stream.

In addition, the H\textsubscript{2}:C\textsubscript{6}H\textsubscript{6} formation rate ratio shown in Figure 4.2-3, shows a much more pronounced maximum compared to the standard catalyst, 3\%MoO\textsubscript{3}/ZSM-5, with a sharper and more continual decline. This is an indication that hydrogen producing side reactions, such as coke formation, decline at a faster rate than for benzene production. The generally higher ratio for the Fe\textsuperscript{3+} doped 3\%MoO\textsubscript{3}/H-ZSM-5 catalyst compared to the standard...
The catalyst also shown in Figure 4.2-3 indicates that the relative formation of coke is in fact higher on the addition of iron, this is consistent with the CHN analysis given in section 4.2.6. Contrary to these observations, Ichikawa and co-workers claim that their Fe modified Mo/H-ZSM-5 catalyst enhances benzene production through reduced coking [55].

Weckhuysen et al. have shown that, iron oxide impregnated onto ZSM-5 (with no molybdenum oxide species present) is an active MDA catalyst [27, 28, 114]. It was suggested that the active form of the catalyst consisted of dispersed Fe$_2$O$_4$ entities on the ZSM-5 matrix. Methane activation is reported to occur on the supported iron oxide clusters, once the catalyst is partially reduced from Fe$_2$O$_3$ to Fe$_3$O$_4$. They reported that in another experiment where the Fe/H-ZSM-5 catalyst had been prepared by solid-state ion exchange, that the catalyst was completely inactive for methane activation.

In the results reported in this work there are at least a couple of effects which may explain any promotional effect of iron doping, for example, there may be segregated phases of Mo and Fe. In this case the activity of the Mo component may cause activation of the Fe species by providing the CO and/or H$_2$ required to reduce them by reaction with methane. Another possibility may be that there is the formation of a mixed phase i.e. Fe-Mo, which exhibits different behaviour from the Mo containing phase alone. From XRD measurements of the catalysts given in section 4.2.2, it has not been possible to observe any molybdenum or iron segregated or mixed phases, as only reflections indicative of the zeolite framework are visible. However, future studies using EXAFS experiments may resolve this issue.

Another dopant, which has been investigated in this work, is gallium. Ga/ZSM-5 is an active catalyst in the Cyclar Process [115, 116], where aromatics are formed from C$_3$ and C$_4$ alkanes. The role/nature of the gallium phase is presently not well understood, one suggestion being facilitated hydrogen desorption. There have also been reports of synergistic effects between Ga$_2$O$_3$ and MoO$_3$ in alkane oxidation [117, 118]. Therefore, it is possible that Ga doping may have promotional effects when used as a dopant in this system.

The data for the Ga$^{3+}$ doped MoO$_3$/H-ZSM-5 catalyst is shown in Figure 4.2-3 to Figure 4.2-5. It is clear to see that the Ga$^{3+}$ doped MoO$_3$/H-ZSM-5 catalyst has an improved benzene production rate. Figure 4.2-3 indicates that there is a slight decrease in the H$_2$: C$_6$H$_6$ ratio on gallium addition, which indicates that there is a relative reduction in the hydrogen producing side reactions, such as coke formation. This is consistent with the
CHN analysis, which shows that gallium doping does reduce coking of the MoO$_3$/H-ZSM-5 catalyst. In addition, as was seen before there is a constant H$_2$: C$_6$H$_6$ ratio, indicating that both benzene and hydrogen producing side reactions decrease at a similar rate with time on stream.

It should be noted that there is a difference between the pH of the impregnation solutions of the dopants, for example, ca. pH 3 for iron, pH 4 for gallium versus pH 7 for cobalt.
Iron and gallium give acidic impregnation solutions. Acidic impregnation may lead to dealumination of the zeolite framework. However, the XRD patterns show that the zeolite structure remains intact, so if dealumination does occur it is only to a limited extent. It is interesting that the doped catalysts, which have had a beneficial effect, have all been prepared from acidic precursor solutions.

In view of the possibility that dopants display a beneficial effect due to acidic impregnation, another dopant, aluminium, which also gives a relatively acidic impregnation solution (pH=5), has been tested in this work. From reviewing the literature it does not appear that aluminium doping of MoO3/H-ZSM-5 aromatisation catalysts has been carried out before. Promotional effects have been observed with the use of an aluminium dopant, Figure 4.2-6 and Figure 4.2-7, in that benzene production was enhanced. However the Al³⁺ doped MoO3/H-ZSM-5 catalyst does not display reproducible results between reaction runs of the same or different batches of the catalyst, this is shown using the hydrogen and benzene formation rate profiles of the catalyst in Figure 4.2-6 and Figure 4.2-7. From studying the catalysts’ preparation procedure there appears to be no correlation between the lengths of time the catalyst is in the fresh/calcined form and catalytic activity i.e. any ageing effects.

![Figure 4.2-6 Hydrogen formation rate as a function of time on stream for Al³⁺ doped 3%MoO3/H-ZSM-5 (Al/Mo atomic ratio of 0.25).](image-url)
The characterisation analysis given in the following sections has been focused on the Fe$_{3+}$ doped 3%MoO$_3$/H-ZSM-5 catalyst. Characterisation has been concentrated on the iron doped catalyst, since, iron addition to Mo/H-ZSM-5 has previously been reported in the literature. As already mentioned, Fe addition to Mo/H-ZSM-5 was shown to enhance benzene, which was attributed to reduced coking \[55\]. Furthermore, iron addition to MoO$_3$/H-ZSM-5 in this work has also shown promotional effects regarding benzene production. In this case addition of iron was seen to enhance coking. Therefore, it is an interesting investigation to attempt to elucidate the promotional effect of iron.

### 4.2.2 XRD patterns

X-ray powder diffraction studies were performed on calcined and post reaction catalysts, the patterns are given in Figure 4.2-8 and Figure 4.2-9 respectively. The patterns of the calcined catalysts show the characteristic reflections of H-ZSM-5 with the main 2θ values of ca. 8, 9 and 23-25°. No molybdenum or dopant metal containing crystallites could be detected. This suggests that MoO$_3$ crystallites are highly dispersed on the surface or in the channels of the H-ZSM-5 zeolite and have a particle size too small to be detected by the XRD technique.

It is noticeable that there are differences between the relative intensities of the reflections at 8-9 and 23-25°2θ between the different catalysts. In patterns where the reflections at 8-
9 \( ^\circ 2\theta \) are comparably lower in intensity, there may be material occluded within the channel structure resulting from dealumination.

As the XRD patterns of the calcined standard catalyst and doped catalysts all only show reflections indicative of the zeolite, it is not possible to verify any active phases of the catalysts. As stated previously, it may be that the dopants interact directly with the molybdenum containing phases or that they form some sort of isolated phase having a more indirect effect.

The XRD patterns of the post reaction catalysts, Figure 4.2-9, show no reflections indicative of molybdenum oxide or carbide species. This was to be expected, as no MoO\(_3\) reflections were visible in the patterns of the calcined catalysts. Reflections indicative of the formation of \( \beta \)-Mo\(_2\)C would appear at 34.3, 37.3 and 39.4 \( ^\circ 2\theta \) and for \( \alpha \)-MoCl\(_x\) at 36.8 and 41.2 \( ^\circ 2\theta \). Reflections indicative of H-ZSM-5 i.e. main 2\( \theta \) values of ca. 8, 9 and 23-25\( ^\circ \) are still visible. In general the reflections are much less intense than those of the calcined patterns, indicating that the crystallinity of ZSM-5 has decreased, and that there is deposition of coke on the catalyst.

It has been reported in the literature, that coke formation occurs both externally and internally, i.e. within the channels of ZSM-5, on MoO\(_3\)/H-ZSM-5 based catalysts. It has
been suggested that coke formation within the zeolite can lead to blockage of channels and the covering of the acid sites, leading to catalyst deactivation \[35\].

Evidence of internal coke is given by the post reaction XRD patterns. It has been reported that ZSM-5 undergoes a displacive transformation from monoclinic to orthorhombic when it occludes organic molecules \[119\]. This effect results in the loss of a shoulder on the reflection at 23°20. On closer examination of this reflection, it is noticeable that in the XRD pattern of the calcined catalysts, Figure 4.2-8, that there is a shoulder on this reflection, however, this shoulder has diminished on the reflection in the XRD patterns of the post reaction catalysts, Figure 4.2-9. Therefore it can be said that ZSM-5 has undergone a phase transformation of monoclinic to orthorhombic due to the deposition of coke.

![Figure 4.2-9 post reaction XRD patterns of 3%MoO₃/H-ZSM-5, and those doped with Co³⁺, Fe³⁺, Ni²⁺, Ga³⁺ and Al³⁺ (dopant metal ion/Mo atomic ratio of 0.25).](image)

The XRD patterns of the calcined and post reaction Al³⁺ doped 3%MoO₃/H-ZSM-5 catalyst are given in Figure 4.2-8 and Figure 4.2-9. In the calcined pattern of Al doped 3%MoO₃/H-ZSM-5 catalyst the molybdenum species are highly dispersed and the characteristic peaks of H-ZSM-5, main 2θ values of ca. 8, 9 and 23-25°, are visible.

The post reaction XRD pattern of the Al-doped catalyst, exhibits in general less intense peaks, indicating a decrease in crystallinity of the sample compared to the pattern of the
catalyst prior to methane aromatisation. However, the zeolite structure does remain intact, as all the main reflections indicative of H-ZSM-5 are still visible.

4.2.3 $^{27}$Al and $^{29}$Si MAS NMR spectra

In order to gain a greater insight into the origin of the promotional effects observed upon $\text{Fe}^{3+}$ addition a MAS NMR investigation was undertaken. The $^{27}\text{Al}$ MAS NMR spectra of the calcined 3%MoO$_3$/H-ZSM-5 catalyst together with the $\text{Fe}^{3+}$ doped 3%MoO$_3$/H-ZSM-5 catalyst are shown in Figure 4.2-10. Quantification of the NMR spectra was not attempted because of uncertainty about the NMR visibility of aluminium species in distorted coordination. Referring to previously published $^{27}\text{Al}$ MAS NMR studies relating to MoO$_3$/H-ZSM-5 based catalysts published in the literature as described in Chapter 3, the peak at ca. 53 ppm in the spectra is typical for tetrahedrally coordinated framework aluminium in the ZSM-5 zeolite and the peak at ca. -1.5 ppm is typical of octahedral non-framework aluminium, i.e. extra framework aluminium.$^{[50, 53, 98, 99]}$

The $^{27}\text{Al}$ MAS NMR spectra of the $\text{Fe}^{3+}$ doped 3%MoO$_3$/H-ZSM-5 catalyst is similar to that of the standard catalyst, 3%MoO$_3$/H-ZSM-5, indicating a high stability of the ZSM-5 framework upon incorporation of the dopant. These spectra agree well with the XRD patterns of the catalysts previously shown, which indicate that the zeolite structure remains intact upon incorporation of the molybdenum and the dopant species.

On comparing the peak at -1.5 ppm for the standard catalyst with the $\text{Fe}^{3+}$ doped catalyst, it can be seen that the relative intensity is greater for the Fe doped catalyst. This implies that there is a greater degree of non-framework aluminium for the $\text{Fe}^{3+}$ doped 3%MoO$_3$/H-ZSM-5 catalyst. The greater degree of non-framework aluminium is confirmed by the Si/Al ratios of these catalysts given in the next section. Therefore doping with iron causes an increase in the extractability of the framework Al compared to that of the standard catalyst.

It is interesting to observe that the signal at ca. -1.5 ppm for the both the iron doped catalyst and the standard catalyst has a "liquid-like" NMR appearance, this "liquid-like" signal is more pronounced for the Fe doped catalyst. As discussed in Chapter 3, this signal rather than being due to the conventional octahedral non-framework aluminium may be due to some form of "disordered" octahedral aluminium. For example, it would be consistent with $[\text{Al(H}_2\text{O)}_6\text{]}^{3+}$ wherein deprotonation was suppressed by the inherit acidity.
of the zeolite host. However, additional $^{27}$Al MAS NMR studies would be required to elucidate this remark any further.

An $^{27}$Al NMR study by Masierak et al.$^{120}$ found that exchange with divalent (or greater) cations leads to distortions of the zeolite framework and the formation of an extra-framework aluminium species. Although their study was conducted on type A zeolites, it is possible that the same effect occurs for other zeolites, such as ZSM-5.

![Figure 4.2-10 $^{27}$Al MAS NMR spectra of calcined: (a) 3%MoO$_3$/H-ZSM-5 (b) Fe$^{3+}$ doped 3%MoO$_3$/H-ZSM-5](image)

As previously mentioned in Chapter 3, the framework Si/Al ratio of zeolites can be determined from the $^{29}$Si MAS NMR spectra. The $^{29}$Si MAS NMR spectra are shown in Figure 4.2-11 for calcined 3%MoO$_3$/H-ZSM-5, and for those doped with Fe$^{3+}$ and Al$^{3+}$. The corresponding chemical shifts and Si/Al ratio for each sample are given in Table 4.2.3-1. From Figure 4.2-11, it can be seen that there are two peaks in the $^{29}$Si MAS NMR
spectra with chemical shifts at ca. -106 ppm and -113 ppm. The first peak can be attributed to Si(1Al) and the second peak can be attributed to Si(0Al).

From visual inspection, it appears that incorporation of iron and aluminium dopants causes a slight diminution in the low field shoulder (-106 ppm), due to Si(1Al), compared to the standard catalyst, 3%MoO₃/H-ZSM-5, implying a loss of aluminium from the zeolite lattice upon incorporating Fe and Al dopants. A similar effect to this signal was reported by Zhang et al. [53] upon calcination.

