Chapter 6

Results from the nonoxidative conversion of methane over Mo/H-ZSM-5 catalysts

In this chapter the results obtained from the studies of the nonoxidative conversion of methane over Mo/H-ZSM-5 catalysts are presented and discussed. The preparation, characterisation and catalytic evaluation of the catalysts were described in Chapter 5. The typical products analysed from the reaction of

methane were ethene, ethane, benzene and coke. As already stated in Chapter 5, coke refers to the solid carbonaceous species deposited on the catalyst as well as the condensable aromatic products which were not detected in our system.

The effects of various parameters, such as the support material, the molybdenum content, the reaction temperature, the flow rate of the feed, the crystallinity and the SiO_2/Al_2O_3 ratio of H-ZSM-5, the catalyst preparation procedure, addition of dopants, the molybdenum precursor, silanation of H-ZSM-5 on the reaction were investigated. The regenerability of Mo/H-ZSM-5 catalysts and the possible replacement of Mo with W were also evaluated. The results of the various characterisation techniques used in this study are also presented and discussed. Unless stated otherwise the SiO_2/Al_2O_3 ratio of the zeolites used in this study was 70 and the molybdenum loading was kept at 2 wt%.

6.1 The effect of the support

The results of the effect of the catalyst support on the catalytic activity of supported molybdenum catalysts are summarised in Table 6.1 for a time on stream of 1 h and a molybdenum loading of 2 wt%.

Table 6.1 The effect of the support on the nonoxidative dehydroaromatisation of methane at 750°C over 2%Mo/Support catalysts for a time on stream of 1 h

| Support | %Conversion | %Selectivity | | | Ethene/Ethane ratio |
		C_2 hydrocarbons	Aromatics	Coke	
SiO_2	14.4	1.2	12.5	86.3	∞
Al_2O_3	10.5	1.8	3.7	94.4	3.5
SiO_2-Al_2O_3	17.0	0.7	1.1	98.2	1.3
H-Silicalite	1.4	3.0	0.0	97.0	∞
H-MOR	10.2	5.2	24.0	70.9	1.9
H-ZSM-5	14.7	2.2	66.4	31.4	3.4
H-SAPO-34	11.5	3.3	2.2	94.5	3.7

The catalytic conversion of methane decreased in the order SiO_2-Al_2O_3 > H-ZSM-5 ≈ SiO_2 > H-SAPO-34 > H-MOR ≈ Al_2O_3 > H-Silicalite. However, the highest selectivity for aromatics was obtained over the 2%Mo/H-ZSM-5 catalyst. Although, the catalyst based on SiO_2-Al_2O_3 showed the highest conversion, the selectivity for aromatics was about 1% with a selectivity to coke of 98.2%. When SiO_2 and silicalite were used as supports, ethane was not produced but ethene was produced, while the other supports which are believed to have Brønsted acidity produced ethane (see Table 6.1). This observation suggests that the formation of ethane requires Brønsted acidity.

The ethene/ethane ratios in the product stream were also monitored and the results are also shown in Table 6.1. Ethane was not produced over silica and silicalite supports, but was produced when the support materials used had a possibility of having Brønsted acid sites. This suggests that Brønsted acid sites are probably involved in the processes that lead to the production of ethane. The fact that silicalite, which gave the lowest conversion in the series, produced only ethene suggests that ethane is produced via hydrogenation of ethene and in some way the Brønsted acid sites are involved in its production.

The aromatisation of methane is believed to occur via a bifunctional mechanism requiring both the Mo component and the Brønsted acid sites of the support [1]. It is, therefore, interesting to note that the formation of aromatic was also observed in the case of 2%Mo/SiO_2 catalyst, which is not expected to have Brønsted acidity. The formation of aromatics products over 2%Mo/SiO_2 was also previously noted by some researchers [2,3]. There has been a suggestion of the participation of Lewis acid sites in the aromatisation reactions over 2%Mo/SiO_2 catalysts [4]. On the other hand other researchers [5] reported that Lewis acid sites were not involved in the aromatisation reaction. Although, the participation of Lewis acid sites in the aromatisation of methane is still a matter of debate [4-6], the importance of Brønsted acid sites in the aromatisation of methane has been acknowledged [1,7-10]. On the other hand, silicalite, which is

isostructural with ZSM-5, showed the lowest activity in the series. This may be due to the fact that there are no Brønsted acid sites in silicalite.

The catalytic stability of the Mo/H-ZSM-5 catalysts with time on stream (TOS) was also higher than those for the other supported systems, as shown in Figure 6.1.
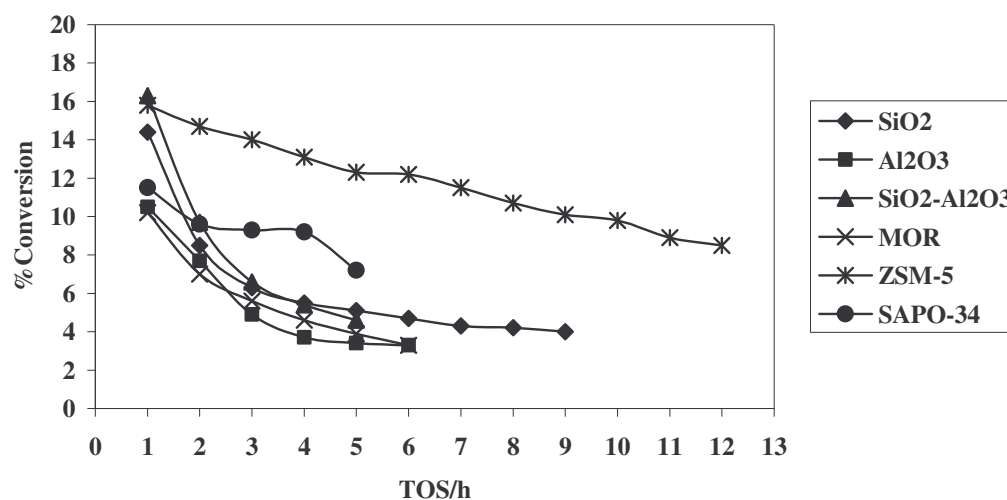

Figure 6.1 The effect of the support on the catalytic conversion and stability of supported molybdenum catalyst at 750°C.

The better catalytic performance of H-ZSM-5-supported catalysts compared with the other support systems makes the Mo/H-ZSM-5 catalyst one of the promising catalysts for the aromatisation of methane, as previously noted by other researchers [1].

6.2 The effect of molybdenum loading

Mo/H-ZSM-5 catalysts with molybdenum loadings from 1 to 15 wt% were prepared and then used for the conversion of methane in the absence of oxygen.

The effect of the Mo loading on the catalytic performance of Mo/H-ZSM-5 catalysts was investigated using a ZSM-5 sample with a crystallinity of 66%. The surface area and pore volumes of these catalysts are summarised in Table 6.2.

Table 6.2 The effect of the molybdenum loading on the surface and pore volumes of Mo/H-ZSM-5 catalysts with a crystallinity of 66%

Mo loading (wt%)	BET surface area (m^2/g)	Pore volume (cm^3/g)
0	406	0.41
1	408	0.41
2	399	0.40
4	382	0.40
8	352	0.37
15	305	0.29

The surface area and the pore volumes of the catalysts decreased with an increase in the molybdenum content, decreasing from 406 to 305 m^2/g and 0.41 to 0.21 cm^3/g, respectively, for the molybdenum-free sample and 15%Mo/H-ZSM-5 sample, respectively. The observed decrease in the surface areas and pore volumes in Table 6.2 was also reported by other researchers [7] and has been attributed to the blockage of the pores by molybdenum species. The effect of the amount of molybdenum in the catalysts is discussed below.

The results of the effect of the Mo loading on the catalytic performance of Mo/H-ZSM-5 catalysts for various times on stream are shown in Figure 6.2. After use, the catalyst was black indicating that there was some deposition of species on the catalysts. All the catalysts deactivated with increasing time on stream (TOS), due to the formation of carbonaceous coke [1]. The catalyst with the highest molybdenum loading (15 wt%) had the lowest conversion, and also deactivated faster than the other catalysts. This is in agreement with a significant decrease of the surface area and pore volumes when the molybdenum loading was 15 wt%.
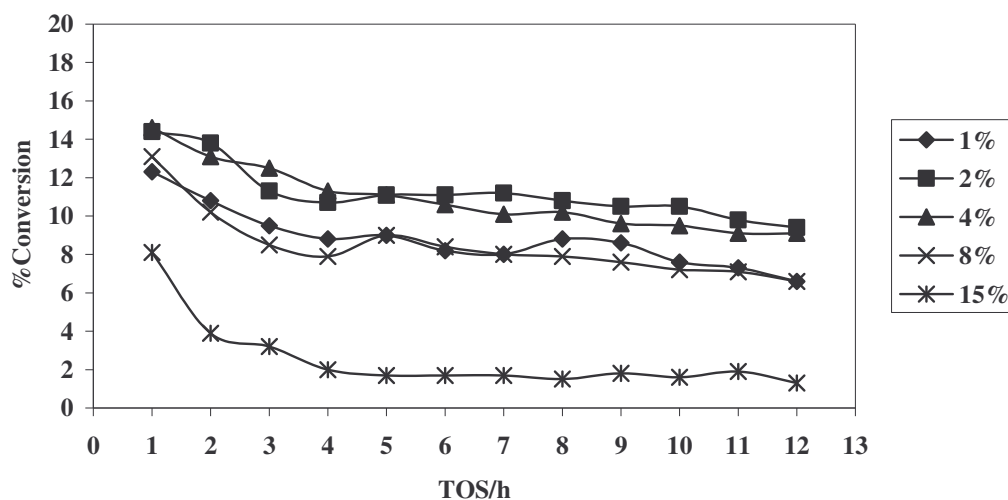
Figure 6.2 The effect of the Mo loading on the catalytic conversion and stability of Mo/H-ZSM-5 catalysts with a crystallinity of 66% for the nonoxidative conversion of methane at 750°C.

The effect of Mo loading on the catalytic activities of the Mo/H-ZSM-5 catalysts is more clearly shown in Figure 6.3 after a time on stream of 5 h.
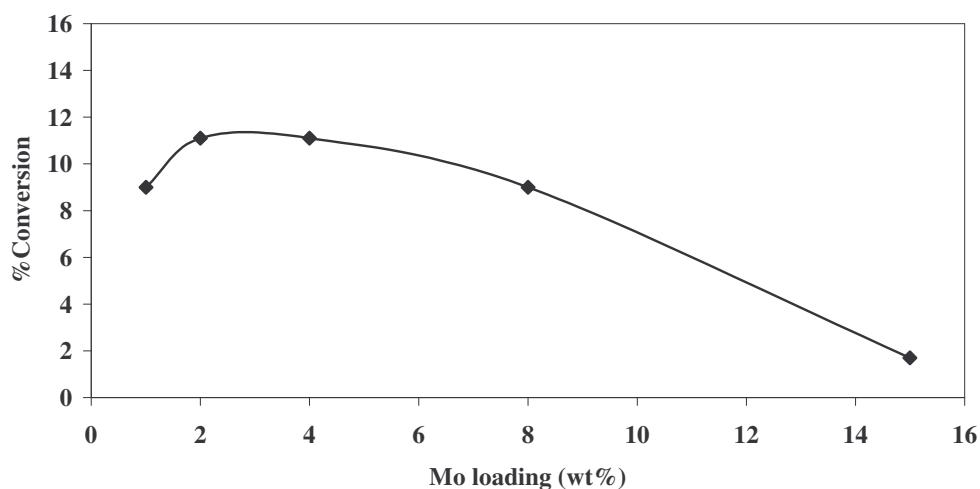

Figure 6.3 The effect of Mo loading on the conversion of methane at 750°C over Mo/HZSM-5 catalysts with a crystallinity of 66%, after a time on stream of 5 h.