![Figure 4.2-11 ²⁹Si MAS NMR spectra of calcined: (a) 3%MoO₃/H-ZSM-5 (b) Fe³⁺ doped 3%MoO₃/H-ZSM-5 (c) Al³⁺ doped 3%MoO₃/H-ZSM-5.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si(nAl)</th>
<th>δ (ppm)</th>
<th>Si/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>3%MoO₃/HZSM-5</td>
<td>Si(1Al)</td>
<td>-109.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si(0Al)</td>
<td>-116.0</td>
<td>50</td>
</tr>
<tr>
<td>3%MoO₃-Fe/HZSM-5</td>
<td>Si(1Al)</td>
<td>-106.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si(0Al)</td>
<td>-113.0</td>
<td>70</td>
</tr>
<tr>
<td>3%MoO₃-Al/HZSM-5</td>
<td>Si(1Al)</td>
<td>-105.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si(0Al)</td>
<td>-112.9</td>
<td>57</td>
</tr>
</tbody>
</table>

Table 4.2.3-1 The results of ²⁹Si MAS NMR
Moreover, it can be seen that the framework ratio of Si/Al increases sharply when Fe$^{3+}$ is doped onto 3%MoO$_3$/H-ZSM-5 i.e. Si/Al of 70 for Fe$^{3+}$ doped 3%MoO$_3$/H-ZSM-5 compared to a Si/Al ratio of 50 for the standard catalyst. As already mentioned the Fe$^{3+}$ doped catalyst was prepared by acidic impregnation. Al$^{3+}$ doped 3%MoO$_3$/H-ZSM-5 was also prepared by acidic impregnation, this catalyst also exhibited an increase in the Si/Al framework ratio compared to the standard catalyst. Therefore, it appears that doped catalysts prepared by acidic impregnation cause an increase in the framework Si/Al ratio of the MoO$_3$/H-ZSM-5 catalyst.

It was proposed in Chapter 3 through Al EXAFS studies that incorporation of Mo species into H-ZSM-5 causes significant distortion of the framework aluminium, which is drawn from the framework towards the molybdenum oxo species. Evidence for the extraction of framework aluminium from the zeolite was given by the N$_2$ adsorption isotherms of the parent zeolite, H-ZSM-5 and the standard catalyst, 3%MoO$_3$/H-ZSM-5, through the increase in mesoporosity upon molybdenum incorporation. It was believed that by addition of extra aluminium in the form of a dopant, that some of the lost framework aluminium might be replaced, or else the concentration of active extra-framework Al species would be increased. The NMR studies have shown that the Al doped catalyst has a greater degree of dealumination than the standard catalyst, as a higher Si/Al ratio is seen for the Al doped catalyst. A higher Si/Al ratio indicates that the acid site strength has increased upon doping with Fe or Al compared to that of the standard catalyst.

The interaction between the framework aluminium of the zeolite and molybdenum species has also been reported in the literature. Xu et al. have also shown using $^{27}$Al and $^{29}$Si MAS NMR studies, that framework aluminium in the zeolite can be extracted by the introduction of molybdenum species. The extractability of framework aluminium was shown to increase with increasing molybdenum loading. The process leads to the formation of non-framework aluminium species at first and then a crystalline phase of Al$_2$(MoO$_4$)$_3$. In the literature it has been reported that Al$_2$(MoO$_4$)$_3$ phases form for standard methane aromatisation catalysts such as MoO$_3$/H-ZSM-5, this type of phase has been associated with low catalytic activity $^{[50]}$, this effect may also be likely when employing an aluminium dopant. However, the XRD patterns shown earlier, Figure 4.2-8 indicate that the Al$_2$(MoO$_4$)$_3$ phase was not produced for any of the catalysts.

From reviewing the literature, there does not appear to be many $^{27}$Al and $^{29}$Si MAS NMR studies on post reaction MoO$_3$/H-ZSM-5 based catalysts. However, Zhang at al. $^{[51]}$ have presented, but not discussed, post reaction $^{27}$Al and $^{29}$Si MAS NMR spectra of their Mo/H-
ZSM-5 catalyst. Figure 4.2-12 and Figure 4.2-13 give the post reaction $^{27}$Al and $^{29}$Si MAS NMR spectra of 3%MoO$_3$/H-ZSM-5 and those doped with Fe$^{3+}$ and Al$^{3+}$. Generally, all the peaks in the $^{27}$Al spectra of the post reaction catalysts are less intense than the peaks in the $^{27}$Al spectra of the calcined catalysts, Figure 4.2-10.

On comparing the intensity of the signals ascribed to octahedral non-framework aluminium with tetrahedrally coordinated framework aluminium for the post reaction 3%MoO$_3$/H-ZSM-5 catalyst compared to the intensities of these signals in the spectra of the catalyst in the calcined form, Figure 4.2-10, it is clear to see that the relative intensity of octahedral non-framework aluminium is much greater in the post reaction $^{27}$Al MAS NMR spectra. This result indicates that during the MDA reaction framework aluminium from the zeolite is extracted. Again, XRD patterns of the post reaction catalysts, shown earlier, revealed that the zeolite structure remains intact after the MDA reaction. Therefore, the dealumination that occurs during the reaction does not occur to a great enough extent to structurally damage the ZSM-5 zeolite.

It can be seen from Figure 4.2-13 that the shoulder peak (which was attributed to Si(1Al)) which was present in the $^{29}$Si MAS NMR spectra of the catalysts when they were in the calcined form (Figure 4.2-11) is no longer clearly visible in the post reaction spectra. This may imply a loss of Al from the zeolite. However, from the $^{27}$Al MAS NMR of the post reaction catalysts it is evident that all the Al has not been extracted. Furthermore, post reaction XRD patterns confirm that the zeolite structure remains intact after the reaction.

In general on comparing the spectra of the post reaction catalysts with the spectra of the catalysts in the calcined form, it appears that the Si(0Al) peaks of the post reaction catalysts are less intense but slightly broader.
Figure 4.2-12 $^{27}$Al MAS NMR spectra of post reaction: (a) 3\%MoO$_3$/H-ZSM-5 (b) Fe$^{3+}$ doped 3\%MoO$_3$/H-ZSM-5
Figure 4.2-13 $^{29}$Si MAS NMR spectra of post reaction: (a) 3%MoO$_3$/H-ZSM-5 (b) Fe$^{3+}$ doped 3%MoO$_3$/H-ZSM-5 (c) Al$^{3+}$ doped 3%MoO$_3$/H-ZSM-5.

4.2.4 NH$_3$-TPD profiles

NH$_3$-TPD experiments were conducted on the Fe doped 3%MoO$_3$/H-ZSM-5 catalyst prior to reaction, to examine any differences in acidity between this catalyst and the standard catalyst, 3%MoO$_3$/H-ZSM-5. NH$_3$-TPD experiments may also help elucidate the origin of the "liquid like" $^{27}$Al MAS NMR signals shown in the previous section, Figure 4.2-10. Changes in acidity between the two catalysts may help explain the differences in their catalytic activity, since in the currently accepted mechanism, acid catalysed reaction of C$_2$H$_4$ intermediates is proposed to yield the C$_6$H$_6$ product. It should be noted that FTIR activation studies conducted on 3%MoO$_3$/H-ZSM-5, which were presented in Chapter 3, demonstrated that all the acidity relating to this type of catalyst is of the Bronsted type and not Lewis.

The NH$_3$-TPD profile of the Fe$^{3+}$ doped MoO$_3$/H-ZSM-5 catalyst is shown in Figure 4.2-14, the profiles for H-ZSM-5 and 3%MoO$_3$/H-ZSM-5 are also given for comparison (the TPD profiles were deconvoluted by the Gaussian curve fitting method. The numerical
data of the fittings are listed in Table 4.2.4-1). It should be noted that direct area comparisons cannot be made between samples. The profile of H-ZSM-5, exhibits the double-peak characteristic of zeolites with the MFI structure [121]. The two fairly well resolved peaks are centered at ca. 237 and 444 °C. However, on closer analysis in view of the data apparent for MoO₃/H-ZSM-5, it actually appears that the low temperature peak may be fitted into two peaks when using the Gaussian curve fitting method.

Figure 4.2.14 NH₃-TPD profile (ramp rate 15°C/min) of (a) H-ZSM-5 (b) 3%MoO₃/H-ZSM-5 (c) Al³⁺ doped 3%MoO₃/H-ZSM-5 (d) Fe³⁺ doped 3%MoO₃/H-ZSM-5. The deconvoluted curves are also shown.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Peak position (°C)</th>
<th>Relative peak area (%)</th>
<th>A₁</th>
<th>A₂</th>
<th>A₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM-5</td>
<td>193  250  444</td>
<td>18  21  61</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3%MoO₃/H-ZSM-5</td>
<td>196  250  430</td>
<td>12  37  51</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3%MoO₃-Al/H-ZSM-5</td>
<td>184  245  405</td>
<td>14  33  53</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3%MoO₃-Fe/H-ZSM-5</td>
<td>230  430</td>
<td>55  44</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2.4-1 Numerical results of the NH₃-TPD profiles by the Gaussian curve fitting method.
In measurement studies of acidity of zeolites, Hidaglo et al. have reported that the peak desorbed at high temperature is always associated with the ammonia adsorbed on the bridging hydroxyl group $\text{Si-OH-Al}$. However, the assignment of the low temperature peak is not clear, possibilities include, physisorbed ammonia, chemisorbed ammonia or from Si-OH groups.\(^{121}\)

The ascription of the moderate temperature peak in the NH$_3$-TPD profiles is also still not well understood. For example, it may be ascribed to the desorbed ammonia on extra-framework Al or Si-OH.\(^{102}\) It may also be possible to attribute it to the ammonia adsorbed on the medium acid sites, which are created from the interaction of Mo species and the strong acid sites.

The temperature of a TPD peak is used as a rough measure of the acid strength of the sorption sites. Caution must be applied in this analysis as, it is generally assumed that acid-base interactions dominate the adsorption of NH$_3$ on acidic materials and that the strength of interaction relates to the acid strength. However, it should be noted that other interactions may be occurring and that these may be as strong as the conventionally assumed acid-base interactions. For instance, ammonia dissociation on adsorption of CaO has been reported, resulting in high TPD temperatures.\(^{122}\)

It can be seen in Figure 4.2-14 that there is an apparent decrease in acidity when Mo species have been loaded onto H-ZSM-5, as there is a decrease in the desorption temperature of A$_3$, which relates to the strongest acid sites of the zeolite i.e the Bronsted acid sites. Bao et al. have also reported a decrease in the area and temperature of the high temperature peak after the incorporation of molybdenum species in ZSM-5.\(^{102}\) The decrease in the relative area of the high temperature peak has been reported to be due to the interaction of Mo species with the Bronsted acid sites of the zeolite.

The results of the Al EXAFS experiments of the standard catalyst, 3\%MoO$_3$/H-ZSM-5, given in Chapter 3, reveal that a distortion of framework aluminium does occur when molybdenum oxide is loaded onto H-ZSM-5. This distortion would be expected to influence the strength of the framework Bronsted acid sites.

In the case of the results reported here, it is probable that the decrease in the high temperature peak is due to the lowering of the amount of Bronsted acid sites, which result from a modification/interaction with Mo species. This agrees well with results reported by Bao et al. that have shown using ESR studies that Mo species do migrate into the zeolite.
channels and interact with and replace some Brønsted acid sites \[^{11}\] \textsuperscript{11}, compared to the findings by Lunsford and co-workers that claim molybdenum oxide species are on the external surface and there is no discussion of migration.

The Fe-modified catalyst has an even lower relative area of high temperature peak than the standard catalyst, 3\%MoO\textsubscript{3}/H-ZSM-5, indicating that doping with iron lowers the amount of Brønsted acid sites compared to that of the standard catalyst. There may be a few possible explanations for this, firstly, the molybdenum and iron species on the iron doped catalyst interact/modify the strongest acid sites to a greater extent than the Mo species alone on the parent catalyst. Alternatively, another explanation may be dealumination by Fe\textsuperscript{3+} ions, as evidenced in the NMR studies outlined previously. Therefore, the difference in acidity may be explained through the dealumination of ZSM-5 caused by the presence of iron species.

To compare the acidity of the Al\textsuperscript{3+} doped catalyst with that of the standard catalyst, NH\textsubscript{3}-TPD experiments were carried out and the results are given in Figure 4.2-14. For the aluminium doped catalyst the ammonia adsorbed on the Brønsted acid sites i.e. A\textsubscript{3}, desorbs at lower temperatures compared to that of the standard catalyst. This implies that the strength of acid site, A\textsubscript{3}, has decreased. Therefore it appears that doping Al into 3\%MoO\textsubscript{3}/H-ZSM-5 does in fact lower the strength of the Brønsted acid sites in the catalyst.

Moreover, all desorption peaks in the Al doped sample are at a lower temperature than the corresponding peaks in the standard catalyst, indicating that the strength of all the types of sites have been lowered upon Al doping.

Although the NH\textsubscript{3}-TPD experiments suggest that addition of Fe and Al dopants to 3\%MoO\textsubscript{3}/H-ZSM-5 lowers the strength of Brønsted acid sites compared to that of the standard catalyst, the $^{29}$Si MAS NMR studies shown previously, Table 4.2.3-1, show that the acidity of the 3\%MoO\textsubscript{3}/H-ZSM-5 catalyst increases upon addition of Fe and Al, as the Si/Al ratio of the doped catalysts is greater than that of the standard catalyst.

### 4.2.5 N\textsubscript{2} adsorption isotherms

The N\textsubscript{2} adsorption isotherm of the parent zeolite, H-ZSM-5 and the standard catalyst, 3\%MoO\textsubscript{3}/H-ZSM-5, were discussed in Chapter 3. It was shown that the N\textsubscript{2} adsorption of H-ZSM-5 represented a combination of Type I and IV isotherms, with a slight hysteresis
loop, typical for microporous materials with a very small degree of mesoporosity. Upon incorporation of molybdenum species it was seen that the isotherm developed a more pronounced but still small hysteresis loop, resulting from capillary condensation in mesopores \cite{104}.

The N$_2$ adsorption isotherms of the cobalt, nickel, iron, gallium and aluminium doped 3%MoO$_3$/H-ZSM-5 catalysts are shown in Figure 4.2-15 to Figure 4.2-19. It should be noted that direct comparisons between isotherms should not be made as the batch of ZSM-5 (although the same Si:Al ratio) used varied between the preparation of the catalysts, i.e. the mesopore structure of ZSM-5 may be different from batch to batch. All doped catalysts show a N$_2$ isotherm with a pronounced hysteresis loop, indicating that mesopores along with micropores are present on all doped catalysts, a combination of Type I and IV isotherms.

The catalysts prepared via acidic impregnation i.e. Fe$^{3+}$, Ga$^{3+}$ and Al$^{3+}$ doped 3%MoO$_3$/H-ZSM-5 have a greater size of hysteresis loop than the Co$^{2+}$ and Ni$^{2+}$ doped 3%MoO$_3$/H-ZSM-5 catalysts, indicating a greater degree of mesoporosity for the catalysts prepared via acidic impregnation. A greater degree of mesoporosity suggests that these materials are more dealuminated. It should be noted that, a significant degree of dealumination can occur before it becomes apparent on the powder diffraction patterns of ZSM-5. Dealumination is not occurring to a great extent, as the XRD patterns, of the catalysts reveal that the zeolites structure remains intact after the incorporation of the molybdenum and/or dopant species.

In all isotherms, the increase in sorption is gradual until at approaching P/P$_0$ = 1, where the isotherms exhibit a steep increase in sorption, which is characteristic of liquid-phase condensation in macropores \cite{123}.
Figure 4.2-15 Adsorption isotherm plot for calcined Co$^{2+}$ doped 3%MoO$_3$/H-ZSM-5.

Figure 4.2-16 Adsorption isotherm plot for calcined Ni$^{2+}$ doped 3%MoO$_3$/H-ZSM-5.
Figure 4.2-17 Adsorption isotherm plot for calcined Fe$^{3+}$ doped 3%MoO$_3$/H-ZSM-5.

Figure 4.2-18 Adsorption isotherm plot for calcined Ga$^{3+}$ doped 3%MoO$_3$/H-ZSM-5.
4.2.6 Post reaction CHN, TGA analysis and TEM images

The post reaction CHN analysis of the doped catalysts and the 3%MoO₃/H-ZSM-5 catalyst are shown in Table 4.2.6-1. Aside from the gallium-doped catalyst, all doped catalysts have more carbon deposited on them after reaction (duration of 390 min on stream) compared to the non-doped standard catalyst, 3%MoO₃/H-ZSM-5. The Ga³⁺ doped catalyst has a significantly lower amount of carbon than the standard catalyst. The reduced coking of the gallium doped catalyst may explain the enhanced hydrogen and benzene production of this catalyst. The higher carbon content in the Fe doped catalyst compared to that of the standard, is in conflict with the work reported by Ichikawa and co-workers, where they attribute the beneficial effect of iron to reduced coking [55], but is consistent with the enhanced H₂:C₆H₆ ratio reported in Figure 4.2-3.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>3%MoO₃/H-ZSM-5</td>
<td>4.21</td>
<td>0.14</td>
<td>-</td>
</tr>
<tr>
<td>Co²⁺ doped 3%MoO₃/H-ZSM-5</td>
<td>5.50</td>
<td>0.15</td>
<td>-</td>
</tr>
<tr>
<td>Fe³⁺ doped 3%MoO₃/H-ZSM-5</td>
<td>5.69</td>
<td>0.15</td>
<td>-</td>
</tr>
<tr>
<td>Ga³⁺ doped 3%MoO₃/H-ZSM-5</td>
<td>3.09</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni²⁺ doped 3%MoO₃/H-ZSM-5</td>
<td>5.26</td>
<td>0.27</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.2.6-1 Post-reaction CHN analysis of catalysts after 390 min on stream.
The TGA profiles of the post reaction catalysts are given in Figure 4.2-20 to Figure 4.2-22. The TGA results are consistent with the post reaction CHN analysis. The post reaction iron doped 3%MoO₃/H-ZSM-5 catalyst has the greatest amount of carbon deposited on it after the reaction i.e. the highest value of carbon content from CHN analysis, 5.69% and the largest decrease in weight in the burning off coke region in Figure 4.2-20. It should be noted that the general trend in the amount of carbon deposited on the different catalysts is the same for the post reaction CHN analysis and TGA profiles. However, exact wt.% for the two techniques are not the same. This is most likely due to the small amount of material required to perform these post reaction techniques. This indicates that there is a degree of inhomogeneity on the dispersion of carbon on the catalysts.

The first derivative weight changes are also given for the post reaction catalysts (Figure 4.2-21 and Figure 4.2-22) as any differences between the samples will be more apparent than those in Figure 4.2-20. From Figure 4.2-22 by looking at the areas under the peaks, it appears that the much of the coke in the gallium-modified catalyst appears to be of the low temperature kind, whereas, the majority of coke in the iron-modified catalyst appears to be of the high temperature kind.
From reviewing the literature there does not appear to be any studies on the analysis of the post reaction MDA catalysts by TEM, with the exception of [37], for which microscopy was performed on non-conventionally prepared samples. TEM analysis reveals that some of the carbon deposition of the Fe$^{3+}$ doped 3%MoO$_3$/H-ZSM-5 catalyst has the form of carbon nanotubes after the reaction, as shown in Figure 4.2-23. The micrograph image shows a cluster of nanotubes. It appears that one end of the carbon nanotube is attached to the
catalyst and the other end is open and detached from the catalyst. It appears that the nanotubes are in the form of multi walled carbon nanotubes (MWNT).

![Figure 4.2-23 post reaction TEM image of (a) Fe$^{3+}$ doped 3%MoO$_3$/H-ZSM-5 and (b) Al$^{3+}$ doped 3%MoO$_3$/H-ZSM-5.](image)

The diameter of the nanotubes range from approximately 17 to 78 nm, this is a much greater value than that of the channel diameter of ZSM-5 (0.55nm). This implies that the nanotubes do not originate from within the zeolite channels. If this was the case it would be expected that there would be some sort of structural collapse of the zeolite, however, the post-reaction XRD patterns given in section 4.2.2 reveal that the zeolite structure remains intact after the reaction, as all the main reflections indicative of ZSM-5 are apparent. However, further TEM images on these types of systems are desirable to fully elucidate their route of formation and final structure, as it this point that is currently not well understood. These observations are consistent with the earlier proposals of Lunsford et al.\textsuperscript{261}, that one form of carbon originates from molybdenum carbide dispersed on the external surface of ZSM-5. The dense phases apparent in Figure 4.2-23 are related to the zeolite component.

Yang et al. reported a similar TEM micrograph to that shown in Figure 4.2-23 for a Mo/H-ZSM-5 catalyst prepared by microwave heating after the methane aromatisation reaction\textsuperscript{37}.

A recent study by Serp et al. has shown that Fe$_2$O$_3$/Al$_2$O$_3$ and FeMo/Al$_2$O$_3$ catalysts when used in the methane decomposition reaction selectively produce single wall carbon nanotubes (SWNT)\textsuperscript{124}. In this case, it was reported that the selective production of the
SWNT is linked with the creation of small iron clusters during the reduction step of an oxide phase, which would not appear to be applicable here.

A post reaction TEM image of the Al$^{3+}$ doped 3%MoO$_3$/H-ZSM-5 catalyst is given in Figure 4.2-23. The nanotube displayed is generally similar to the one produced for the Fe$^{3+}$ doped 3%MoO$_3$/H-ZSM-5 catalyst also shown in Figure 4.2-23.

4.3 Results and discussion - molybdenum precursors

4.3.1 Reaction data

Figure 4.3-1 and Figure 4.3-2 give the formation rate data for hydrogen and benzene production for 2, 5, 10 and 15wt.%MoO$_3$/H-ZSM-5 catalysts prepared from a phosphomolybdic acid precursor (the P/Mo molar ratio is dictated by the formula of the Keggin unit, $[\text{PMo}_{12}\text{O}_{40}]^{3-}$, and is therefore 0.08). The data for the standard catalyst, 5%MoO$_3$/H-ZSM-5, prepared from ammonium heptamolybdate is also given for comparison. It should be noted that this is a different standard catalyst to the one used in section 4.2. The reason being that phosphomolybdic acid, silicomolybdic acid (SMA) and sodium molybdate were all prepared via impregnation onto a different ZSM-5 from the one used in the previous section. These catalysts were prepared by Dr. K. M. Parida, using a ZSM-5 (Zeolyst) zeolite with a Si/Al ratio of 50:1, whereas all of the catalysts discussed in section 4.2 were prepared using a ZSM-5 (Catal) zeolite with a Si/Al of 40:1. It should be noted that the percentages refer to wt% of MoO$_3$ i.e. 5wt%MoO$_3$/H-ZSM-5 and 5%phosphomolybdic-acid/H-ZSM-5 are comparable.

It is clear from the data that the inclusion of very low levels of phosphorus dopant has produced a decrease in both the hydrogen and benzene formation rates. This can be seen clearly when comparing the 5%MoO$_3$/H-ZSM-5 standard catalyst and the 5%MoO$_3$/H-ZSM-5 catalyst prepared from a phosphomolybdic acid precursor. The effect is more prominent for benzene than it is for hydrogen.

On comparing the catalysts prepared by phosphomolybdic acid, the lower loadings of 2 and 5wt.% have a greater hydrogen and benzene formation rate compared to the catalysts with the higher loadings of 10 and 15wt.%. This is not unexpected, as it has been reported in the literature that metal loading does exhibit an effect on catalytic activity$^{[24, 35]}$, and that the most favourable loading of molybdenum on ZSM-5 for methane dehydroaromatisation
is in the range of 2-6 wt.%. Molybdenum loadings greater than 6 wt.% are reported to lead to blockage of zeolite channels and therefore a loss in catalytic activity.

The relative constancy of the $H_2: C_6H_6$ formation rate ratio for all catalysts, shown in Figure 4.3-3 suggests that both hydrogen and benzene formation decline at similar rates, as was observed for the standard catalyst previously. The $H_2: C_6H_6$ formation rate ratio appears to be slightly higher for the 5% wt catalyst prepared from phosphomolybdic acid compared to the standard 5% MoO$_3$/H-ZSM-5 catalyst, as shown in Figure 4.3-3. This suggests that the selectivity towards benzene is lowered with respect to that for hydrogen. A possible explanation for this effect may be the enhanced coking for the catalyst prepared by phosphomolybdic acid, as a result of the modified acidity of the catalyst.
The ways in which phosphorus affects the acidity are most likely to be dependent upon the level of phosphorus added and the nature of the phase with which it is associated. For instance, it has been shown that phosphorus modification of MoO$_3$ enhances acidity \cite{125}, but on the other hand, phosphorus modification of ZSM-5 has been reported to decrease total acidity due to the removal of the strongest acid sites \cite{126}. In this work it was not possible to conduct NH$_3$-TPD experiments on the phosphomolybdic acid prepared...
catalysts, due to a limited supply of these materials. This was unfortunate, as these experiments would have most likely helped to explain their catalytic behaviour.

Considering that the levels of phosphorus addition are so low, in that they are governed by the stoichiometric ratio of P:Mo in phosphomolybdic acid, the effects on catalytic performance are comparatively dramatic. There are many potential explanations for this. For instance, the dispersion of the molybdenum active phase may be different for the phosphomolybdic acid precursor prepared catalyst compared to that of the standard catalyst. This may be likely as in one case the impregnating ion is $\text{Mo}_7\text{O}_{24}^{6-}$ and $[\text{PMo}_{12}\text{O}_{40}]^3^-$ in the other. Re-dispersion of oxomolybdenum species has been reported to occur on calcination and so this may be expected to have little or no implication.

The thermal decomposition of phosphomolybdic acid supported on silica proceeds via the metastable $\beta$-MoO$_3$ phase, however, this phase has only been observed to be stable at temperatures lower than the calcinations and reaction procedures used in this study. When silica was used as a support, calcination at 500°C was reported to completely transform $\beta$-MoO$_3$ into $\alpha$-MoO$_3$.

From the results reported in this work it is not possible to fully propose the form of the active precursor.

### 4.3.2 XRD patterns

X-ray powder diffraction studies were performed on calcined and post reaction catalysts, the patterns are given in Figure 4.3-4 and Figure 4.3-5. The patterns of the calcined catalysts show the characteristic reflections of H-ZSM-5 with the main 2θ values of ca. 8, 9 and 23-25°. The pattern for 15%wt MoO$_3$/H-ZSM-5 prepared from phosphomolybdic acid has an intense reflection at 27.4°, this is indicative of $\alpha$-MoO$_3$ crystallites, as ca. 27° is the dominant reflection observed for $\alpha$-MoO$_3$, therefore the $\beta$-MoO$_3$ phase can be discounted. This reflection is consistent with the post reaction TGA profile given in Figure 4.3-9 and discussed later, which shows a weight increase in the region where molybdenum carbide is oxidised to molybdenum oxide for the 10 and 15%wt MoO$_3$/H-ZSM-5 catalysts (this increase was not observed for all the lower loading samples).

The reflection indicative of MoO$_3$ crystallites is not visible in the other patterns. This suggests that for the catalysts prepared with lower loadings of molybdenum ($\leq$15%MoO$_3$),
MoO₃ crystallites are highly dispersed on the surface or in the channels of the H-ZSM-5 zeolite and have a particle size too small as to be detected by XRD technique.

The XRD patterns of the post reaction catalysts, Figure 4.3-5, show no reflections indicative of molybdenum oxide or carbide species. The reflection indicative of MoO₃ in the 15%wt catalyst in the pattern prior to reaction with methane has now disappeared. Reflections indicative of H-ZSM-5 are still visible. In general the reflections are much less intense than that of the calcined patterns.

Figure 4.3-4 XRD pattern of calcined 2, 5, 10 and 15 % MoO₃/H-ZSM-5 prepared from phosphomolybdic acid.

Figure 4.3-5 post reaction XRD pattern of calcined 2, 5, 10 and 15 % MoO₃/H-ZSM-5 prepared from phosphomolybdic acid.
4.3.3 Raman spectroscopy

Since no direct observation of molybdenum based compounds could be detected by XRD, due to its high sensitivity to surface molybdenum oxide species, the pre-reaction catalysts were investigated using laser Raman spectroscopy. For all samples tested there were five spot analyses taken, this was done to survey how homogeneous the samples were. The results of the 5 and 15wt.% MoO$_3$/H-ZSM-5 catalysts prepared from a phosphomolybdic acid precursor are shown in Figure 4.3-6. It is clear that the bands at ca. 820 and 995 cm$^{-1}$ which would be expected for the Mo-O-Mo and M=O stretches of α-MoO$_3$ [128] do not occur for the 5 wt.% catalyst, and it is only at much higher loading such as 15 wt.% that these features appear; however it should be noted that this occurs inhomogeneously as they were not observed in every sampling point. The ratio of the intensity of the Mo-O-Mo band to the M=O band is ca. 4:1. M=O species are associated with the side planes and Mo-O-Mo with the basal planes of MoO$_3$ [129], and so this value indicates that such MoO$_3$ species are relatively highly dispersed.