The maximum conversion was obtained for catalysts with Mo loadings between 2 and 4 wt%, and conversions of about 11%. The high activity for Mo/H-ZSM-5 catalysts with molybdenum loadings of 2-4 wt% was reported by other researchers [7,11]. The decrease in the conversion for Mo loadings above 4 wt% was attributed to the formation of MoO_3 species and the partial destruction of the zeolite framework [7,11,12].

The effect of the Mo loading on the selectivities to different products was compared at a conversion level of about 10%, as given in Table 6.3. The effect of the Mo loading on the selectivity for various products is shown in Figure 6.4. The selectivity for C_2 hydrocarbons ranged between 3 and 5%, while the ethene/ethane ratios ranged between 2.5 and 3.5, as shown in Table 6.3.

Table 6.3 The effect of the molybdenum loading on the catalytic performance of Mo/H-ZSM-5 catalysts for the nonoxidative aromatisation of methane at $750^{o}C$, after 5 h on-stream

| Mo loading (wt%) | % Conversion | % Selectivity | | | Ethene/Ethane ratio |
		C_2 hydrocarbons	Aromatics	Coke	
1	9.5	3.5	49.8	47.0	2.5
2	10.5	5.0	44.9	50.1	3.5
4	10.1	4.4	46.3	49.2	3.0
8	10.2	3.6	53.9	42.5	3.0
15	8.1	3.4	35.5	61.0	2.8

The observed variations of the ethene/ethane ratios may be related to the slight difference in the percentage conversion of methane as seen in Table 6.3. The selectivity for aromatics varied between 35 and 54%, while the selectivity for coke varied between 47 and 61%. The results in Figure 6.4 also show that the selectivity for C_2 hydrocarbons did not vary significantly with molybdenum loading.
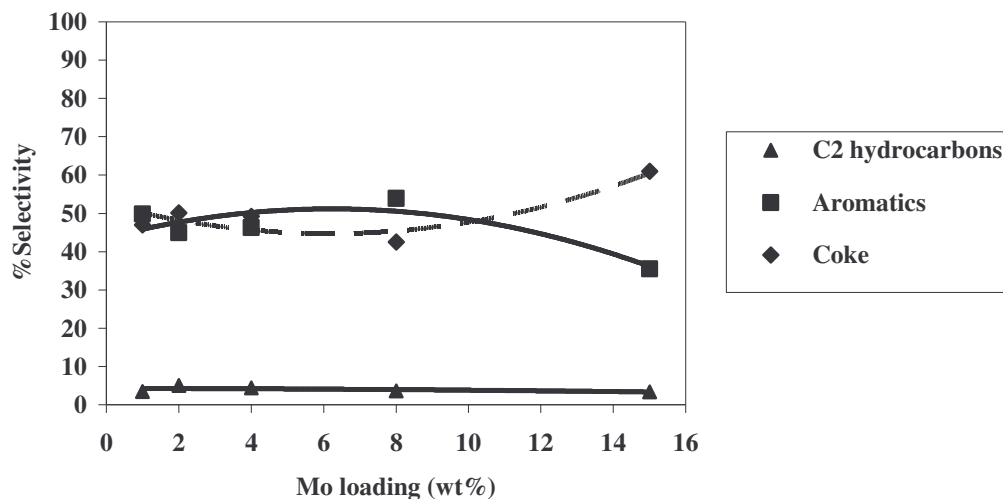
Figure 6.4 The effect of Mo loading on the products selectivity from methane aromatisation over Mo/H-ZSM-5 catalysts for a time on stream of 5 h at 750°C, for a conversion of 10%.

Similarly, the selectivity for aromatics and coke was not significantly affected by the molybdenum content, though a slightly higher aromatic selectivity was observed when the Mo loading was 8 wt%. It is also interesting to note that there is an inverse relation between the selectivity to coke and aromatics. This indicates that coke is mainly formed from the aromatic products. The ethene/ethane ratio observed at various levels of molybdenum loadings were not significantly affected by the molybdenum content in Mo/H-ZSM-5 catalysts. The slightly lower values observed for the catalysts with molybdenum loadings of 1 and 15 wt% seems to be in line with the slightly lower conversions observed over these samples in relation with the other catalysts in the series.

In order to understand some of the observed catalytic properties of the Mo/H-ZSM-5 catalysts with different molybdenum loadings the catalysts were characterised using different techniques. The results obtained for each characterisation method used are reported and discussed below.

The X-ray diffractograms of the Mo/H-ZSM-5 catalysts of different molybdenum contents are shown in Figure 6.5, together with that of the molybdenum oxide and H-ZSM-5. The results indicate that the framework of the H-ZSM-5 zeolite was maintained at all molybdenum loadings. No molybdenum species were detected by X-ray diffraction for molybdenum contents up to 4 wt%. This is due to the fact that at molybdenum levels below 4 wt% the molybdenum species were well dispersed and smaller than could be detected by X-ray diffraction. However, at molybdenum contents above 4 wt%, new peaks were observed, as shown in Figure 6.5 (marked A, B, and C). These new peaks were attributed to the presence of crystalline MoO_3 phase, and this was also confirmed by comparing the diffractograms with the database of known X-ray structures, as shown in Figure 6.6 for a sample with a molybdenum loading of 15 wt%. It should also be noted that the percentage crystallinity of the catalysts remained almost unchanged for molybdenum loadings up to 4 wt%, changing by only 1%, but decreased significantly when the molybdenum loading was 8 wt%. The crystallinity of the sample decreased by 13% and 21% when the molybdenum loading was 8 and 15 wt%, respectively.
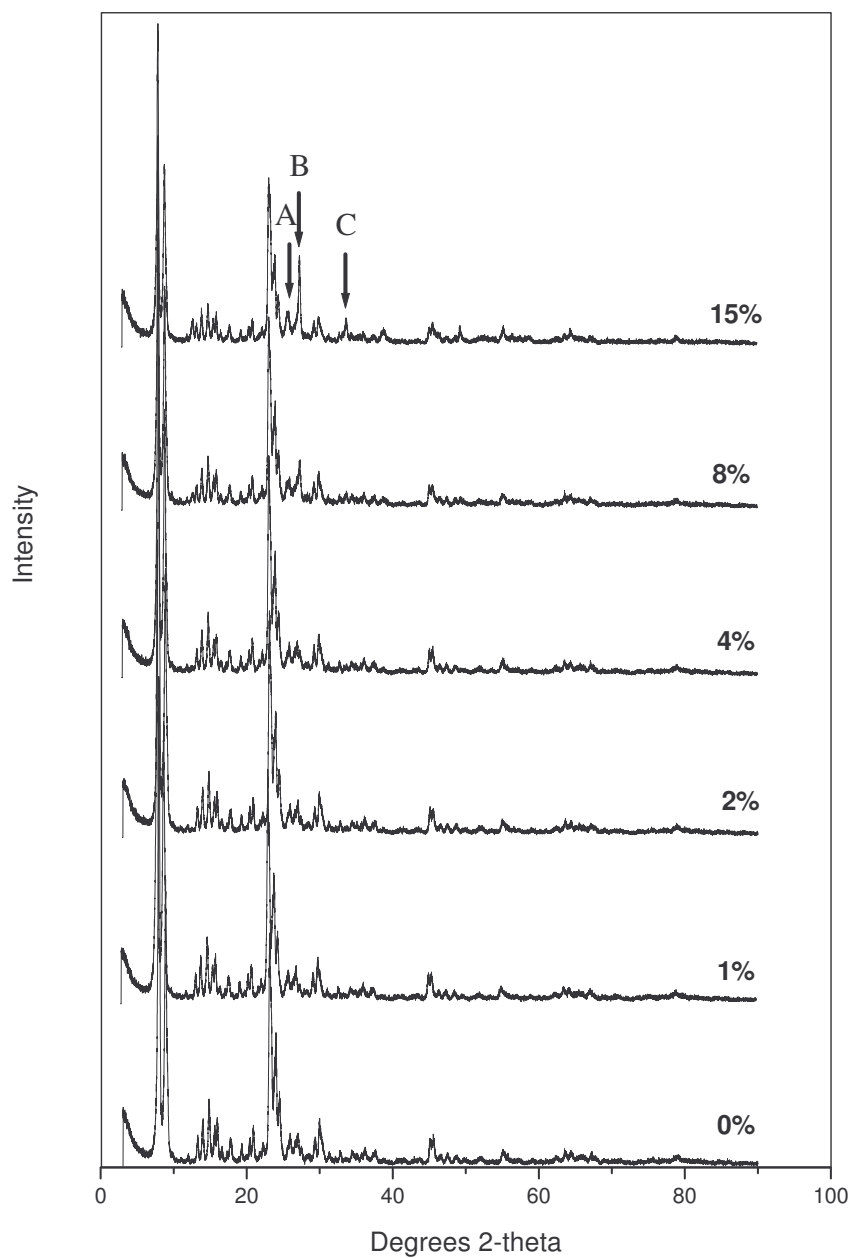
Figure 6.5 The X-ray diffractograms of Mo/H-ZSM-5 catalysts of different molybdenum contents. A, B, and C indicate the peaks due to MoO_3 species
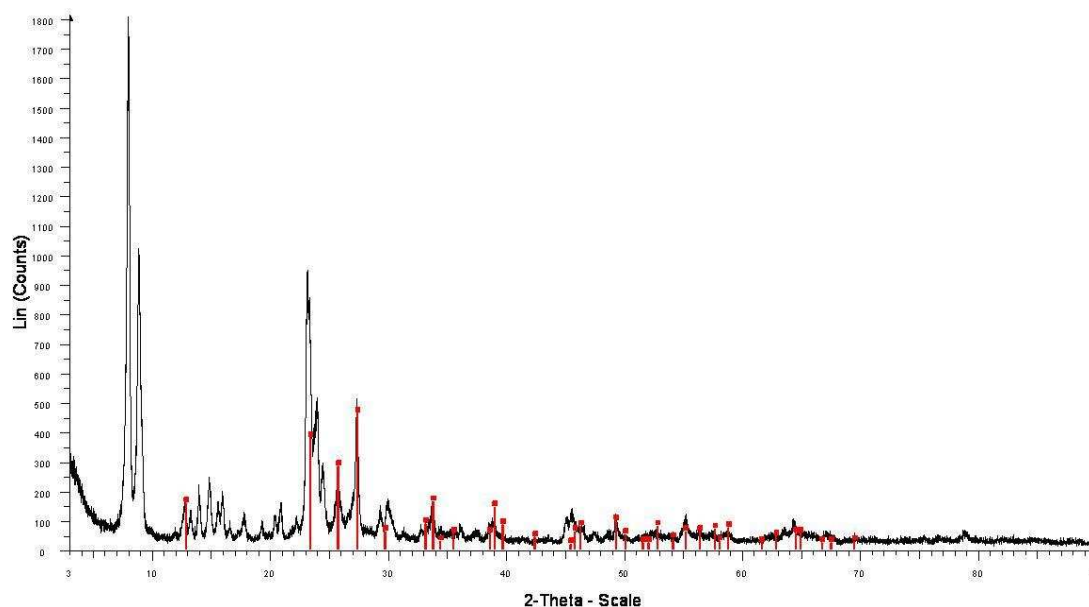
Figure 6.6 The results of the phase identification of the 15%Mo/H-ZSM-5 catalyst using database of X-ray structures: the sample profile [diffractogram] and MoO_3 peak positions [red lines].