Throughout this work, the samples mentioned above are the only ones to be analysed by this technique. This was due to restrictions on the number of materials that could be analysed on the single session that was kindly offered by Strathclyde University, where Dr Ann Robin carried out the laser Raman spectroscopy analysis.
4.3.4 N₂ adsorption Isotherms

The N₂ adsorption isotherm of the standard 5%MoO₃/H-ZSM-5 catalyst and the 5%MoO₃/H-ZSM-5 catalyst prepared from phosphomolybdic-acid are given in Figure 4.3-7 and Figure 4.3-8 respectively. On comparing the isotherm of the standard catalyst, 5%MoO₃/H-ZSM-5, with the isotherm of the catalyst prepared from phosphomolybdic-acid, it can be seen that the overall N₂ uptake is lower for the catalyst prepared from the phosphomolybdic-acid precursor. Both isotherms display a hysteresis loop, indicating that mesopores along with micropores are present, indicating a combination of Type I and IV isotherms. The hysteresis is more pronounced for the catalyst prepared using phosphomolybdic-acid than the standard catalyst. Therefore, the phosphomolybdic-acid prepared catalyst has a greater degree of mesoporosity, and therefore may be dealuminated to a greater extent than 5%MoO₃/H-ZSM-5.

It can be seen that the overall uptake is lower for the phosphomolybdic-acid prepared catalyst (ca. 90 cm³/g) compared to the standard catalyst (ca. 100 cm³/g), this may suggest that the overall adsorption capacity is reduced for the phosphomolybdic-acid prepared catalyst.
4.3.5 Post reaction CHN and TGA analysis

The post reaction CHN analysis of the phosphomolybdic acid precursor prepared catalysts are given in Table 4.3.5-1, the data for the standard catalyst, 5%MoO$_3$/H-ZSM-5 prepared from ammonium heptamolybdate is also given for comparison. It was shown in Figure 4.3-1 and Figure 4.3-2 that the 5%phosphomolybdic-acid/H-ZSM-5 catalyst has a lowered activity compared to that of the standard catalyst, however as can be seen from the CHN data a comparable amount of carbon was deposited on this catalyst compared to the standard.

It is noticeable that the catalysts with a higher loading of molybdenum i.e. 10 and 15wt %MoO$_3$, have a lower amount of carbon, this is due to their lower reaction rates.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%Phosphomolybdic-acid/H-ZSM-5</td>
<td>4.57</td>
<td>0.20</td>
<td>-</td>
</tr>
<tr>
<td>5%Phosphomolybdic-acid/H-ZSM-5</td>
<td>5.67</td>
<td>0.22</td>
<td>-</td>
</tr>
<tr>
<td>10%Phosphomolybdic-acid/H-ZSM-5</td>
<td>4.37</td>
<td>0.19</td>
<td>-</td>
</tr>
<tr>
<td>15%Phosphomolybdic-acid/H-ZSM-5</td>
<td>4.19</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5%Silicomolybdic-acid/H-ZSM-5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5%Sodium-molybdate/H-ZSM-5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5%Ammonium-heptamolybdate/H-ZSM-5</td>
<td>5.70</td>
<td>0.11</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.3.5-1 Post-reaction CHN analysis of catalysts after 390 min on stream.
Again, the TGA profiles have been assigned on the basis of the study by Liu at al.\(^{44}\). The TGA profiles of the post reaction catalysts are given in Figure 4.3-9 and Figure 4.3-10. In Figure 4.3-9, the weight increase in the region of 450°C resulting from the oxidation of the carbide is only visible for the higher loaded MoO\(_3\) catalysts i.e 10 and 15 wt% MoO\(_3\). Apart from the 2 wt% MoO\(_3\) catalyst, all other catalysts lose weight in the 750-900°C region, indicating sublimation of MoO\(_3\).

![Figure 4.3-9 TGA profile for the post reaction 5%MoO\(_3\)/H-ZSM-5 and 2, 5, 10 and 15% MoO\(_3\)/H-ZSM-5 prepared from phosphomolybdic acid after 390 min on stream.](image)

![Figure 4.3-10 TGA profile for the post reaction 5%MoO\(_3\)/H-ZSM-5 and 2, 5, 10 and 15% MoO\(_3\)/H-ZSM-5 prepared from phosphomolybdic acid after 390 min on stream.](image)
The first derivative weight changes for the post reaction catalysts are shown in Figure 4.3-10. In these profiles the differences between the catalysts become more apparent. For example, the weight increase for the 10 and 15wt%MoO₃ catalysts can clearly be seen. It appears that much of the coke on the 15wt%MoO₃ catalyst is of the high temperature kind. The profiles for the 5%MoO₃/H-ZSM-5 catalysts prepared from AHM and phosphomolybdic-acid precursors are very similar, indicating that the types of coke on these catalysts are similar.

4.3.6 Reaction data - silicomolybdic acid and sodium molybdate

An additional study has been carried out on investigating the catalytic behaviour of catalysts that were supplied, by Dr. K. M. Parida, using silicomolybdic acid (SMA) and sodium molybdate as the molybdenum precursors.

The hydrogen formation rate profiles of the catalysts are shown in Figure 4.3-11, it is clear that neither the silicomolybdic acid or sodium molybdate precursor prepared catalysts are as active for hydrogen formation as the standard catalyst. The sodium molybdate precursor prepared catalyst has the same shape of profile as the standard catalyst, in that there is an induction period observed before the maximum in hydrogen production.

The hydrogen formation rate for H-ZSM-5 is also given in Figure 4.3-11, however a direct comparison between activity of the H-ZSM-5 zeolite shown and the catalysts should not be made as the Si/Al ratio of the ZSM-5 is 40:1 whereas, the Si/Al of the ZSM-5 in the three other materials is 50:1. Ideally it would be best if H-ZSM-5 with a Si/Al ratio of 50:1 was tested under the same conditions as that used on the catalysts in Figure 4.3-11 so that a direct comparison between the parent zeolite and the catalysts could be made.
No benzene was detected for the sodium molybdate precursor prepared catalyst. This may be an indication that sodium may possibly be destroying/poisoning or altering the acidity of the Bronsted acid sites that are required for the production of benzene.

Some benzene was detected for the catalyst prepared from the SMA precursor. However, to a far lesser extent than the catalyst prepared from the standard AHM precursor and it was only detected on the first analysis point. It has been reported in the literature that at high temperature SMA decomposes to SiO$_2$ and molybdenum oxide. However, in the
presence of water, SMA regenerates \cite{130}. However, due to the high calcination and reaction temperatures this is probably not an issue in this system. It is more likely that the active molybdenum carbide phase cannot be made from this precursor.

CHN analysis of post reaction 5%MoO$_3$/H-ZSM-5 prepared from both sodium molybdate and silicomolybdic acid, Table 4.3.5-1, reveal that no carbon at all was deposited on these catalysts during the 390 minute run time. One possible explanation for the absence of carbon lay down may be that these two catalysts may be resistant to forming a carbide. Molybdenum carbide has been suggested to be the active species in the formation of ethylene and ethylene is subsequently aromatised to benzene \cite{29}, therefore without the formation of molybdenum carbide benzene cannot be produced under this proposed mechanism. From reviewing the literature there appear to be no studies based on the carbiding characteristics of silicomolybdic acid. Alternatively, in the case of 5%MoO$_3$/H-ZSM-5 prepared from sodium molybdate, it may be that Na$^+$ poisons the acidity, so molybdenum carbide could form but C$_2$H$_4$ and H$_2$ could be the reaction products.

It should be noted that there was a slight colour change of white to grey/white upon calcination of 5%MoO$_3$/H-ZSM-5 prepared from both sodium molybdate and silicomolybdic acid, compared to no colour change on calcination of H-ZSM-5. This is direct evidence that there are molybdenum species present in these materials.

Consequently from this work, it is clear to see that the starting material of the molybdenum component strongly influences catalytic performance in methane aromatisation.

### 4.3.7 N$_2$ adsorption isotherm

The N$_2$ adsorption isotherm of the 5%MoO$_3$/H-ZSM-5 catalyst prepared from SMA is given in Figure 4.3-13. The overall N$_2$ uptake is lower for the 5%MoO$_3$/H-ZSM-5 catalyst prepared from SMA compared to the standard catalyst, but it is similar to that of the catalyst prepared by phosphomolybdic acid. The isotherm displays a hysteresis loop, indicating that mesopores along with micropores are present, indicating a combination of Type I and IV isotherms. The hysteresis is distinctly more pronounced for this catalyst compared to the standard catalyst, 5%MoO$_3$/H-ZSM-5, prepared from ammonium heptamolybdate as the starting material of the molybdenum component (Figure 4.3-7). Therefore, preparing the MoO$_3$/H-ZSM-5 catalyst with silicomolybdic-acid as the precursor creates more mesoporosity compared to when ammonium heptamolybdate is used as the starting material of the molybdenum component.
4.4 Silver doping of MoO$_3$/H-ZSM-5

An additional investigation on doping the standard MDA catalyst, MoO$_3$/H-ZSM-5, with silver has been carried out. It was proposed that by adding a small amount of silver to the standard catalyst, (Ag/Mo atomic ratio = 0.25), that the induction period would be shortened. It was hoped that the addition of silver would improve the reducibility of the catalysts by forming the following redox couple:

$$\text{Ag}^0 + \text{Mo}^{6+} \rightleftharpoons \text{Ag}^{+} + \text{Mo}^{5+}$$

In the MDA reaction, Ma et al.$^{[13]}$ reported that, Mo$^{6+}$ species are partially reduced during the induction period. They showed that during the induction period, reduction of Mo$^{6+}$ to Mo$^{5+}$ and Mo$^{4+}$ takes place. Since Mo$^{6+}$ species are reduced into Mo$_2$C, which has been proposed as an active phase of MDA, then if the process of reduction of molybdenum could be accelerated, then the activity of the catalyst at the early stages of reaction could possibly be enhanced. Consequently the addition of silver as a promoter on redox properties to the standard MDA catalyst was carried out.
4.4.1 Reaction data

Figure 4.4-1 shows the hydrogen formation rate versus time on stream for the silver doped 3%MoO$_3$/H-ZSM-5 catalyst, the profile for the standard catalyst, 3%MoO$_3$/H-ZSM-5, is given for comparison. It should be noted that the ZSM-5 employed in this study was prepared using a ZSM-5 (Catal) zeolite with a Si/Al of 40:1. The hydrogen produced for the two catalysts is very similar, although initially the silver doped catalyst clearly produces more hydrogen. It appears that the induction period is similar for the two catalysts. Overall there appears to be no significant promotional effect on hydrogen formation when silver is doped onto the standard 3%MoO$_3$/H-ZSM-5 catalyst at longer times on stream.

Figure 4.4-1 Hydrogen formation rates as a function of time on stream for 3%MoO$_3$/H-ZSM-5 and Ag doped 3%MoO$_3$/H-ZSM-5.

Figure 4.4-2 gives the benzene formation rate for the Ag doped 3%MoO$_3$/H-ZSM-5 and standard 3%MoO$_3$/H-ZSM-5 catalysts. The silver doped catalyst has a noticeably greater benzene formation rate than the standard catalyst. Clearly doping silver onto the standard catalyst results in a prominent increase in the benzene production. Further investigations are required to help explain why the Ag doped 3%MoO$_3$/H-ZSM-5 catalyst exhibits a greater benzene formation compared to the standard catalyst.
Figure 4.4-2 Benzene formation rates as a function of time on stream for 3%MoO$_3$/H-ZSM-5 and Ag doped 3%MoO$_3$/H-ZSM-5.

Figure 4.4-3 shows the H$_2$:C$_6$H$_6$ formation rate ratio for Ag doped 3%MoO$_3$/H-ZSM-5 catalyst, the profile for the standard catalyst is also given. The lower ratio for the Ag doped 3%MoO$_3$/H-ZSM-5 catalyst (after ca. 50 minutes on stream) implies that the relative coke formation decreases compared to that of the standard catalyst. Therefore it appears that loading silver onto 3%MoO$_3$/H-ZSM-5 not only increases the benzene formation rate but also reduces the amount of coke produced compared to that of the standard catalyst.

Figure 4.4-3 The ratio of hydrogen to benzene formation rates for 3%MoO$_3$/H-ZSM-5 and Ag doped 3%MoO$_3$/H-ZSM-5.
4.4.2 XRD Patterns of 3%Mo-Ag/H-ZSM-5

The XRD patterns of 3%Mo-Ag/H-ZSM-5 in the fresh/calcined and post reaction form are shown in Figure 4.4-4. The patterns of 3%Mo-Ag/H-ZSM-5 in both states are similar. In both patterns there are no isolated molybdenum or silver species i.e. only the H-ZSM-5 phase is observed. This suggests that the Mo/Ag species are finely dispersed on the surface or locate in the channels of the H-ZSM-5 zeolite.

As the silver was added to the ready prepared MoO$_3$/H-ZSM-5 catalyst, it is difficult to say if silver interacts with any molybdenum containing phases, or if it forms an isolated phase having a more indirect effect. As the XRD patterns only show reflections indicative of the zeolite, it is not possible to verify any active phases of the Ag doped 3%MoO$_3$/H-ZSM-5 catalyst.

![Figure 4.4-4 XRD pattern of calcined and post reaction Ag doped 3%MoO$_3$/H-ZSM-5.](image)
4.5 Summary

In this study, the effect of a number of different dopants on the activity of MoO$_3$/H-ZSM-5 dehydroaromatisation catalysts has been investigated. Promotional effects were observed for Fe$^{3+}$, Al$^{3+}$ and Ga$^{3+}$, the impregnation solutions of these dopants were all acidic. No promotional effect was seen for the Co$^{2+}$ and Ni$^{2+}$ doped catalysts, apart from an initial high conversion and burst of hydrogen at the beginning of the reaction. This work has been found to contradict previous observations, which claim Co$^{2+}$ doping of MoO$_3$/H-ZSM-5 does produce promotional effects. The use of an iron dopant leads to an increase in the benzene formation rate at longer times on stream, which again contradict previous observations, where the promotional effect was attributed to reduced coking, but as can be seen from this study the coking in fact increases upon iron addition. The use of an aluminium dopant leads to an increase in benzene formation rate, however there were reproducibility issues with this catalyst. Gallium doping was also found to have a beneficial effect, with an increase in methane conversion and reduced coking observed for this catalyst.

In all of the doped catalysts, the molybdenum and dopant metal were found to be highly dispersed, as only reflections indicative of the ZSM-5 framework are visible in the XRD patterns. TEM images of both Fe and Al doped catalysts reveal that some of the carbonaceous deposition on these catalysts is in the form of carbon nanotubes.

NH$_3$-TPD experiments carried out on the Fe and Al doped catalysts indicate that in both cases the amount of Bronsted acid sites has been altered when compared to the standard catalyst. In the case of Fe doping, the amount of Bronsted acid sites has been lowered compared to that of the standard catalyst, however, Al doping appears to replace some of the lost Bronsted acid sites that occurs when Mo is loaded onto H-ZSM-5.

$^{27}$Al MAS NMR of the Fe$^{3+}$ doped MoO$_3$/H-ZSM-5 catalyst reveals this catalyst has a greater degree of non-framework Al than the standard catalyst. Thus doping with iron causes an increase in the extractability of framework Al compared to that of the standard catalyst. $^{29}$Si MAS NMR of the Al$^{3+}$ and Fe$^{3+}$ doped 3%MoO$_3$/H-ZSM-5 catalyst shows that the framework ratio of Si/Al increases when Al$^{3+}$ or Fe$^{3+}$ is added to the standard catalyst. Since both Fe$^{3+}$ and Al$^{3+}$ doped MoO$_3$/H-ZSM-5 catalysts were prepared by acidic impregnation it appears that catalysts prepared by acidic impregnation cause an increase in the framework Si/Al ratio of MoO$_3$/H-ZSM-5.
The co-impregnation of phosphorus and molybdenum through impregnation using a phosphomolybdic-acid precursor leads to a catalyst of lowered catalytic activity. In that the observed hydrogen to benzene formation rate ratio is increased, which has been attributed to enhanced coking.

Catalysts prepared using both silicomolybdic acid and sodium molybdate as the molybdenum precursors have been shown to have very poor activity as methane aromatisation catalysts.

Doping the standard catalyst, 3%MoO\textsubscript{3}/H-ZSM-5, with silver was seen to increase the benzene formation rate and reduce the coke formation compared to the standard catalyst.
5 Phosphorus doping of MoO$_3$/H-ZSM-5 and the preparation of phosphide catalysts

5.1 Introduction

5.1.1 Phosphorus doping of MoO$_3$/H-ZSM-5

As was shown in Chapter 4, very low levels of phosphorus addition in the form of a phosphomolybdic acid precursor leads to lower catalytic activity. At that level of phosphorus addition, benzene is suppressed with respect to hydrogen, so it may be expected that at higher levels of P addition benzene may be fully eliminated while hydrogen production is maintained. In this Chapter the effect of higher loadings of phosphorus doping on the activity of MoO$_3$/H-ZSM-5 based dehydroaromatization catalysts has been investigated. In the study in Chapter 4, phosphorus was incorporated simultaneously with the molybdenum component. In this chapter, phosphorus has been added via impregnation using ammonium dihydrogen phosphate to the ready prepared MoO$_3$/H-ZSM-5 catalyst precursor.

From reviewing the literature, it is clear that the addition of phosphorus in different dehydroaromatization catalysts has been shown to cause different effects dependent upon its form. For example, when phosphate is added as a framework species in the zeolite host, it has been reported to enhance the production of aromatics $^{[132,133]}$. In this work, Shu et al. reported that high calcination temperature and high molybdenum loading enhanced the replacement of framework silicon atoms by phosphorus atoms, which subsequently lead to altering the environment of the aluminium nuclei in the zeolite framework, resulting in a modification of the acidic property of the catalyst. However, when added to MoO$_3$/H-ZSM-5 as a dopant via impregnation with phosphoric acid, it was shown to lower but not eliminate the benzene production $^{[35]}$. In that work, Chen et al. reported that the decrease in catalytic activity was due to poisoning effects. They suggested that phosphorus modification of MoO$_3$/H-ZSM-5 decreased the acidity of the catalyst. Elsewhere, it has been reported that phosphorus modification of MoO$_3$ enhances acidity $^{[125]}$. 
5.2 Results and discussion – phosphorus dopant study

5.2.1 Reaction data

Figure 5.2.1-2 displays the hydrogen formation rate against time on stream for a 5wt.%P/5%wt. MoO3/H-ZSM-5 catalyst. The results for the non-doped standard catalyst, 5%MoO3/H-ZSM-5 are also given for comparison in Figure 5.2.1-1. At this level of phosphorus addition, benzene formation was completely suppressed. As can be seen from Figure 5.2.1-2 initially there was a very low level of hydrogen production for this catalyst. However, the hydrogen production was found to increase gradually with time on stream.

To evaluate the maximum hydrogen production for this catalyst it was tested over a longer run time. The hydrogen production was found to pass through a maximum, which corresponds to >5% of the exit product stream at about 510 min on stream. Off-line gas-phase FTIR analysis of the effluent indicated that only very small traces of carbon oxides were formed during reaction. However, past this maximum traces of benzene and higher hydrocarbons could be seen from the gc analysis, but these were present in concentrations estimated to be < 0.02%. This is a very interesting observation in that it could possibly indicate a potential CO-free route to hydrogen. This maximum in hydrogen formation was associated with the emergence of a pungent-smelling orange deposit from the catalyst on the reactor wall. Dr. David Rycroft, University of Glasgow, kindly analysed this solid following dissolution in DCM (dichloromethane), using 31P NMR, it was found to be a phosphite. In addition, the absence of any signals in the 13C NMR spectrum confirmed it to be an inorganic phosphite.

Subsequently, a 5%P/H-ZSM-5 sample was prepared and tested under the same conditions as those used for the 5%P5%MoO3/H-ZSM-5 catalyst. It was found that no benzene or hydrogen was produced at all in this case. Therefore, the inclusion of molybdenum is crucial for this behaviour. It should also be noted that the parent ZSM-5 material was tested and that hydrogen was produced for this material, albeit at very low quantities, as shown in Figure 5.2.1-2. Therefore, doping phosphorus on ZSM-5 hinders any hydrogen formation that is produced for the parent zeolite alone.
The XRD patterns of both the calcined/fresh and post reaction 5wt.%P/5wt.%MoO$_3$/H-ZSM-5 materials are shown in Figure 5.2.1-3. In both patterns, reflections of H-ZSM-5 are visible. However, there is no evidence for any other phase other than H-ZSM-5. This suggests that any molybdenum and/or phosphorus containing species are either highly dispersed and/or amorphous. Therefore, it is difficult to say if binary phases are formed, if there are additive effects on activity between isolated Mo and P containing phases or if the addition of the phosphorus dopant is having an effect on the dispersion or distribution of the molybdenum containing species.
These results led on to the investigation of a 5wt.% P doped bulk MoO₃ sample. The results for this material are shown in Figure 5.2.1-4. It can be seen, that in terms of the production of hydrogen, the overall activity pattern with time on stream appears similar to that reported in Figure 5.2.1-2, which may imply a similar formation route. However, unlike the zeolite system, the burst in hydrogen formation rate was found to be associated with simultaneous bursts of CO and CO₂ as determined by of-line FTIR analysis of the reactor effluent gas. Moreover, an inorganic phosphite phase was not evolved for this system.
5.2.2 XRD patterns

Figure 5.2.2-1 and Figure 5.2.2-2 show the XRD patterns of the bulk 5%P/MoO₃ material in the calcined form and following reaction. The patterns were checked using the database of the Joint Committee on Powder Diffraction Standards (JCPDS). Prior to reaction the bulk P/MoO₃ material can be indexed to molybdenum trioxide, with no reflections indicative of any P containing phases visible. Following reaction, the bulk P/MoO₃ material can be indexed to a mixture of molybdenum phosphide and eta-molybdenum carbide phases. This suggests that the evolution of hydrogen and carbon oxides as shown in Figure 5.2.1-4, is associated with the carbiding and/or phosphiding of the MoO₃ component, i.e. oxygen from the molybdenum oxide is removed as CO and CO₂. Water is also likely to be produced however the set up used is not optimised to analyse this product. However, the carbide formed in Figure 5.2.2-2 is not the usual β-Mo₂C phase, which is expected. For example, when Choi et al. [134], prepared a series of molybdenum carbides by the temperature-programmed carburisation of bulk MoO₃ with pure methane, the resultant carbide was in the β-Mo₂C phase.
Figure 5.2.2-1 XRD pattern of calcined bulk 5%P/MoO$_3$.

Figure 5.2.2-2 XRD pattern of 5%P/MoO$_3$ following carburisation.
From reviewing the literature, there appears to be very few studies regarding the isothermal carbiding of MoO$_3$ with methane. Most studies have followed the process using temperature-programmed routes with H$_2$/CH$_4$ mixtures, e.g. \cite{72,74}. Using temperature programming, Xiao et al. reported a complete phase transition of MoO$_3$ to molybdenum carbide, in which the carbide produced has mainly the hcp structure, i.e. the $\beta$-Mo$_2$C phase. They reported that the phase transition of molybdenum oxide to molybdenum carbide is topotactic.

The nature of the phase transition with time on stream shown in Figure 5.2.1-4 is consistent with reports that the isothermal reduction of the bulk MoO$_3$ phase involves an induction period which has been ascribed to rate-determining nucleation or autocatalytic effects \cite{75}. Lacheen and Iglesia \cite{71} have reported that the carburisation process in MoO$_3$/$\text{H-ZSM-5}$ methane aromatisation catalysts is autocatalytic, with intermediate olefins being formed which enhance the rate of carburisation.

Due to the similarity of the general evolution/burst of hydrogen between 5\%P/5\%MoO$_3$/H-ZSM-5 and 5\%P/MoO$_3$ it may seem credible that the formation of hydrogen is due to carbiding or phosphiding in the case of 5\%P5\%MoO$_3$/H-ZSM-5. However the lack of carbon oxides throws uncertainty over this suggestion. An additional feature, which requires thought, is the evolution of the phosphite co-product. Its formation requires the reduction of phosphate, which would result in an oxidised co-product. Whilst this may be water, the alternative of an oxidised organic product being formed by, e.g., a Mars-van Krevelen type process, which has not been detected, cannot be discounted.

### 5.2.3 NH$_3$-TPD Profiles

In view of the previous literature, NH$_3$-TPD measurements have been conducted to examine the effect which phosphorus has on the acidity of the catalyst. Changes in acidity between the two catalysts may help explain the differences in their catalytic activity. The NH$_3$-TPD profile of the 5\%P5\%MoO$_3$/H-ZSM-5 catalyst is shown in Figure 5.2.3-1. The profile for the 5\%MoO$_3$/H-ZSM-5 catalyst is also given for comparison (the TPD profiles were deconvoluted by the Gaussian curve fitting method and numerical data of the fittings are listed in Table 5.2.3-1). It should be noted that in these experiments, the thermocouple at the catalyst bed, was not linked/connected to the mass spectrometer, the temperature was recorded manually. Ideally, it is best if the thermocouple is linked to the mass spectrometer, as more data points would be recorded in this way and thus the profiles would be more precise.
Figure 5.2.3-1 NH₃-TPD profile (ramp rate 15°C/min) of (a) 5%MoO₃/H-ZSM-5 (b) 5%P5%MoO₃/H-ZSM-5, the deconvoluted curves are also shown.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Peak position (°C)</th>
<th>Peak area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T₁</td>
<td>T₂</td>
</tr>
<tr>
<td>5%MoO₃/H-ZSM-5</td>
<td>151</td>
<td>232</td>
</tr>
<tr>
<td>5%P5%MoO₃/H-ZSM-5</td>
<td>190</td>
<td>268</td>
</tr>
</tbody>
</table>

Table 5.2.3-1 Numerical results of the NH₃-TPD profiles by the Gaussian curve fitting method.

As mentioned in Chapter 4, the temperature of an NH₃-TPD peak can be used as a rough measure of the acid strength of the sorption site. It can be seen that there is a decrease in the temperature of the peak maximum of the strongest acid site, A₃ i.e. Bronsted acid site, when P is loaded onto 5%MoO₃/H-ZSM-5.

The relative area of A₃ upon incorporation of phosphorus into 5%MoO₃/H-ZSM-5 is roughly the same as it is for the undoped 5%MoO₃/H-ZSM-5 catalyst, while the relative area of A₂ is enhanced with respect to that of A₁ upon P addition to the 5%MoO₃/H-ZSM-5 catalyst.

The low temperature peak, A₁, may be ascribed to physisorbed ammonia or ammonia bonded to Si-OH groups. Whereas, the ascription of the moderate temperature peak, A₂, is not clear, it may be ascribed to ammonia desorbed on extra-framework Al or it may be due to the ammonia adsorbed on a new type of acid site that was created by the interaction between Mo and possibly also P species with the strongest acid sites.
There is an increase in the desorption temperature maxima of A₁ and A₂, indicating that P modification of 5%MoO₃/H-ZSM-5 increases the strength of both A₁ and A₂ interactions. The increase in the relative area of A₂, if this peak is due to extra-framework Al, suggests that modification of MoO₃/H-ZSM-5 with phosphorus actually increases the extractability of framework Al of the catalyst.

Chen et al.²⁵ have reported that phosphorus addition to Mo/H-ZSM-5 catalysts results in a decrease in the ammonia uptake of the catalyst. Consistent with the observations reported here, they also reported that the maximum desorption temperature decreased upon phosphorus modification, suggesting a decrease in the acidity of the catalyst upon P modification.

### 5.2.4 Post reaction carbon and TGA analysis

The post-reaction carbon analysis and TGA profiles of the 5%P5%MoO₃/H-ZSM-5, 5%P/MoO₃ and 5%P/H-ZSM-5 materials are given in Table 5.2.4-1 and Figure 5.2.4-1 to Figure 5.2.4-3 respectively. It should be noted that these materials were not on stream for the same length of time, therefore, direct comparisons of the degree of coking should not be made between them. As discussed in Chapter 3, if the stoichiometry of the molybdenum-containing phase is assumed as Mo₂C, as it is often proposed in the literature, e.g. ³³ then the amount of contribution of carbidic carbon can be calculated. For the 5%P5%MoO₃/H-ZSM-5 sample, from the table it is apparent that the overall carbon content is close to that which would be expected if indeed the Mo₂C phase formed. However from this we cannot confirm that it is in fact formed, although future studies using EXAFS experiments may help clarify this.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%C</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%P5%MoO₃/HZSM-5</td>
<td>0.22</td>
</tr>
<tr>
<td>5%P/HZSM-5</td>
<td>0.24</td>
</tr>
<tr>
<td>5%P/MoO₃</td>
<td>5.71</td>
</tr>
<tr>
<td>5%MoO₃/HZSM-5</td>
<td>5.70</td>
</tr>
</tbody>
</table>

Table 5.2.4-1 Carbon analysis of post-reactor materials.