The hydrogen temperature programmed reduction profiles of the catalysts with different molybdenum contents are shown in Figure 6.7, together with the profile of bulk MoO_3. The TPR profile of MoO_3 showed a major reduction peak at a temperature of $765^{o}C$ and a shoulder at $712^{o}C$. The profiles also show that there is a third reduction peak which developed at temperatures above $800^{o}C$. Molybdenum oxide is reduced to Mo in a simplified two-step reduction process [13]:

$$MoO_3 + H_2 \rightarrow MoO_2 + H_2O \tag{1}$$

$$MoO_2 + 2H_2 \rightarrow Mo + 2H_2O \tag{2}$$

Reaction (1) is observed at a lower reduction temperature than reaction (2). From the TPR profile of MoO_3, the calculated molar H_2/Mo consumption ratio of the
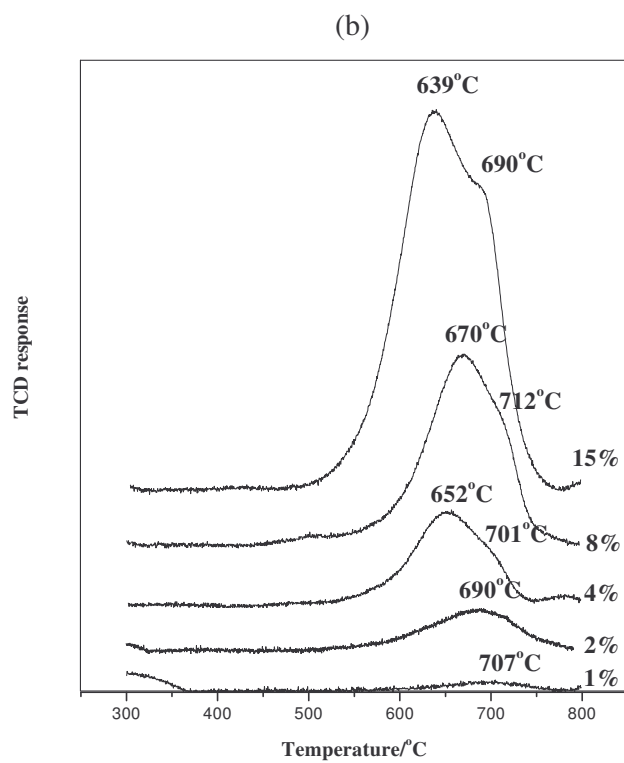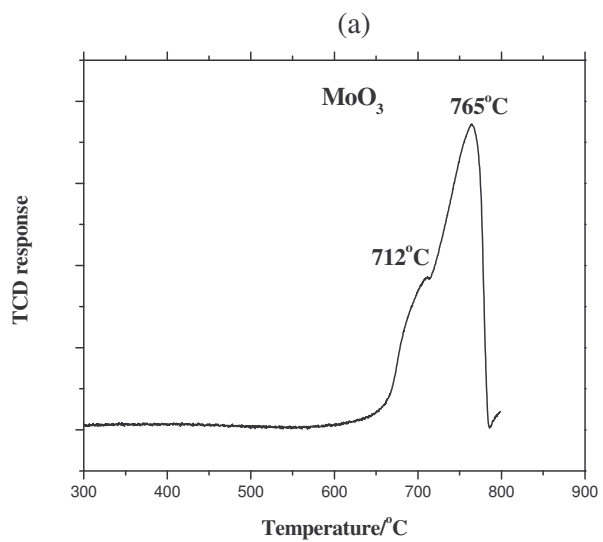
Figure 6.7 H$_2$-TPR profiles of (a) MoO$_3$, together with the profile for (b) Mo/H-ZSM-5 catalysts of different Mo contents.

bulk MoO_3 was found to be 0.8. This suggests that MoO_3 was only reduced to MoO_2, following equation (1). As already mentioned Figure 6.7(a) suggests that there is third peak appearing at temperatures above 800°C. This peak is probably due to the further reduction of MoO_2 species.

The TPR profiles of Mo/H-ZSM-5 catalysts showed the presence of two reduction peaks appearing at temperatures lower than that for the bulk MoO_3, suggesting that dispersed MoO_3 on the surface and in the channels of H-ZSM-5 was easily reduced. Similar observations were reported by Liu et al. [14]. The reducibility of the catalysts were calculated based on reaction (1) and are summarised in Table 6.4.

Table 6.4 A summary of the effect of the Mo loading on the reducibility of the Mo/H-ZSM-5 catalysts

Mo loading (wt%)	Reduction temperature (^{o}C)	%Reduction
1	701	17
2	690	34
4	652; 701	33
8	670; 712	36
15	639; 685	43

The reducibility of the catalysts increased with increasing molybdenum content. The lower reducibility at lower Mo content could be due to the high degree of dispersion of molybdenum species in the samples. The reduction profiles of the Mo/H-ZSM-5 catalysts also show the appearance of a shoulder peak with increasing molybdenum content. The appearance of the shoulder may be due to the increasing heterogeneity of the molybdenum species resulting in poor dispersion of molybdenum species. This is in agreement with the results of X-ray studies, which indicated the presence of crystalline MoO_3 species at higher molybdenum loadings.

The mode of coordination of the molybdenum species in Mo/H-ZSM-5 catalysts was characterised by diffuse reflectance spectroscopy (DRS). It is known that oxomolybdenum compounds give strong absorption bands in the UV-vis region due to the charge transfer: $O^{2-} \rightarrow Mo^{6+}$ [15]. The position of this electronic transition depends on the ligand field symmetry surrounding the Mo center. In general, three bands at 220–250, 280, and 320 nm are detected in the UV–vis diffuse reflectance spectrum of supported molybdate ions [16]. The bands at 220–250 nm are commonly attributed to the tetrahedral molybdate, $Mo(T_d)$, while the band at 320 nm is assigned to the Mo–O–Mo bridge bond of the octahedral molybdate $Mo(O_h)$. The band at 280 nm has been assigned to monomer, dimer, and polymerised molybdate species, respectively, but the assignment is not well clarified [16].

It is known that molybdenum species in sodium molybdate are in the tetrahedral coordination environment while ammonium heptamolybdate (AHM) are in octahedral coordination environment [17]. The DRS spectra of sodium molybdate (Na_2MoO_4), AHM and MoO_3 are shown in Figure 6.8, together with the spectra for Mo/H-ZSM-5 catalysts. Figure 6.8(a) indicate that the molybdenum in sodium molybdate is in a $Mo(T_d)$ site and molybdenum in ammonium heptamolybdate is in a $Mo(O_h)$ site while MoO_3 has both types of molybdenum species. The diffuse reflectance spectra in Figure 6.8 (b) suggests that the molybdenum species in Mo/H-ZSM-5 catalysts were predominantly in the $Mo(T_d)$ coordination site irrespective of the molybdenum content, showing absorption at wavelengths of 212 and 238 nm. However, a small shoulder at the wavelength of 320 nm was observed for the sample with molybdenum loadings from 4 wt% and above, suggesting the presence of small amounts of molybdenum species in octahedral coordination. This is in line with the presence of crystalline MoO_3 species as the molybdenum loading was increased.
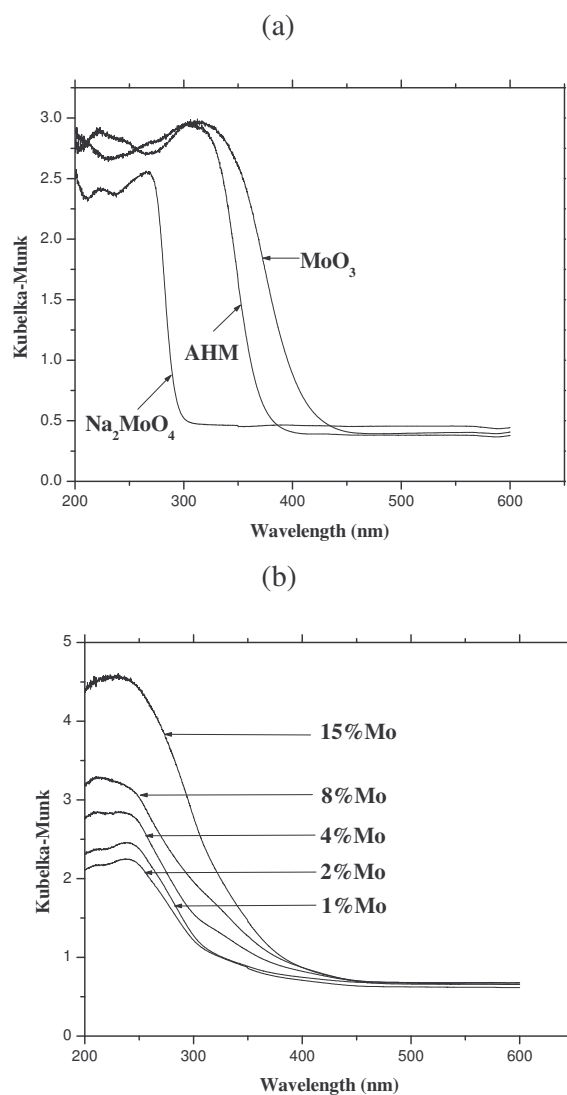
(a)

(b)

Figure 6.8 The UV-Vis diffuse reflectance spectra of (a) MoO_3, sodium molybdate (Na_2MoO_4) and ammonium heptamolybdate (AHM), and (b) Mo/H-ZSM-5 catalysts with different molybdenum contents.

The position of the absorption edge for charge-transfer transitions is known to reflect the average size of the of the MoO_x domains [18]. The absorption edge energies of the samples were determined from the UV-vis DRS spectra by the procedure reported by Weber [18], by finding the energy intercept of the straight

line extrapolated from the plot of $[F(R_\infty) \times h\nu]^2$ versus $h\nu$, where $F(R_\infty)$ is the Kubelka-Munk function and $h\nu$ is the incident photon energy. The absorption edge energies of AHM, Na_2MoO_4 and MoO_3 were found to be at 3.30, 4.23 eV and 2.98 eV, respectively. These values are in agreement with the values reported in the literature [18]. Sodium molybdate is dominated by the monomeric $[MoO_4]^{2-}$ species, whereas polyoxomolybdates exist in AHM and MoO_3 samples[18]. The variation of the edge energies with the molybdenum content of Mo/H-ZSM-5 catalysts is shown in Figure 6.9.
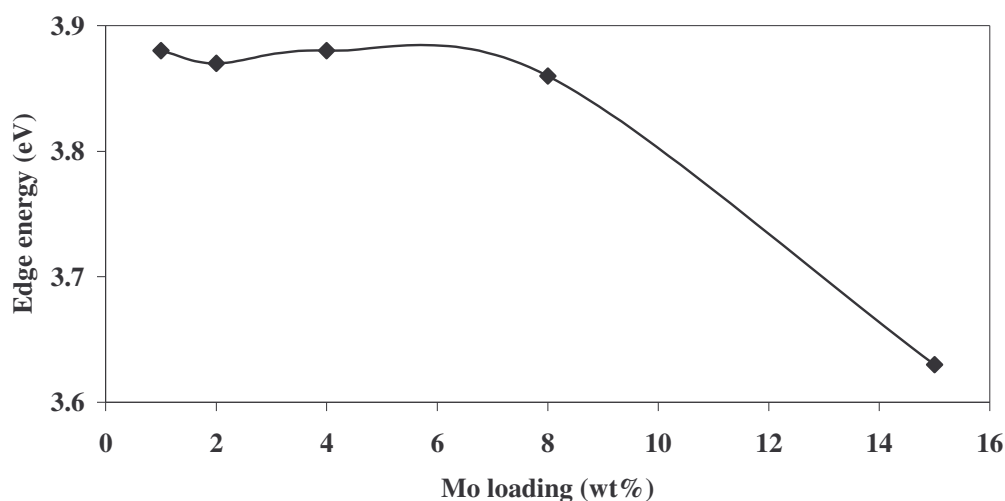

Figure 6.9 The variation of the absorption UV-Vis absorption edge energies of Mo/H-ZSM-5 catalysts with the molybdenum content.

These results show that the absorption energies of the catalysts remained constant for molybdenum loadings up to 4 wt% and decreased slightly when the molybdenum loading was 8 wt%. The character of the molybdenum species did not vary significantly for molybdenum contents from 1 to 8 wt%. A more significant decrease in the absorption edge energy was observed when the molybdenum loading was 15 wt%. This decrease in the edge energies corresponds to the increase in the domain size of the MoO_x species, since it is known that the estimated average degree of aggregation of the MoO_x species increases with increasing molybdenum loading [18].

The effect of molybdenum loading on the acidity of Mo/H-ZSM-5 catalysts was studied by means of temperature programmed desorption of ammonia (NH_3-TPD). The NH_3-TPD profiles of zeolites generally show peaks in two regions; the low-temperature region (LT), below 300^oC, and the high-temperature region (HT), above 400^oC [19]. The peak in the HT region has been ascribed to desorption of ammonia from strong Brønsted and Lewis acid sites [20], while assignment of the LT peak remains controversial. According to Niwa et al. [20] the LT peak is due to weakly bound ammonia, probably hydrogen bonded, but not ammonia adsorbed on the acid sites. Lónyi and Valyon [19] on the other hand concluded that the LT peak may characterise the base strength of the zeolite framework, and indirectly, the strength of the Brønsted acid sites, which generated the NH_4^+ ions. The TPD profiles of the Mo/H-ZSM-5 catalyst containing different amounts of Mo are shown in Figure 6.10.
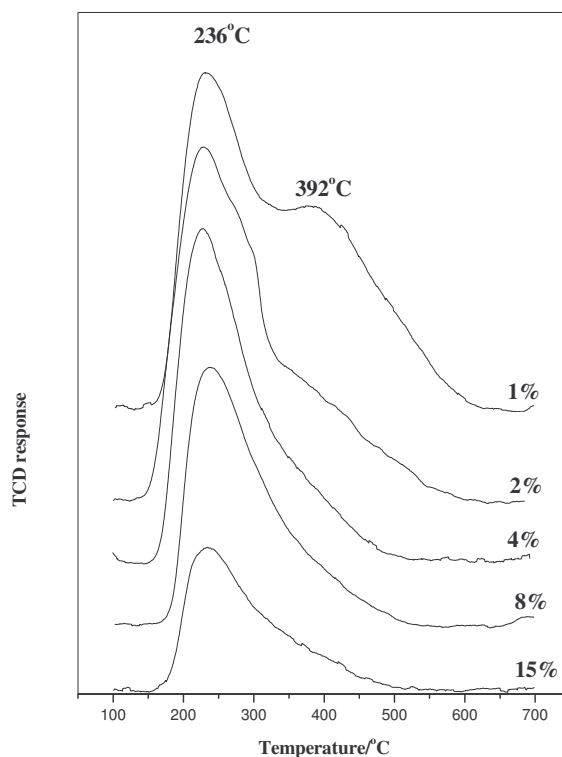

Figure 6.10 The NH_3-TPD profiles of Mo/H-ZSM-5 catalysts with different molybdenum contents.

The results show that for molybdenum loading of 1 wt% the profile showed two peaks at 236 and 392°C. The HT peak (392°C) decreased in intensity when the molybdenum loading was increased to 2 wt% and was suppressed when the molybdenum content was increased further above 2 wt%. The intensity of the LT peak was also decreased when the molybdenum content was above 2 wt%. These results indicated that the molybdenum species were interacting with the Brønsted acid sites and the interaction became stronger with increasing Mo loading. This is in agreement with the observations by other researchers [21,22].

It is accepted that the formation of carbonaceous species on Mo/H-ZSM-5 catalysts is one of the factors that contribute to the deactivation of the catalysts. The quantity of carbon that was deposited on the catalysts after use for 12 hours on stream was determined by means of a CHNS analyser. The results obtained are summarised in Table 6.5.

Table 6.5 The amounts of carbon that remained on the catalysts after use in the dehydroaromatisation of methane at 750°C

Mo loading (wt%)	Carbon deposited (wt%)
1	7.99
2	10.7
4	8.25
8	7.21
15	5.96

The results suggest that more carbonaceous deposits were obtained when the molybdenum loading was 2 wt%, while the lowest carbon quantity was obtained when the molybdenum loading was 15 wt%. These results also suggest that the fast deactivation observed in Figure 6.2 for the catalyst with a Mo loading of 15 wt% was probably not only due to the deposition of carbonaceous matter but

other factors. The nature of the carbonaceous species was studied by using temperature programmed oxidation and the results are shown in Figure 6.11.
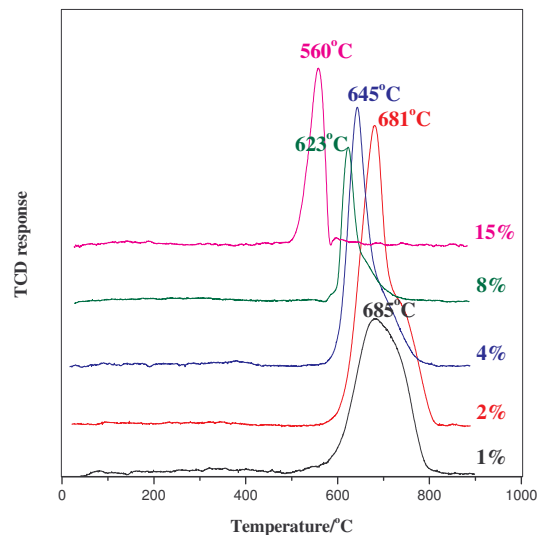

Figure 6.11 The TPO profiles of Mo/H-ZSM-5 catalysts with different molybdenum contents that were used for the conversion of methane at 750°C.

The character of the deposited carbonaceous material changed with an increase in the molybdenum loading as shown by the change in the shape of the TPO profiles and the shift in the oxidation temperatures. The intensity of the oxidation peaks which is related to the amount of carbon on deposited on the catalysts changed in accordance with the results shown in Table 6.5. The TPO profile of the catalysts with molybdenum loadings of 2, 4 and 8 wt% exhibited two oxidation peaks, one at lower temperature and a shoulder at a higher temperature. The peak at a lower temperature has been attributed to the oxidation of carbon associated with molybdenum species while the peak at a higher temperature is due to the oxidation of the carbon associated with the Brønsted acid sites [23]. It should be noted that the intensity of the shoulder in the high-temperature end decreased

with increasing Mo loading, suggesting that the deposition of carbon on the Brønsted acid sites decreased with increasing molybdenum content. The oxidation peaks also shifted to lower temperatures with increasing Mo. The catalyst with a molybdenum loading of 1 wt% showed one peak at 685°C and the peak appeared unsymmetrical suggesting the presence of a shoulder in the high-temperature zone. When the molybdenum loading was 15 wt% only one peak was observed at 560°C, which may be attributed to the carbon associated with Mo species. These results suggest that as the molybdenum loading increased the deactivation of the catalyst was not due to the deposition of carbon on the Brønsted acid sites.

Since it is possible for the structure of the zeolite to collapse at high Mo loadings and high temperatures [24], in order to establish if this was the case, the spent catalysts were characterised by means of X-ray powder diffraction. The diffractograms of the samples after their use in a catalytic reaction are shown in Figure 6.12. It can be seen that the zeolites structure was retained for the samples with Mo contents from 1 to 4 wt%, although a partial decrease in the peak intensities was observed for the sample with a Mo content of 4 wt%. Significant changes are observed when the molybdenum loading was 8 and 15 wt%. When the molybdenum loading was 8 and 15 wt% the peaks characteristic of H-ZSM-5 significantly decreased in intensity and also became broader, suggesting amorphotisation was occurring as well. This effect was more pronounced for the sample with the highest Mo loading.