Figure 5.2.4-1 and Figure 5.2.4-2 display the TGA profiles for the post reaction 5%MoO₃/H-ZSM-5 and 5%P5%MoO₃/H-ZSM-5 catalysts. The TGA profiles are assigned as described in previous chapters. It can be seen in Figure 5.2.4-1 that the shape of the
weight loss profiles of the two catalysts are relatively similar, however there is a greater weight loss for the undoped catalyst compared to the P doped catalyst. The first derivative weight changes are also given for the post reaction catalysts, Figure 5.2.4-2. In this profile, we can see that for the standard catalyst, 5%MoO$_3$/H-ZSM-5, that there are two weight loss regions i.e. low and high temperature combustion of carbon, at ca. 450 and 550°C respectively. However, for the P modified catalyst, there is only one region where there is a weight loss, in this region the weight loss is ca. 4%. All of this weight loss is not due to burnt off carbon alone as the post reaction carbon analysis results show that only 0.22% of the catalyst after the reaction is carbon, therefore this higher value of weight loss can be attributed to the burning off of both carbon and phosphorus.

Figure 5.2.4-1 TGA profiles for the post reaction 5%MoO$_3$/H-ZSM-5 and 5%P5%MoO$_3$/H-ZSM-5 catalysts.

Figure 5.2.4-2 TGA profiles for the post reaction 5%MoO$_3$/H-ZSM-5 and 5%P5%MoO$_3$/H-ZSM-5 catalysts.
Figure 5.2.4-3 displays the TGA profile after the isothermal carburisation of 5%P/MoO₃ at the reaction conditions employed in Figure 5.2.1-4. The increase in weight is due to the oxidation of the molybdenum carbide and/or molybdenum phosphide into molybdenum oxide. The decrease in weight after ca. 750°C is likely to be due to the sublimation of MoO₃.

![TGA profile after the isothermal carburisation of 5%P/MoO₃ at the reaction conditions employed in Figure 5.2.1-4.](image)

**Figure 5.2.4-3 TGA profile after the isothermal carburisation of 5%P/MoO₃ at the reaction conditions employed in Figure 5.2.1-4.**

### 5.3 Results and discussion – Molybdenum phosphide catalysts

There have been many methods reported for the preparation of phosphides [135]. The most frequent being combination of the elements (Equation 5-1), which can be carried out in various ways such as ampoule techniques and arc melting. Other routes include, reaction with phosphine (Equation 5-2) and reduction of phosphates with H₂ (Equation 5-3) [135].

\[
\begin{align*}
M^0 + xP^0_{(red)} & \rightarrow MP_x & \text{Equation 5-1} \\
MCl_x + PH_3 & \rightarrow MP + HCl + H_2 & \text{Equation 5-2} \\
MPO_4 + 4H_2 & \rightarrow MP + 4H_2O & \text{Equation 5-3}
\end{align*}
\]

For catalytic applications many preparation routes are impractical, due to the high temperatures required and the use of expensive starting materials or other species which can contaminate the phosphide are produced. The synthesis route of phosphides most
frequently used in catalytic systems is reduction of phosphates. In this process bulk or supported phosphides are produced by reduction of the phosphate precursors in a flow of hydrogen \[^{135-139}\].

Recently, much attention has been paid towards transition metal phosphide catalysts as these types of materials have been found to be stable and sulfur resistant with a high performance in hydrodenitrogenation (HDN) and hydrodesulfurisation (HDS) \[^{136, 137}\]. Both HDS and HDN are very important industrial processes, which aim to improve the quality of rapidly declining feedstocks and meet increasingly strict environmental regulations. Transition metal phosphides may be the next generation of hydroprocessing catalysts.

The main binary transition metal phosphides, which have recently been synthesised to be tested as hydroprocessing catalysts are MoP, Ni\(_2\)P, WP and CoP. Ternary phosphides such as NiMoP and CoMoP have also been synthesised and tested as hydroprocessing catalysts \[^{138}\]. Prins and co-workers have recently shown that the intrinsic HDN activity of surface Mo atoms of MoP is 6 times higher than that of the conventional supported MoS\(_2\) catalyst \[^{137}\].

From reviewing the literature there does not appear to be any publications regarding the preparation of phosphides from phosphates via reduction in methane as opposed to hydrogen. It appears that the method reported here has not been investigated before. It potentially permits for a more economic method of getting to the phosphide without using hydrogen to pre-reduce the sample. It should be noted that the hydrogen required to produce the phosphides is synthesised from methane anyhow (steam reforming of methane is the main route of hydrogen production). The advantage of using methane to reduce the phosphate as opposed to hydrogen is that hydrogen is produced in the former as shown in section 5.3.2.

Stuart Hunter (University of Glasgow, 4th year project student) kindly assisted with some of the phosphide work presented in this chapter.
5.3.1 XRD Patterns

Following on from section 5.2.2, where it was shown that the isothermal carburisation of 5%P/MoO$_3$ using methane produces a mixed phase of molybdenum phosphide and molybdenum carbide, the preparation of molybdenum phosphide catalysts using methane has been examined. The preparation of nickel phosphide using methane as the reducing agent has also been investigated. Nickel phosphide is also of interest as a potential hydoprocesing catalyst. The preparation of phosphides using methane (and hydrocarbons in general) as the reductant has previously not been reported.

The materials discussed in this section were prepared using the precursors and procedures outlined in Chapter 2. The phosphide precursors were prepared by a similar method to that reported by Green and co-workers\cite{136}. Essentially, the molybdenum phosphide and nickel phosphide precursor materials were prepared by using a 1:1 and 2:1 molar ratio of MoO$_3$ or NiO to NH$_4$H$_2$PO$_4$ (Aldrich, 98+%) for molybdenum phosphide and nickel phosphide respectively. The required amount of NH$_4$H$_2$PO$_4$ was dissolved in ca. 15ml of deionised water and was impregnated onto MoO$_3$ or NiO for the preparation of the MoP or NiP precursors respectively, followed by drying at 100°C overnight and then calcined in air at 500°C for 5 hours.

The phosphide precursors were then reacted with methane at 750°C (as described in the experimental section). The resultant XRD patterns of the materials after reaction with methane were checked using the database of the Joint Committee on Powder Diffraction Standards (JCPDS).

The XRD pattern of the synthesised molybdenum phosphide is given in Figure 5.3.1-1, the pattern reveals that the phosphate precursor material following its reduction in methane is transformed into molybdenum phosphide. The pattern shows that the material is very crystalline with little amorphous material. The XRD pattern of MoP shows reflections at 28.0, 32.2, 43.2, 57.3, 64.9, 67.4 and 74.0°20.
This pattern agrees very well with the reference pattern of MoP, (PDF 24-0771) and the recent report by Green and co-workers \[136\]. Molybdenum phosphide crystallises in the form of the hexagonal tungsten carbide structure (WC) \[139\]. The surface area of the MoP in Figure 5.3.1-1, as determined by N\textsubscript{2} adsorption, is 15 m\textsuperscript{2}g\textsuperscript{-1} which compares favourably to the 2 m\textsuperscript{2}g\textsuperscript{-1} reported by Prins and co-workers for their synthesised MoP, which was prepared via reducing the metal oxide/phosphate precursors in a flow of H\textsubscript{2} \[138\].

From Figure 5.3.1-1 it has been shown that molybdenum phosphide can be synthesised through the in-situ reduction under methane at 750°C from the doped metal oxide phosphate, to yield the XRD pattern shown. Typically, it has been reported that when phosphides are produced via the reduction of phosphates, hydrogen is used as the reducing agent \[135-139\].

The XRD pattern given in Figure 5.3.1-2 was yielded after the reduction under methane at 750°C of a mixture of nickel oxide and ammonium dihydrogen phosphate. This material was prepared using a Ni:P ratio of 2:1.
The pattern shows that a nickel phosphide with a Ni$_{12}$P$_5$ stoichiometry has been produced (PDF 22-1190), all the main reflections indicative of this phase are visible, i.e. 38.3, 41.6, 44.4, 46.9 and 48.9°2θ. However, there are some low angle reflections indicative of nickel phosphate (PDF 19-0835), this implies that the material yielded is not a pure phosphide. It should be noted that the “bump” in the baseline at ca. 35°2θ is not a true feature/reflection of the sample, its occurrence is due to a fault in the XRD equipment.

The material produced in Figure 5.3.1-2 was not the expected phosphide phase. Based on the work by Green and co-workers it was expected that the phosphide would have the Ni$_2$P stoichiometry as opposed to Ni$_{12}$P$_5$. It is possible that the Ni$_2$P phase was not produced, as some loss of P may have occurred.

The preparation of ternary transition metal phosphides via the corresponding metal phosphates using methane as the reducing agent, as opposed to hydrogen has also been investigated. It was hoped that NiMoP, FeMoP and CoMoP could all be prepared by this way. The precursor materials consisted of a 1:1:1 molar ratio of Ni/Fe/Co:Mo:P. In the preparation of the ternary phosphides the first step involved impregnation of the 2nd metal nitrates i.e cobalt, nickel or iron onto molybdenum trioxide, followed by calcination and then impregnation with ammonium dihydrogen phosphate followed by calcination. The XRD patterns given in Figure 5.3.1-3 were yielded after the reduction of the precursor materials in methane at 750°C.
The XRD patterns of the NiMoP, CoMoP and FeMoP materials all consist of mixed phases. All materials exhibit reflections indicative of MoP, i.e. 32.2, 44.2, and 53.7°2θ. The NiMoP and CoMoP materials both have an intense reflection at 39.7°2θ, which is indicative of Mo2C. They also have reflections indicative of Ni2P (PDF 03-0953) and Co2P (PDF 06-0595) for the NiMoP and CoMoP materials respectively.

The FeMoP material produced a mixed carbide phase. Reflections indicative of Fe2MoC (PDF 17-0911) are visible, with main 2θ values of 39.6, 43.2 and 57.5°. This material also consisted of phases indicative of Fe2P (PDF 33-0670).

In the case of the binary phosphides i.e. MoP, it has been shown that the in-situ reduction of phosphates to phosphides is successful when methane is used as the reducing agent at 750°C. In view of this, it was hoped that phosphides could be prepared from phosphates using a more reactive hydrocarbon source such as, propane or propene, as the reducing agent. If a more reactive hydrocarbon is employed as the reducing agent it may allow for the temperature of reduction to be lowered, in turn facilitating preparation of high surface area phosphides, which could be a technologically important route to phosphide catalysts.

Therefore, the initial stage of this study was to attempt to prepare a phosphide using the same precursor materials and reduction temperature (750°C) as that used for the MoP material prepared by reduction of the phosphate under methane as shown in Figure 5.3.1-1, however with propane being employed as the reducing agent rather than methane. It
should be noted that both methane and propane reactions were carried out for the same length of time on stream (i.e. 390 min).

The resultant XRD pattern when using propane as a reductant at 750°C, is shown in Figure 5.3.1-4. The pattern has an amorphous appearance, although it does exhibit reflections indicative of MoP, i.e. 32.2, 43.2, 57.3, 64.9 and 76.4 °2θ. When comparing Figure 5.3.1-4 with Figure 5.3.1-1 it is clear to see that the MoP material prepared using propane has less intense peaks, this is an indication that the material is less crystalline, than when methane is used as a reductant.

An attempt to prepare molybdenum phosphide using an alkene (propene) rather than an alkane as the reducing agent, was also investigated. The resultant XRD pattern is shown in Figure 5.3.1-5. There are no reflections indicating that MoP has been produced. There are reflections, although not very intense, which can be indexed to molybdenum (IV) oxide, MoO₂. This implies that under the reducing conditions employed, MoP cannot be prepared from reduction of the corresponding phosphate under propene. It is, however, possible that amorphous MoP has been prepared using the propene as the reductant.

![Figure 5.3.1-4 XRD pattern of a mixture of molybdenum oxide and ammonium dihydrogen phosphate reduced at 750°C under propane.](image-url)
5.3.2 Reaction data

The hydrogen and carbon oxides formed during the synthesis of the phosphide materials are presented in Figure 5.3.2-1 to Figure 5.3.2-5. The evolution of the hydrogen and carbon oxides is associated with the phase transition.

It can be seen in Figure 5.3.2-1 that the products formed during the transformation to the molybdenum phosphide phase all undergo a similar shape in their formation rate profile, with the maximum in formation of products at ca. 200 min on stream. At the maximum in formation of products 15 times more CO is produced compared to CO₂. Carbon oxides still being evolved when the reaction is stopped indicates an incomplete transformation, yet a good quality diffraction pattern was obtained and this sounds caution for sole reliance on diffraction pattern as an indication of total phase transformation.

The profile for the products formed during the transformation to the nickel phosphide is shown in Figure 5.3.2-2. It can be seen that the maximum in the formation of products is seen at a shorter time on stream for the synthesis of nickel phosphide compared to molybdenum phosphide. This result is somewhat similar to the one reported in Chapter 4, where a Ni doped MoO₃/H-ZSM-5 catalyst displayed a similar burst of hydrogen formation at the beginning of the reaction when methane was flowed over the catalyst at high temperature. It appears that the nickel phosphide is produced faster than the molybdenum phosphide.
Although the maximum in the formation of products comes at an earlier time on stream for the synthesis of the nickel phosphide catalyst compared to the synthesis of the molybdenum phosphide catalyst, in the reduction of the NiMoP precursor material, Figure 5.3.2-3, nickel actually delayed the burst in hydrogen formation until longer times on stream compared to the MoP catalyst. It can be seen that in some respects the profile for this mixed phase looks like the profiles in Figure 5.3.2-1 and Figure 5.3.2-2 added together.
The maximum in hydrogen and carbon oxide formation in the reduction of the FeMoP precursor material, Figure 5.3.2-4, comes around the same time for that of the MoP material. It is unfortunate that there are only a few data points in Figure 5.3.2-4, it would be better if more points were taken for a more accurate analysis of the phase transformation.
Figure 5.3.2-5 gives the formation rates of products formed during the reduction of the CoMoP precursor material. It can be seen that the maximum hydrogen production comes around the same time as it did for the MoP material. The addition of cobalt to the precursor material results in a burst of hydrogen formation at the beginning of the reduction process. Again this is similar to results reported in Chapter 4, where addition of a divalent metal, results in a burst of hydrogen at early times on stream.