The results of Figure 6.12 also indicate that molybdenum carbide formed during the reaction, for the catalysts with molybdenum loadings of 8 and 15 wt%, marked by arrows. This is also shown in Figure 6.13 for the sample with a Mo loading of 15 wt%. This observation is consistent with the results of temperature programmed oxidation in Figure 6.11, which showed that the carbon in the sample with a molybdenum loading of 15 wt% is associated with molybdenum species. Therefore, the deactivation of Mo/H-ZSM-5 catalysts was mainly due to carbonaceous coke when the molybdenum content was lower than 4 wt%, and
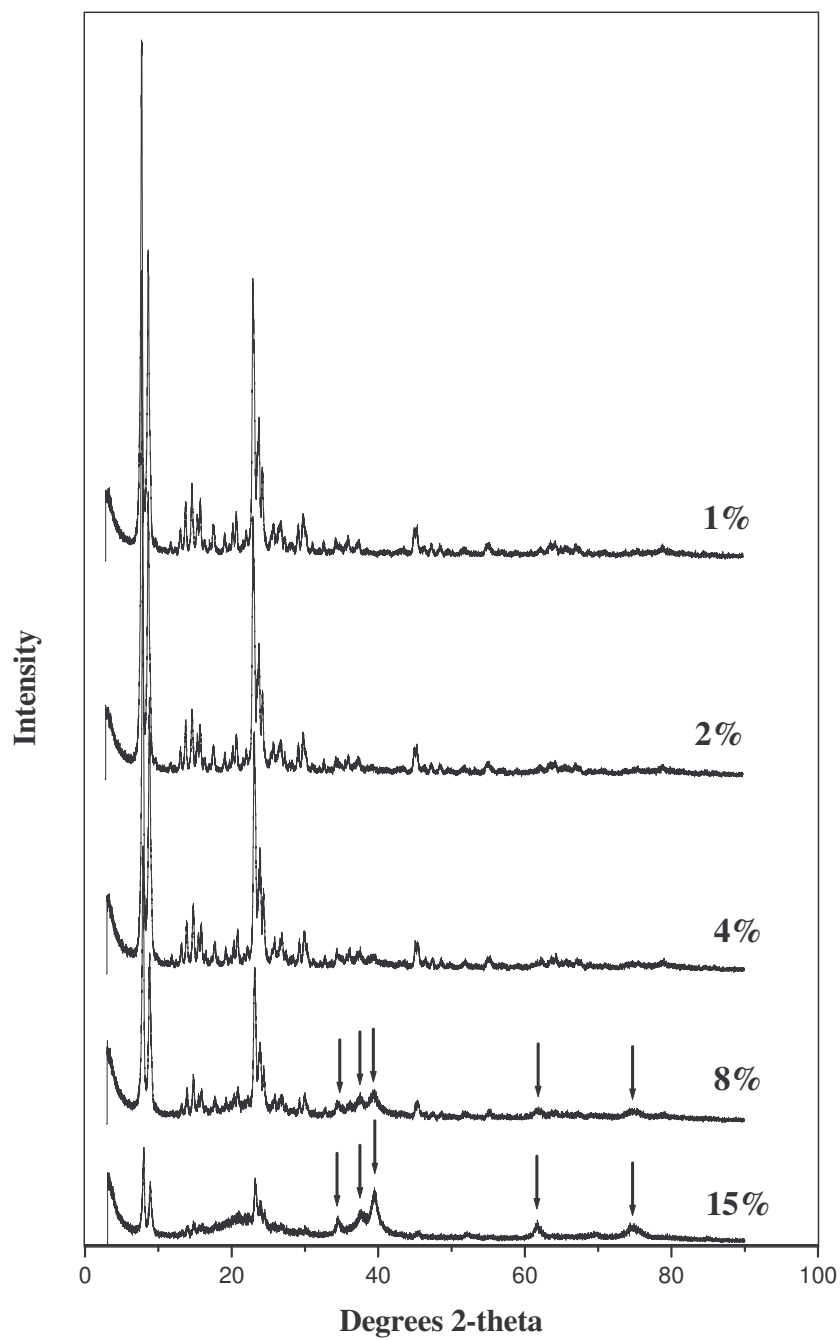
Figure 6.12 The X-ray diffractograms of the used Mo/H-ZSM-5 catalysts of different Mo contents.
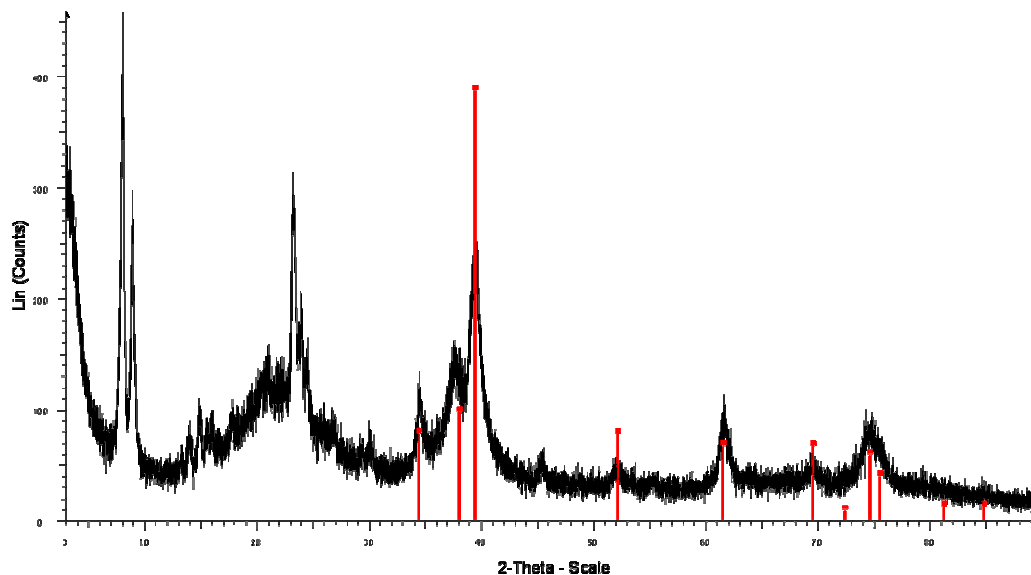
Figure 6.13 The results of the phase identification of the used 15%Mo/H-ZSM-5 catalyst using database of X-ray structures: the sample profile [diffraction profile] and Mo_2C Peak positions [red lines].

was mainly due to the collapse of the zeolite structure when the molybdenum loading was higher than 4 wt%.

6.3 The effect of flow rate

The effect of varying the flow rate on the activity of Mo/HZSM-5 was also studied and the results obtained are summarised in Table 6.6, collected after an interval of 1 h. The crystallinity of H-ZSM-5 used for these studies was 54%. The molybdenum loading of the catalyst was 2 wt%. The results show that the conversion of methane at a flow rate of 6.5 ml/min was lower than that for a flow rate of 13 ml/min. The low conversion observed for a flow rate of 6.5 ml/min may be attributed to the fact that the induction period was not complete when the data was collected (after 1 h of flow). It has also been reported that the

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Table 6.6 The effect of the flow rate of the feed on the catalytic performance of 2%Mo/H-ZSM-5 catalysts with a crystallinity of 54% for the conversion of methane at 750°C

Flow rate (ml/min)	Flow rate^{-1} (h/L)	%Conversion	%Selectivity				
			Ethene	Ethane	Benzene	Toluene	Coke
6.5	2.56	12.2	1.5	0.8	27.8	0.8	69.1
13	1.28	19.6	1.0	0.5	22.0	0.9	75.6
26	0.641	14.6	2.4	0.7	28.4	1.5	67.0
39	0.427	11.3	4.5	0.8	26.0	1.9	66.7
52	0.321	9.3	5.9	0.7	21.8	1.8	69.8
65	0.256	7.8	7.2	0.5	19.2	1.7	71.3
91	0.183	6.3	7.6	0.4	13.5	1.5	77.0
117	0.142	6.0	6.5	0.3	9.1	1.0	82.9
130	0.128	5.2	6.5	0.5	6.9	0.0	86.1
178	0.0936	4.7	5.3	0.6	4.3	0.0	89.9
208	0.0801	4.4	5.3	0.6	2.6	0.0	92.5
234	0.0712	4.4	3.6	0.6	1.9	0.0	94.0

lower the methane space velocity the longer the induction period [25,26]. As a result, this point was not included when analysing the data obtained. The percentage conversion of methane decreases with an increase in the flow rate of the feed gas as shown in Figure 6.14. The conversion increased with increasing contact time and reached a semi-plateau at higher contact times. This means methane dehydroaromatisation is inhibited by the products due to their strong adsorption and slow desorption from the catalyst surface, and their slow diffusion in the channels [27]

The variation of the percentage product selectivity with percentage conversion of methane obtained by varying the flow rate of the catalyst is shown in Figure 6.15, for ethene, ethane and toluene, and in Figure 6.16, for benzene and coke.
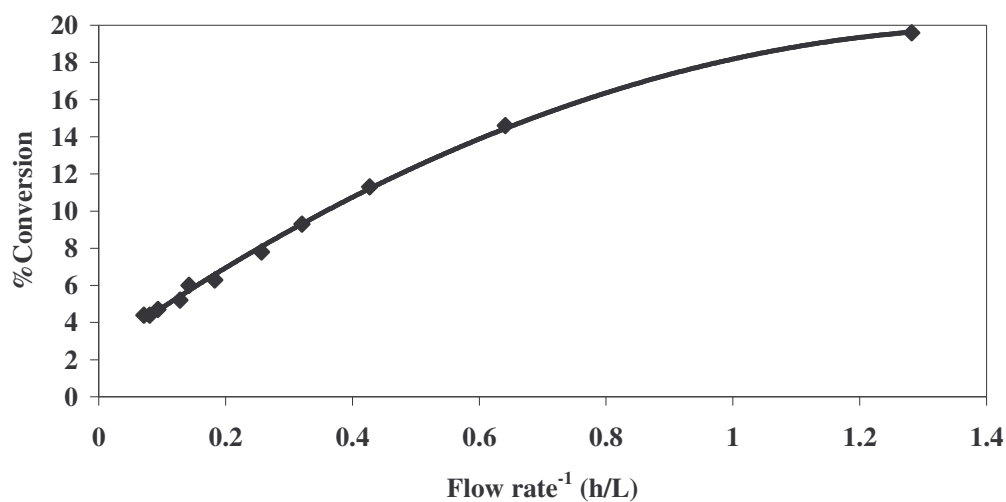
Figure 6.14 The variation %conversion of methane with the flow rate of the feed during the nonoxidative conversion of methane over 2%Mo/H-ZSM-5 catalysts with a crystallinity of 54% at 750°C.
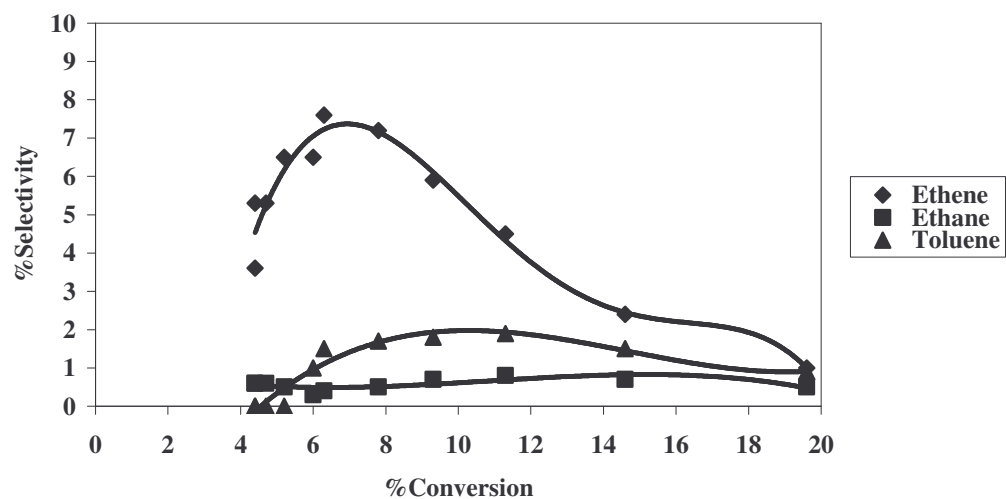

Figure 6.15 The variation of %selectivity for ethene, ethane and toluene with %conversion from the nonoxidative conversion of methane over 2%Mo/H-ZSM-5 catalysts with a crystallinity of 54% at 750°C.
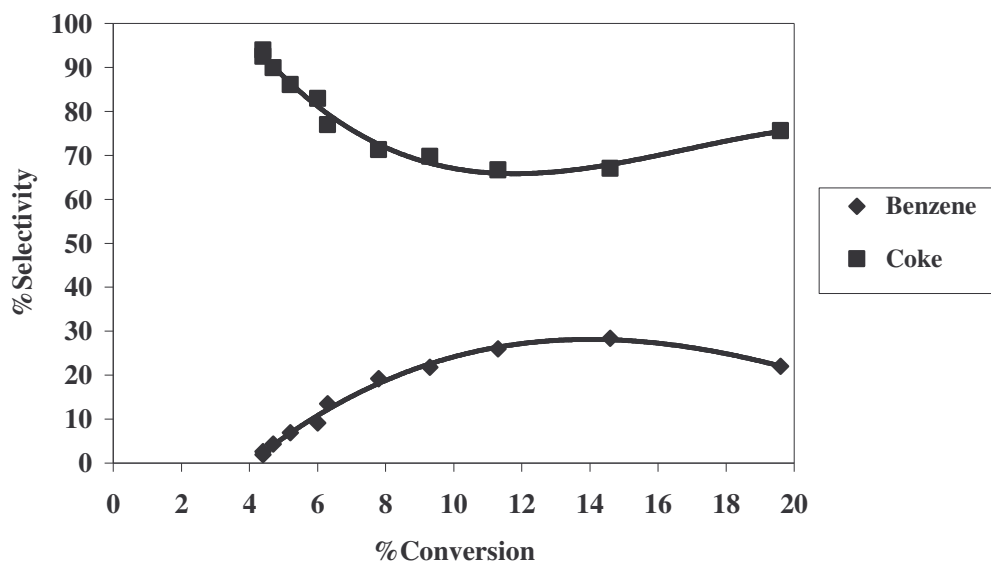
Figure 6.16 The variation of the %selectivity for benzene and coke with %conversion from the nonoxidative conversion of methane over 2%Mo/H-ZSM-5 catalysts with a crystallinity of 54% at 750°C.