Generally, it can be seen from Figure 5.3.2-1 to Figure 5.3.2-5, that there is a critical stage of the reaction that results in a “burst” of activity. This burst in activity is associated with the transformation of the phosphate to phosphide and its appearance with time on stream varies depending on the precursor material employed i.e. the burst in activity is seen at ca. 200 min in the preparation of MoP compared to ca. 50 min for the preparation of Ni12P5.

It is interesting to note that in the preparation of these phosphides and mixed phosphide materials via reduction of the corresponding phosphates in methane, CO is the major product of the reaction, with only low levels of CO2 being observed and the H2 formation rate being lower than the CO formation rate. In the isothermal carburisation of 5%P/MoO3, where a mixed phase of molybdenum phosphide and molybdenum carbide is produced, H2 is the major product of the transformation, with the formation rate of CO being lower than that of H2, Figure 5.2.1-4. Therefore, these results demonstrate that the...
product distribution of CO to H₂ can vary depending upon the amount of phosphorus in the starting material compared to molybdenum, i.e. 5%P loaded onto MoO₃ gives different product distributions of CO to H₂ when reduced under methane, compared to when the molar ratio of Mo:P is 1:1. It is a noteworthy observation that the formation of CO has not completely ceased by the end of each synthesis, although by this stage the hydrogen production has peaked and decreased. This along with Figure 5.3.1-1 suggests incomplete reduction, which is associated with a well defined diffraction pattern. It is interesting to note that incomplete phase transformations have been proposed in other catalytic and solid-state systems. For example, some “nitrides” may be more correctly described as oxynitrides.[140]

It was shown in Chapter 3 that the hydrogen formation rate is greater than the CO formation rate in the isothermal carburisation of MoO₃ to molybdenum carbide, whereas in this chapter, it has been shown that the CO formation rate is greater than the H₂ formation rate during the preparation of MoP using methane as the reductant. Therefore it has been shown that the product distribution of H₂ to CO is different in phosphiding as it is in carbidng of molybdenum using methane at high temperatures.

The general observations reported in this work are interesting in that methane may be utilised as a reductant for phosphide synthesis yielding CO and H₂ as significant reaction products. Studies on the preparation of phosphides via reduction of phosphates using more reactive hydrocarbons i.e. propane and propene, as the reducing agents have proved more difficult.
5.4 Summary

In this study, higher levels of phosphorus doping of MoO$_3$/H-ZSM-5 catalysts have been investigated. It was shown that when 5wt.% phosphorus (in the form of ammonium dihydrogen phosphate) was doped onto 5%MoO$_3$/H-ZSM-5, initially hydrocarbon formation was completely suppressed and hydrogen was the sole gas phase product. Although the hydrogen formation rate is low, it increased throughout the run and reached a maximum of >5% of the exit stream concentration. The appearance of this maximum is associated with the evolution of an inorganic phosphite phase from the catalyst. The decrease in hydrogen formation from this maximum is associated with the production of trace levels of benzene (<0.02%) and carbon oxides. Further studies on 5%P/MoO$_3$ showed that this material exhibits a similar pattern of hydrogen evolution. But, in this case, carbon oxides are formed in greater quantities and the relative ratios of the products are similar to recent reports of the carburisation of oxomolybdenum ZSM-5 catalysts, although the timescales are much greater.

This chapter has also reported a novel method for the production of phosphides from the corresponding phosphate doped oxide through reduction using methane. The gas phase products evolved during the transformation process demonstrate that CO and H$_2$ are major components, indicating the involvement of secondary reactions pathways in the process. In addition, CO is still evolved at the end of the synthesis which coupled with powder diffraction patterns, illustrates that good quality diffraction patterns can be obtained with materials where the transformation is not totally complete.

In the production of high surface area carbides and nitrides, phase transformations are carried out using high flow rates of the corresponding reductants applying controlled low temperature ramp rates. These considerations are important for the generation of high surface area materials. The high flow rates result in low partial pressure of water being produced in the transformation, minimising hydrothermal sintering. By analogy, it can be considered that high methane space velocities and controlled temperature ramp rates could yield very high surface area phosphides, which is an area of current significant interest.

Studies on the preparation of phosphides via reduction of phosphates using more reactive hydrocarbons i.e. propane and propene, as the reducing agents were met with less success. Future studies could try and prepare phosphides using these gases but using a lower temperature with longer times on stream.
From reviewing the literature, it does not appear that this method of phosphide preparation has been carried out before. Generally, for catalysis applications, it has been reported that phosphides are prepared via reduction of phosphates under a hydrogen flow. The advantage of the method shown in this work is that, along with producing the phosphide, hydrogen is also produced.
6 Hydrogen scavenging study

6.1 Introduction – LTA study

Zeolite A exhibits the LTA (Linde type A) structure, Figure 6.1-1. This zeolite has a 3-dimensional pore structure with pores running perpendicular to each other in the x, y, and z planes, and is made up of secondary building units. The pore diameter is defined by an eight-membered oxygen ring and is small at 4.1 Å. This leads into a larger cavity of 11.4 Å in diameter. This cavity is surrounded by eight sodalite cages, which are connected by their square faces in a cubic structure.

![Figure 6.1-1 framework structure of LTA, Viewed along [100] taken from [141].](image)

Although the inner cavity of LTA is larger than the molecular diameter of benzene (5.9 Å), benzene cannot travel into the cavity due to the small pores. However, the small entry pores will permit hydrogen to travel into the cavity. Figure 6.1-2, taken from reference [141], shows the kinetic diameters for selected molecular species contrasted with the effective pore size of selected zeolites (the darker shadings in the figure indicate increases that accompany a temperature rise). It can be seen that H₂ is within the range to enter the pores of all the types of zeolites given in Figure 6.1-2. It should be noted that the pore size of zeolite A is different depending on the cation employed, the differences between potassium (3A), sodium (4A) and calcium (5A) zeolite A reflect the presence of non-framework cations in partially blocking window sites.
By incorporating a 50:50 mixture of 3%MoO$_3$/H-ZSM-5 with a reducible cation dispersed within the pore structure of H-LTA as a catalyst in a methane aromatisation reaction run, it could be expected that the transition metal exchanged LTA zeolite, with its small pore dimensions, may act as a hydrogen storage vessel as it could capture the hydrogen that is produced from methane reacting with the standard methane aromatisation catalyst. As a result of the LTA component capturing the hydrogen produced from the methane dehydroaromatisation reaction, the product distribution could possibly move towards benzene as the main product were the reaction catalysed to equilibrium. This possibility is dependent upon the LTA system being inert with respect to reaction with methane. However, as shown in Figure 6.1-2 the pore size of zeolite A and molecular diameter of methane are close.

As previously mentioned in the Chapter 1, the MDA reaction is equilibrium limited with the limit of conversion being 11.5% at atmospheric pressure and 700°C [25]. The MDA reactions presented in this project using MoO$_3$/H-ZSM-5 based catalysts have a maximum methane conversion of ca. 6% then the conversion declines to ca. 3% for the remaining time the catalysts are kept on stream. Thus the experiments shown in this work do not reach equilibrium conversions, but the effects of selective H$_2$ removal are still worthy of investigation.

![Figure 6.1-2 Kinetic diameter of selected molecular species contrasted with the pore size of some zeolites, taken from[141].](image)
6.2 Results and discussion – LTA study

6.2.1 Reaction data

The hydrogen formation rate for a physical mixture of 3%MoO$_3$/H-ZSM-5 and Ni(II)/H-LTA is given in Figure 6.2-1. The hydrogen formation rate for the standard catalyst, 3%MoO$_3$/H-ZSM-5 is also given for comparison. It should be noted that the formation rates in this chapter are calculated based on the total mass employed i.e. the hydrogen formation rate is based on the total mass of the combined bed. As can be seen from Figure 6.2-1 the hydrogen production is greater for the combined catalyst than it is for the standard catalyst, 3%MoO$_3$/H-ZSM-5.

It can be seen that for this combined material that there is a burst in hydrogen at the beginning of the reaction. This is most likely due to the Ni$^{2+}$ feature of the LTA catalyst, which is being reduced. To investigate this further, the activity of Ni(II)/H-LTA was investigated (Figure 6.2-1). As can be seen, there is also a burst in hydrogen formation at the beginning of the reaction, which is associated with the reduction of Ni$^{2+}$. Aside from the initial burst in hydrogen formation, the standard catalyst, 3%MoO$_3$/H-ZSM-5 is more active for hydrogen formation than the Ni(II)/H-LTA catalyst.

![Figure 6.2-1 Hydrogen formation rate as a function of time on stream for 3%MoO$_3$/H-ZSM-5, Ni(II)/H-LTA and 3%MoO$_3$/H-ZSM-5 and Ni(II)/H-LTA combined.](image-url)
The benzene formation rate for the physical mixture of 3%MoO$_3$/H-ZSM-5 and Ni(II)/H-LTA is given in Figure 6.2-2. The benzene formation rate for the standard catalyst, 3%MoO$_3$/H-ZSM-5 is also given for comparison. The benzene formation rate for the combined catalyst increases throughout the length of time it was on stream and did not reach its maximum in benzene formation during the time it was kept on stream. At ca. 225 minutes on stream its benzene formation was greater than that of the standard catalyst. It would be interesting to run this sample for a greater length of time to see where in fact benzene production would reach its maximum and where the catalyst would begin to deactivate. No benzene was detected for Ni(II)/H-LTA.

![Figure 6.2-2 Benzene formation rate as a function of time on stream for 3%MoO$_3$/H-ZSM-5 and 3%MoO$_3$/H-ZSM-5 and Ni(II)/H-LTA combined.](image)

The combined reaction bed of 3%MoO$_3$/H-ZSM-5 and Ni(II)/H-LTA, results in an increase in the hydrogen and benzene (at longer times on stream) formation rates compared to the standard methane aromatisation catalyst, 3%MoO$_3$/H-ZSM-5. It does not appear that using this combined catalyst, that the LTA system acts as a hydrogen trap, as more hydrogen was produced for the combined catalyst compared to that of the standard catalyst alone. One possible explanation for this may be that ethylene, which is commonly agreed to be the reactive intermediate in the MDA reaction [29], is produced by the MoO$_3$/ZSM-5 catalyst and then goes on to further react in the LTA system and a kinetic coupling effect occurs. Alternatively, a catalytically active form of carbon, which increases with time on stream, may be formed with the mixed-bed.
Therefore, due to the interesting results that combining MoO$_3$/H-ZSM-5 with Ni(II)/H-LTA gave, another transition metal containing LTA system was investigated, this time 3%MoO$_3$/H-ZSM-5 was combined with Fe(III)/H-LTA.

The hydrogen formation rate for a physical mixture of 3%MoO$_3$/H-ZSM-5 and Fe(III)/H-LTA is shown in Figure 6.2-3. The hydrogen formation rate for the standard catalyst, 3%MoO$_3$/H-ZSM-5 is also given for comparison. It can be seen that the combined catalyst has a much greater hydrogen formation rate than the 3%MoO$_3$/H-ZSM-5 catalyst alone. There appears to be an induction period in the hydrogen formation for the combined catalyst, and then the hydrogen formation increases gradually throughout the remaining time on stream. The combined catalyst did not reach its maximum in hydrogen production during the time it was tested.

To determine the hydrogen produced from only Fe(III)/H-LTA, this material was tested under the same conditions as that of the combined catalyst. Initially, no hydrogen was detected for this material then only trace amounts were detected after 200 minutes on stream.

![Figure 6.2-3 Hydrogen formation rate as a function of time on stream for 3%MoO$_3$/H-ZSM-5, Fe(III)/H-LTA and 3%MoO$_3$/H-ZSM-5 + Fe(III)/H-LTA combined.](image)

The benzene formation rate for the 3%MoO$_3$/H-ZSM-5 and Fe(III)/H-LTA combined catalyst is given in Figure 6.2-4. The combined catalyst has a considerably smaller
benzene formation rate compared to the standard catalyst alone, 3%MoO₃/H-ZSM-5. No benzene was detected for Fe(III)/H-LTA.

These combined catalysts appear to be behaving differently from each other. The 3%MoO₃/H-ZSM-5 and Ni(II)/H-LTA combined sample increases the hydrogen formation rate compared to the standard catalyst. Initially there is no benzene for the 3%MoO₃/H-ZSM-5 and Ni(II)/H-LTA combined sample then the benzene starts to increase throughout the time on stream. However, the 3%MoO₃/H-ZSM-5 and Fe(III)/H-LTA combined sample increases the hydrogen formation rate but decreases the benzene formation rate compared to the standard catalyst, 3%MoO₃/H-ZSM-5.

As already mentioned, it can be seen from Figure 6.1-2 that the pore size of zeolite A and the molecular diameter of methane are close. Furthermore, when taking into consideration the ionic radii of Ni²⁺ and Fe³⁺, which are as follows: 0.69 and 0.64 Å for 4 co-ordinated Ni²⁺ in tetrahedral and square planar geometry, 0.63, 0.69 and 0.79 Å for Fe³⁺ in 4 co-ordinated (high spin), 6 co-ordinate (low spin) and 6 co-ordinate (high spin) geometry, the pore mouth would be expected to be wider in the case of the transition metal exchanged zeolites, in comparison, the atomic radius of 6 co-ordinated Ca²⁺ is 1.14 Å. It may well be that the pore size of the Ni(II) and Fe(III)/H-LTA catalysts are in fact too large for selective H₂ scavenging.
Due to the promotional effects in terms of an increase in both hydrogen and benzene formation for the Ni(II)/H-LTA and MoO$_3$/H-ZSM-5 combined sample, the next stage in this investigation was to examine the effect of combining nickel with the standard catalyst in the absence of the LTA system. For this study a 50:50 mixture of NiO and 3%MoO$_3$/H-ZSM-5 was employed. The results of this investigation are given in the following section.

6.3 Results and discussion - NiO study

6.3.1 Reaction data

The hydrogen formation rate versus time on stream for 3%MoO$_3$/H-ZSM-5, NiO and 3%MoO$_3$/H-ZSM-5 combined and NiO and H-ZSM-5 combined systems are given in Figure 6.3-1. As can be seen from the profiles the hydrogen formation for the standard catalyst mixed with nickel oxide i.e. NiO and 3%MoO$_3$/H-ZSM-5 combined, is very different to that of the standard catalyst alone, 3%MoO$_3$/H-ZSM-5.