It should also be noted that the flow rates were changed at 1 h intervals while the catalyst was also deactivating on-stream. The selectivity for ethene increased with conversion and then reached a maximum followed by a decrease, while the selectivity for ethane remained unchanged, as seen in Figure 6.15.

The observed trend of the variation of ethene with conversion could be an indication that ethene is transformed into a secondary product when it reached a given threshold value. The selectivity for benzene and toluene showed similar trends and they both increased until reaching a plateau at high conversion levels, as shown in Figures 6.15 and 6.16. The selectivity for coke is inversely related to the selectivity for benzene, suggesting that some of the coke is produced from benzene. The results also suggest that ethane is formed as a primary product of methane conversion reaction as shown in Figure 6.15, which showed that at the selectivity for ethane was independent of the flow rate when the flow rate of the feed was above 130 ml/min. It appears from these results that ethane is not formed via the hydrogenation of ethene. By extrapolating the linear section (at

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higher conversions) of the curves in Figures 6.15 and 6.16, to 0% conversion, the distribution of the products is estimated as approximately 9%, 1%, 34%, 3% and 53% for ethene, ethane, benzene, toluene, and coke, respectively. The high level of aromatics suggests that if aromatics are formed from ethene as suggested in the literature [1], then the aromatisation of ethene is a fast process. As already mentioned, coke included even the carbon which is used up in the formation of molybdenum carbide species, which are generally believed to be the activation sites for methane. The high selectivity for coke at 0% conversion is probably related to the presence of molybdenum carbide species.

Since the flow rate was varied over a deactivating catalyst, the study of the effect of flow rate on the catalytic performance of 2%Mo/H-ZSM-5 for the dehydroaromatisation of methane was studied using a fresh catalyst for each data point, collected after 1 h on-stream. For this purpose a commercial H-ZSM-5 zeolite supplied by Sud-Chemie, was used in the preparation of the catalysts. The results for the effect of flow rate on the conversion of methane are shown in Figure 6.17.
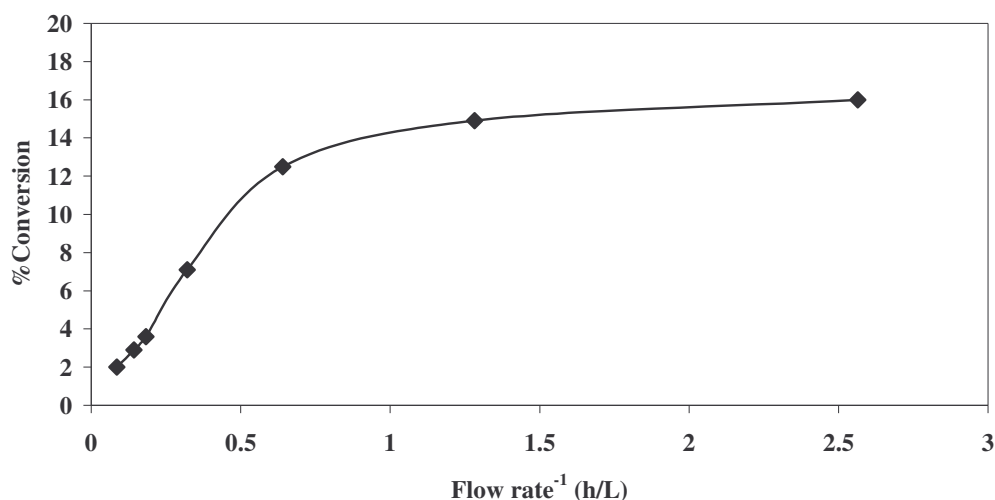

Figure 6.17 The variation of methane %conversion with the flow rate of the feed during the nonoxidative conversion of methane over 2%Mo/H-ZSM-5 catalysts at 750°C.

The variation of the percentage product selectivity with percentage conversion of methane obtained by varying the flow rate of the catalyst is shown in Figure 6.18, for ethene, ethane and toluene, and Figure 6.19, for benzene and coke.
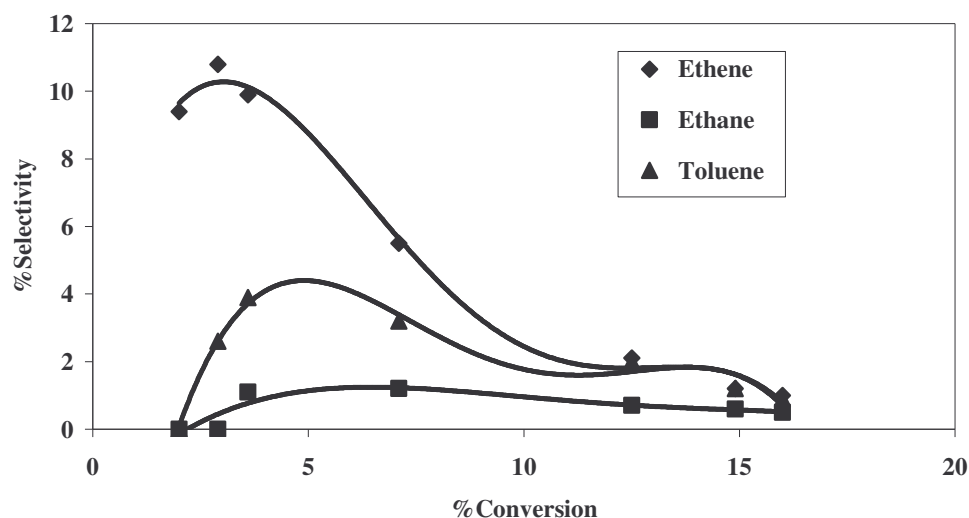

Figure 6.18 The variation of %selectivity for ethene, ethane and toluene with %conversion from the nonoxidative conversion of methane over 2%Mo/H-ZSM-5 catalysts at 750°C.
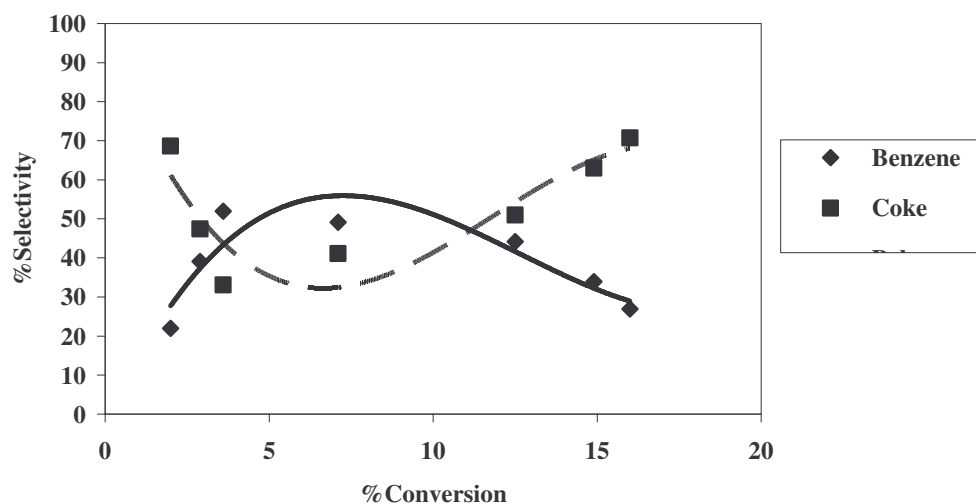

Figure 6.19 The variation of the %selectivity for benzene and coke with %conversion from the nonoxidative conversion of methane over 2%Mo/H-ZSM-5 catalysts at 750°C.

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The general trends of the variations of the product selectivities with conversion observed in Figures 6.18 and 6.19, obtained by using a fresh catalyst for each point are similar to the trends in Figures 6.15 and 6.16, for which the catalyst was also deactivating while the flow rate was varied. However, in this case ethane and ethene are not produced when the flow rate of the feed was very high, suggesting that these products are formed via secondary reactions. These observations indicate that ethane is probably formed as both a primary product and a secondary product, so the situation could be more complicated than supposed normally. It was noted earlier in this thesis that Brønsted acidity might be involved in the formation of this product.

6.4 The effect of the reaction temperature

The effect of the reaction temperature on the catalytic activity of Mo/HZSM-5 was studied using the catalyst with a zeolite crystallinity of 61% with a molybdenum loading of 2 wt%. The results of the effect of the reaction temperature on the activity and stability of Mo/H-ZSM-5 catalysts are shown in Figure 6.20.
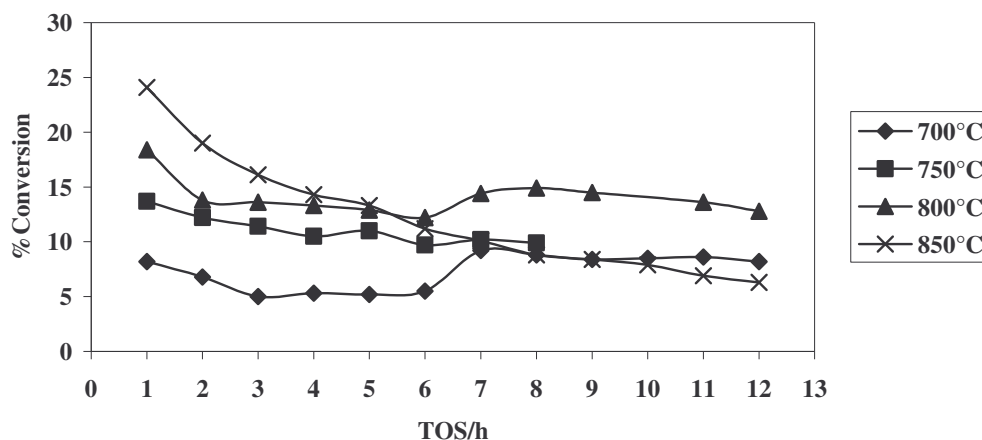

Figure 6.20 The effect of the reaction temperature on the catalytic conversion and stability of 2%Mo/H-ZSM-5 catalysts with a crystallinity of 61% for the nonoxidative conversion of methane at 750°C.