The NiO and 3%MoO$_3$/H-ZSM-5 combined sample exhibits a much greater hydrogen formation rate than the standard catalyst, 3%MoO$_3$/H-ZSM-5. In actual fact, after approximately 100 minutes on stream the NiO and 3%MoO$_3$/H-ZSM-5 combined sample shows a gradual increase in hydrogen formation. At no point during the standard length of reaction time, i.e. 390 minutes, did the hydrogen formation rate reach its maximum. So this sample was left on stream for a longer period of time to assess its activity further. The sample was tested for >800 minutes and still did not reach its maximum in hydrogen production. If possible it would have been interesting to run these samples on stream for a longer period of time. However, time constraints on the length of hours that experiments can be conducted prevented this.
Similarly, a NiO and ZSM-5 combined sample was tested and the general activity pattern is very similar to the NiO and 3%MoO₃/H-ZSM-5 combined sample. The NiO and ZSM-5 combined sample, has an even greater hydrogen production rate than the NiO and 3%MoO₃/H-ZSM-5 combined sample.

Both the NiO and 3%MoO₃/H-ZSM-5 and NiO and ZSM-5 combined materials display a high initial hydrogen formation, which rapidly decreases over time then begins to increase gradually for the remaining time that these materials are left on stream. This sharp initial H₂ activity is associated with the reduction of the nickel oxide species. A similar burst in activity in hydrogen formation was demonstrated in Chapter 4 when Ni²⁺ was doped into 3%MoO₃/H-ZSM-5 and reacted under the same conditions as those used in Figure 6.3-1.

The benzene formation rate versus time on stream for 3%MoO₃/H-ZSM-5 and NiO and 3%MoO₃/H-ZSM-5 combined are given in Figure 6.3-2. The NiO and 3%MoO₃/H-ZSM-5 combined sample only produced a low benzene formation rate for the first 100 minutes on stream then the benzene formation was completely inhibited.
No benzene was detected for the NiO and ZSM-5 combined sample.

Li et al. [143] have demonstrated that NiO samples can be reduced to metallic nickel by reduction in hydrogen, which is then able to carry out methane decomposition.

From Figure 6.3-1 it appears that, as expected, the nickel oxide part of the combined catalysts is acting as a highly active methane decomposition catalyst, where the products of decomposition are hydrogen and carbon. It can be seen that more hydrogen is produced for the NiO and ZSM-5 combined sample than from the NiO and 3%MoO3/H-ZSM-5 combined sample. As can be seen from the profiles benzene was only produced initially for the NiO and 3%MoO3/H-ZSM-5 combined sample. One reasonable explanation may be that the inherent acidity of the two ZSM-5 materials are different.

It is clear from the profiles that hydrogen is produced to a far greater extent for these NiO combined catalysts than for the standard catalyst alone, 3%MoO3/H-ZSM-5. From CHN analysis it is evident that carbon is a product of this reaction. The post reaction XRD patterns show that NiO has been reduced into nickel metal, Figure 6.3-3.

### 6.3.2 Post reaction XRD patterns

The post reaction XRD patterns of the NiO+3%MoO3/H-ZSM-5 and NiO+ZSM-5 combined materials are shown in Figure 6.3-3. It is clear that in both patterns there are low
intensity reflections that are indicative of ZSM-5, implying that the zeolite structure is still intact. The three dominant peaks in both patterns can be indexed to nickel and carbon. The reflections at 44.5° and 51.9°2θ can be indexed to nickel (PDF 03-1051), while the reflection at 26.6°2θ can be indexed to graphite (PDF 26-1080). There are no reflections indicative of a NiO phase in either diffraction pattern, reflections indicative of nickel oxide would be visible at 37.2, 43.3 and 62.88°2θ.

The post reaction XRD patterns of the NiO and 3%MoO3/H-ZSM-5 and NiO and ZSM-5 combined materials shown in Figure 6.3-3 both display a carbon phase. This is consistent with the post reaction carbon analysis of these materials, which is given in Table 6.3.3-1, which reveals that for both materials, more than 50% of the materials are carbon after exposure to methane under the given conditions i.e. 52.8% and 67.4% for NiO and 3%MoO3/H-ZSM-5 and NiO and ZSM-5 combined respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3%MoO3/H-ZSM-5 + NiO combined</td>
<td>52.8</td>
</tr>
<tr>
<td>H-ZSM-5 + NiO combined</td>
<td>67.4</td>
</tr>
</tbody>
</table>

Table 6.3.3-1 Carbon analysis of post-reactor materials.
It should be noted that a direct comparison on the amount of carbon that has been deposited on these materials cannot be made as these material although tested under the same conditions were not on stream for the exact same length of time. The NiO and 3%MoO$_3$/H-ZSM-5 combined material was on stream for ca. 840 minutes whereas the NiO and ZSM-5 combined material was on stream for ca. 800 minutes.

However it can be noted that the NiO and 3%MoO$_3$/H-ZSM-5 combined material is more resistant to the deposition of carbon as this material was on stream for a greater length of time than the NiO and ZSM-5 combined material yet has less carbon deposited on it than the NiO and ZSM-5 combined material. Therefore, the NiO and ZSM-5 sample is much more active for methane decomposition than the NiO and 3%MoO$_3$/H-ZSM-5 combined material. As already mentioned it may be that MoO$_3$ sublimes and slightly covers the NiO surface in the case of the NiO and 3%MoO$_3$/H-ZSM-5 combined material.

It is probable that the form of carbon on these post reaction materials is in the form of carbon nanotubes, since it has been shown that methane decomposition over nickel produces carbon nanotubes \cite{143, 144}, however, future TEM studies on the materials used in this work would be required to clarify this.

### 6.4 Summary

This short study on attempting to elucidate the effect of a reduction in the H$_2$ partial pressure by adding a H$_2$ storage material in the form of Ni(II) or Fe(III)/H-LTA has demonstrated that although the benzene concentration did increase for the Ni(II)/H-LTA and 3%MoO$_3$/H-ZSM-5 combined material so did the hydrogen formation. In this combined system it does not appear that the LTA catalyst acts as a H$_2$ storage vessel. One reasonable explanation for these results may be that ethylene which is formed by the MoO$_3$/ZSM-5 catalyst, goes on to further react with the LTA system. Alternatively, there may be a gradual build up of an active carbonaceous phase in the Ni/LTA and 3%MoO$_3$/H-ZSM-5 materials, which leads to a gradual increase in benzene formation rate with time on stream i.e. carbonaceous phase partially comes from ethylene hence no benzene was observed at first and then benzene increases beyond that expected.

Similarly, the Fe(III)/H-LTA combined catalyst also exhibited a greater hydrogen formation than the standard MDA catalyst, 3%MoO$_3$/H-ZSM-5, but in this case benzene formation was suppressed.
7 Conclusion

Throughout this project, the experimental work undertaken has been focused on two main objectives. Firstly, trying to understand more fundamental aspects of the MoO$_3$/H-ZSM-5 catalyst, for example, through Al K-edge EXAFS experiments of the catalyst upon activation, and secondly, attempting to improve the stability and reactivity of the MoO$_3$/H-ZSM-5 catalyst in methane dehydroaromatization, such as, through the use of dopants. Beneficial insights into both matters were obtained and are summarised below:

- On comparing the catalytic activity of MoO$_3$/H-ZSM-5 with Pd/H-ZSM-5, it has been shown that these two catalysts exhibit little similarity in behaviour in MDA. This suggests that either Mo$_2$C is not the active phase of molybdenum in MoO$_3$/H-ZSM-5 or that there are uncertainties in the comparisons that can be drawn between Mo$_2$C and Pd within this system.

- $^{27}$Al and $^{29}$Si MAS NMR experiments conducted on H-ZSM-5 and MoO$_3$/H-ZSM-5 catalysts showed that there is an extraction of framework Al upon incorporation of Mo species into H-ZSM-5. The appearance of a sharp signal in the $^{27}$Al MAS NMR spectra of MoO$_3$/H-ZSM-5 catalysts is noteworthy. This suggests that such species are "liquid-like" in nature and may be present as either highly disordered species or possibly as hydrated cations.

- It has been shown through Al K-edge EXAFS experiments that the average local environment of framework Al species in activated MoO$_3$/H-ZSM-5 catalyst precursors is significantly distorted, with Al species being drawn towards molybdenum centres. Subsequent FTIR studies revealed that molybdenum remains in the $+VI$ oxidation state under the conditions employed in the EXAFS experiments, and that the acidity displayed by such precursors is exclusively of Bronsted type.

- The effect of a number of dopants on the activity of MoO$_3$/H-ZSM-5 dehydroaromatization catalysts has been investigated. Following previous reports by Ichikawa, Co and Fe dopants have been investigated. Contrary to previous observations, the addition of cobalt has not been observed to produce any promotional effect, other that an initial short burst of activity (which was also observed for the nickel doped MoO$_3$/H-ZSM-5 catalyst). However, promotional
effects were observed with the use of iron dopants at longer times on stream, yet these do not relate to suppression of coke as previously reported. The use of novel Al containing dopants, was seen to result in the enhancement of the benzene formation rate. However, reproducibility issues were observed for this doped catalyst. Gallium doping was also seen to have promotional effects, with reduced coking observed. In all of the doped catalysts, the molybdenum and dopant metal were found to be highly dispersed, as only reflections indicative to the ZSM-5 framework are visible in the XRD patterns. TEM images of both Fe and Al doped catalysts reveal that some of the carbonaceous deposition on these catalysts is in the form of carbon nanotubes. Doping the standard catalyst, 3%MoO\textsubscript{3}/H-ZSM-5, with silver was seen to increase the benzene formation rate and reduce the coke formation compared to the standard catalyst.

- The co-impregnation of phosphorus and molybdenum through impregnation using a phosphomolybdic acid precursor results in a catalyst with lower catalytic activity. In that the observed hydrogen to benzene formation rate ratio is increased, which has been attributed to enhanced coking. Catalysts prepared using both silicomolybdic acid and sodium molybdate as the molybdenum precursors have been shown to have very poor activity as methane aromatisation catalysts.

- Higher levels of phosphorus doping of MoO\textsubscript{3}/H-ZSM-5 catalysts have been investigated. It was shown that when 5wt.% phosphorus (in the form of ammonium dihydrogen phosphate) was doped onto 5%MoO\textsubscript{3}/H-ZSM-5, hydrocarbon formation was completely suppressed initially and hydrogen was the sole gas phase product. The hydrogen formation rate was seen to increase throughout the run and reached a maximum of >5% of the exit stream concentration. The appearance of this maximum is linked with the evolution of an inorganic phosphite phase from the catalyst. The decrease in hydrogen formation from this maximum is associated with the production of trace levels of benzene and carbon oxides. Further studies on 5%P/MoO\textsubscript{3} showed that this material exhibits a similar pattern of hydrogen evolution. But, for this material, carbon oxides are formed in greater quantities and the relative ratios of the products are similar to recent reports of the carburisation of oxomolybdenum ZSM-5 catalysts, although the timescales are much greater.

- A novel method for the production of phosphides through the reduction under methane from the corresponding phosphate doped oxide has been demonstrated.
However, the preparation of phosphides via reduction of phosphates using more reactive hydrocarbons i.e. propane and propene, as the reducing agents have proved more difficult. From reviewing the literature, it does not appear that this method of phosphide preparation has been previously reported. Normally, for catalysis applications, it has been reported that phosphides are prepared via reduction of phosphates under a hydrogen flow. The advantage of the method shown in this work is that, along with producing the phosphide, hydrogen is also produced.

- The inclusion of dispersed reducible cations to LTA, in particular, Ni(II)/H-LTA or Fe(III)/H-LTA was investigated. In all cases, benzene production was generally suppressed, although the Ni (II) system showed interesting effects with time on stream. The increase in the benzene formation rate for the Ni(II)/H-LTA combined catalyst may be due to ethylene which is produced by the MoO3/H-ZSM-5 catalyst going onto further react with the LTA based catalyst.

### 7.1 Future work

This work has generated many novel and interesting findings related to methane conversion under non-oxidative conditions. Future studies relating to this work could possibly include:

- **Mo EXAFS studies** on the Fe/Al/Ga doped MoO3/H-ZSM-5 materials to see if molybdenum species and dopant species are segregated from one another or if the catalysts consist of mixed phases. This type of study may help determine the active phases in these doped catalysts.

- **In-situ XRD studies** to follow the phase transformations, which occur during the production of phosphides from the corresponding phosphate doped oxide through reduction using methane.

- The preparation of phosphides using more reactive hydrocarbons such as propene and propane while using a lower temperature with longer times on stream than was employed while using methane as the reductant in the preparation of phosphides.
8 Appendices

8.1 Appendix 1: Benzene gas calibration

Together with the experimental conditions given in Section 2.3.2, the Clausius-Clapeyron equation can be used so that the gc calibration for benzene can be performed.

The Clausius-Clapeyron equation given below as equation (1), allows the estimation of vapour pressure as a function of temperature, if the enthalpy of vapourisation is known.

\[ P = P^* \exp \left\{ \frac{-\Delta H}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right) \right\} \quad \text{eqn (1)}. \]

The enthalpy of evaporation of benzene is 30.8 kJmol\(^{-1}\) and the boiling point (760mmHg) is \( T_b/K \) is 353.25 K [data taken from, Atkins, Physical Chemistry, 2nd edition].

For example, if the temperature is 294.15 K, then the vapour pressure can be determined as follows:

\[ \frac{P}{760} = \exp \left\{ \frac{-30800}{8.314} \left( \frac{1}{294.15} - \frac{1}{353.25} \right) \right\} \]

Thus, \( P = 92.0 \text{ mmHg} \)
8.2 Appendix 2: Equations for the calculation of reaction data

Using the N\textsubscript{2} internal standard, where applicable, appropriate account was taken of the change in volume on reaction and then data was calculated according to the following:

Methane Conversion (%) = \frac{\text{CH}_4 \text{ (In)} - \text{CH}_4 \text{ (Out)}}{\text{CH}_4 \text{ (In)}} \times 100

Hydrogen formation rate (molH\textsubscript{2}g\textsuperscript{-1}s\textsuperscript{-1}) = \frac{\text{H}_2 \text{ (Out)}\text{ mol min}^{-1}}{\text{mass catalyst (g)}} / 60

Benzene formation rate (molC\textsubscript{6}H\textsubscript{6}g\textsuperscript{-1}s\textsuperscript{-1}) = \frac{\text{C}_6\text{H}_6 \text{ (Out)}\text{ mol min}^{-1}}{\text{mass catalyst (g)}} / 60
9 References