From these results, it can be deduced that the initial conversion of methane increased with increasing reaction temperature. However, deactivation was also favoured by the high reaction temperature. The effect of the reaction temperature on the catalytic properties of 2%Mo/H-ZSM-5 for a time on stream of 1 h is summarised in Table 6.7.

Table 6.7 The effect of the reaction temperature on the catalytic performance of 2%Mo/H-ZSM-5 catalysts with a crystallinity of 61% at 750°C and a time on stream of 1 h

Reaction temperature (^{o}C)	%Conversion	%Selectivity			Ethene/Ethane ratio
		C$_2$ hydrocarbons	Aromatics	Coke	
700	8.2	1.4	17.2	81.4	0.6
750	13.7	1.7	33.0	65.2	1.8
800	18.4	1.6	31.7	66.6	3.0
850	24.1	2.0	23.9	74.1	5.7

There is a near-linear increase in the conversion of methane with increasing reaction temperature as shown in Figure 6.21.
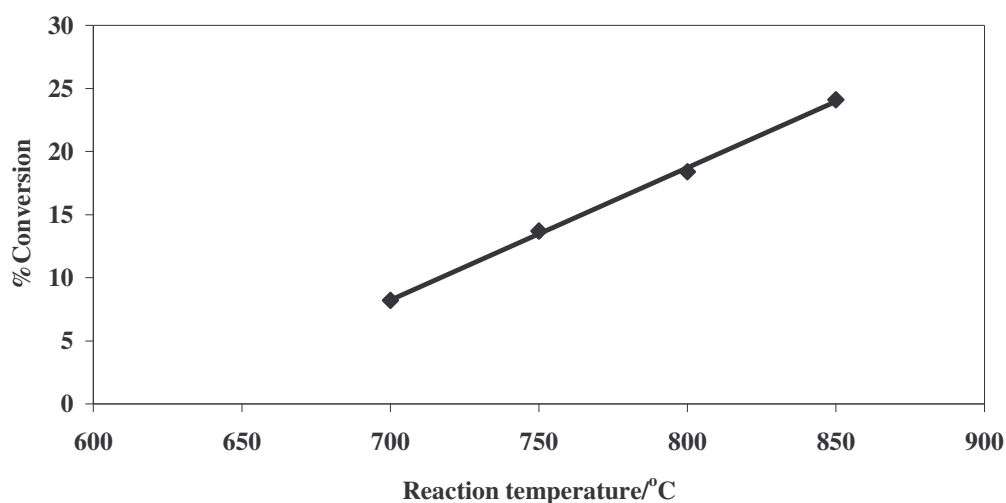

Figure 6.21 The effect of the reaction temperature on the %conversion of methane over 2%Mo/H-ZSM-5 catalysts with a crystallinity of 61%.

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The apparent activation energy determined using the Arrhenius equation was found to be 64.5 kJ /mol, (from Figure 6.22). This value of the activation energy is close to the previously reported value of 71.4 kJ/mol [25]
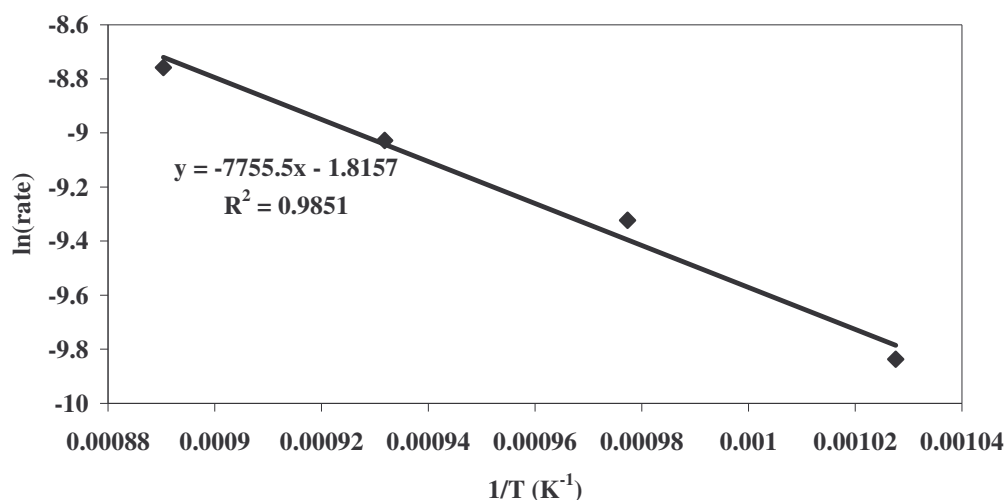

$y = -7755.5x - 1.8157$
$R^2 = 0.9851$

Figure 6.22 The Arrhenius plot from conversion of methane over 2%Mo/H-ZSM-5 catalysts with a crystallinity of 61%.

The effect of the reaction temperature on the selectivity for C_2 hydrocarbons for a time on stream of 1 h is shown in Figure 6.23, and for benzene and coke in Figure 6.24. The selectivity for C_2 hydrocarbons increased linearly with increasing reaction temperature. Thermodynamic calculations show that the equilibrium conversion of methane to benzene will increase as the reaction temperature increased [1]. The equilibrium conversions of 11.3, 15.8, 21, 27 and 33% were predicted for methane to benzene at 700, 750, 800, 850 and 900°C, respectively [28]. This suggests that the selectivity for aromatics will increase with increasing reaction temperature. The selectivity to aromatics increased with increasing reaction temperature until temperatures between 750 and 800°C and then decreased for temperatures above 800°C as shown in Figure 6.24.
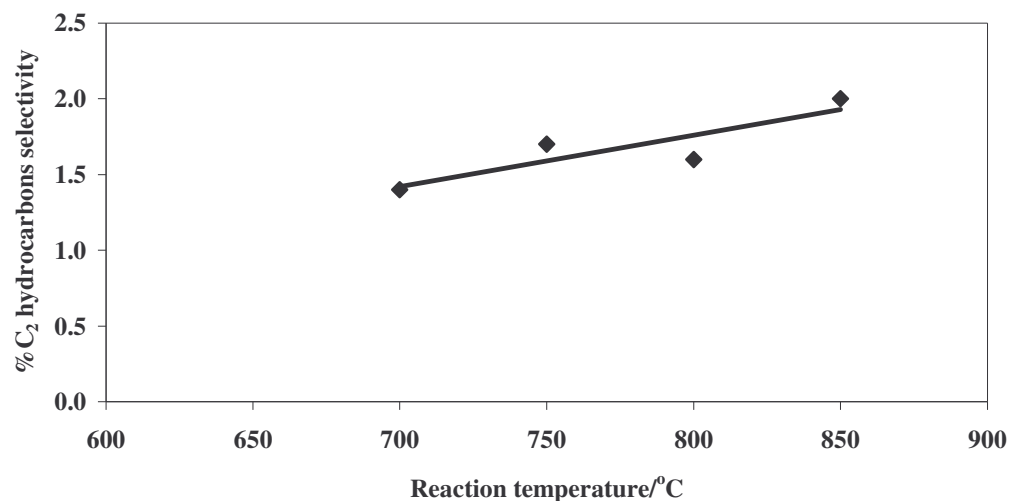
Figure 6.23 The effect of the reaction temperature of the selectivity for C_2 hydrocarbons from the nonoxidative conversion of methane over 2%Mo/H-ZSM-5 catalysts with a crystallinity of 61%, after a time on stream of 1 h.
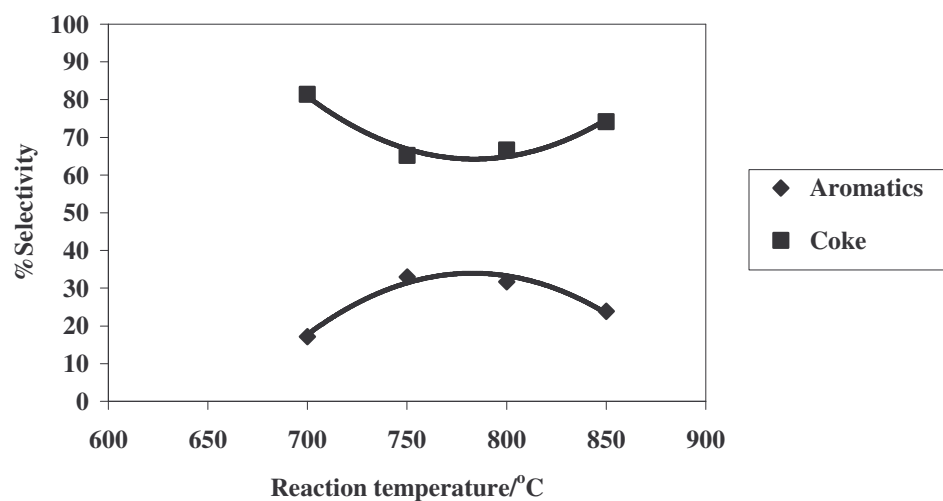

Figure 6.24 The effect of the reaction temperature of the %selectivity for aromatics and coke from the nonoxidative conversion of methane over 2%Mo/H-ZSM-5 catalysts with a crystallinity of 61%, after a time on stream of 1 h.

However, because the formation of coke is favoured at higher reaction temperatures, this is not realised in practice. Figure 6.24 also shows that the selectivity for aromatics and coke are dependent on each other, and coke is more favoured at temperatures above 800°C.

The used catalysts were characterised by means of temperature programmed oxidation (TPO) and the results obtained are shown in Figure 6.25.
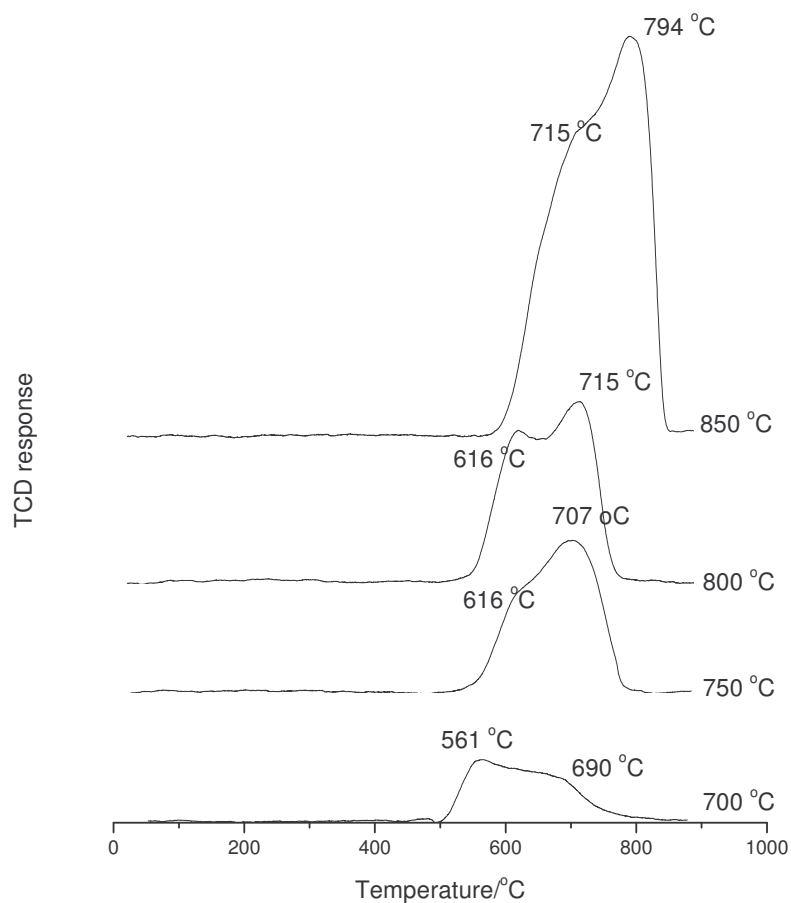

Figure 6.25 The TPO profiles of 2%Mo/H-ZSM-5 catalysts used for the aromatisation of methane at different reaction temperatures.

The profiles exhibited two oxidation peaks, one at lower temperature and one at a higher temperature. As already mentioned, the peak at a lower temperature is due to the oxidation of carbon associated with molybdenum species, while the peak at a higher temperature is due to the oxidation of the carbon associated with the Brønsted acid sites. At lower reaction temperatures, the peak due to the carbon associated with Mo species is more intense than the peak due to the carbon deposited on the Brønsted sites. As the reaction temperature is increased, the intensity of the peak due to the carbon deposited on Brønsted acid sites increased more than the peak due the carbon associated with molybdenum species. This indicates that the formation of carbonaceous species is favoured by the increasing reaction temperature. Therefore the formation of carbonaceous coke was responsible for most of the observed deactivation of the catalysts.

Characterisation of the used catalyst by powder X-ray diffraction shows that the zeolite framework was maintained even at high reaction temperatures as shown in Figure 6.26. However, there was a decrease in the intensity of the peak characteristic of ZSM-5 (between 23 and 25 $^o2\theta$), suggesting a decrease in the crystallinity of the catalyst. These results together with those for the TPO studies indicates that the rapid rate of deactivation observed for the sample reacting at high temperature was due to the high level of coke deposition and the partial collapse of the zeolite framework.
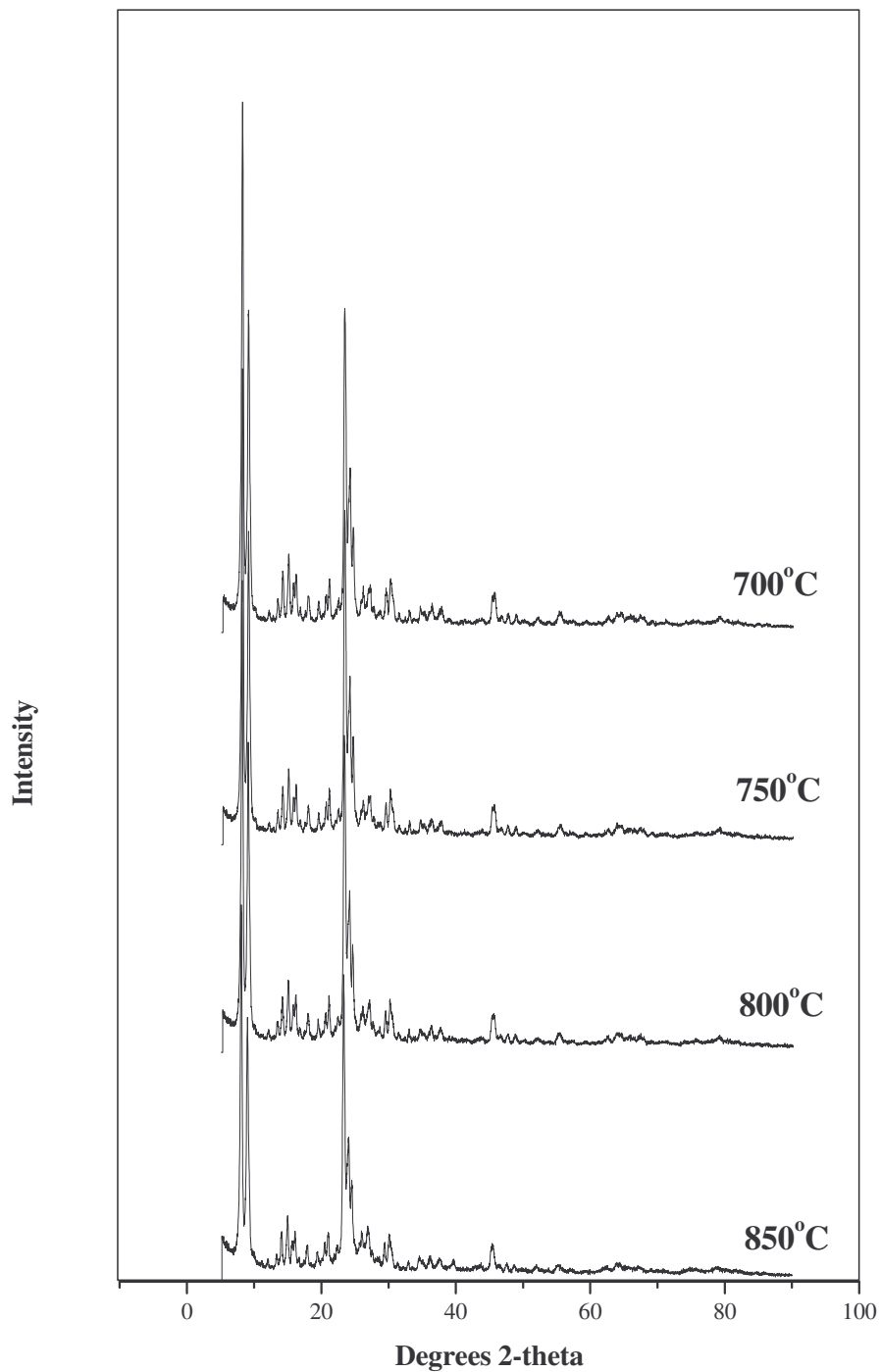
Figure 6.26 The X-ray diffractograms of 2%Mo/H-ZSM-5 catalysts used for the aromatisation of methane at different reaction temperatures.

6.5 The effect of the percentage XRD crystallinity

The effect of the percentage XRD crystallinity on the catalytic performance of ZSM-5 zeolite-based materials has been reported for the cracking of *n*-hexane [29] and propane [29] and for the aromatisation of propane [30,31]. In this study the effect of the percentage XRD crystallinity of ZSM-5 on the catalytic performance of Mo/H-ZSM-5 catalysts was investigated. H-ZSM-5 samples with percentage XRD crystallinities ranging from 5 to 97% were impregnated with molybdenum as described in Chapter 5. The molybdenum loading of 2 wt.% was used for this study.

The results showing the effect of the percentage crystallinity of H-ZSM-5 on the catalytic performance of Mo/H-ZSM-5 for the aromatisation of methane at 750°C are shown in Figure 6.27.
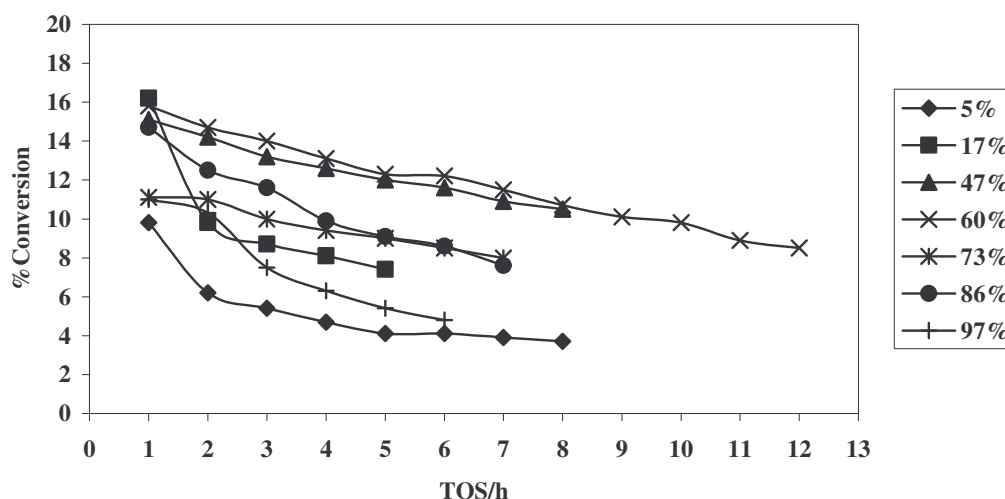

Figure 6.27 The effect of %XRD crystallinity on the stability of 2%Mo/H-ZSM-5 catalysts during the conversion of methane at 750°C.

All the catalysts deactivated with increasing time on stream and the deactivation was independent of percentage XRD crystallinities of the catalysts. The effect of

the percentage XRD crystallinity on the catalytic conversion of methane is summarised in Table 6.8 and illustrated in Figure 6.28, for a time on stream of 5 h. Data recorded after a time on stream of 5 hours was used for because the induction period is most likely to be complete by then.
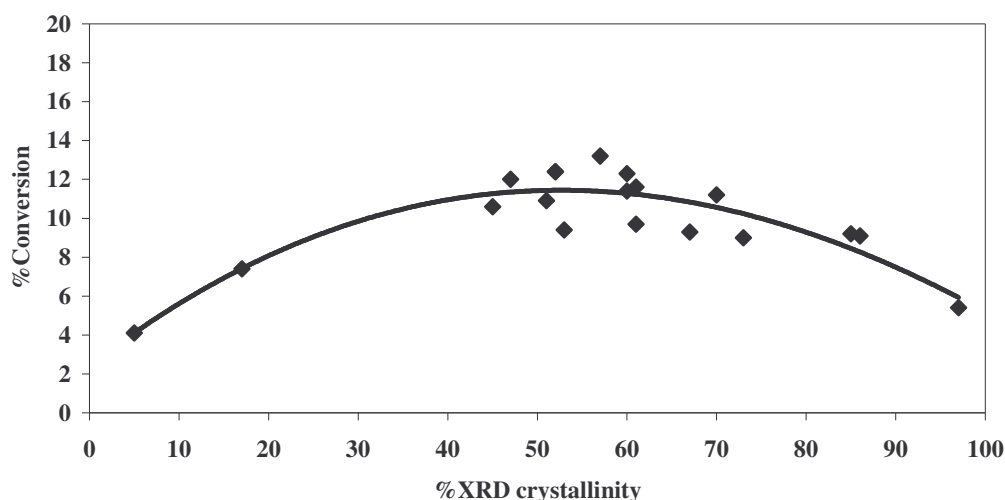

Figure 6.28 The effect of the %XRD crystallinity on the percentage conversion of methane over Mo/H-ZSM-5 catalysts at 750°C, after a time on stream of 5 h.

There is an increase in the percentage conversion of methane with increasing percentage XRD crystallinity until a maximum conversion was attained for crystallinities between 40 and 60% followed by a decrease in conversion for higher crystallinities. Similar conclusions were reached in the studies on the aromatisation of propane over Ga/H-ZSM-5 catalysts of different crystallinities [30,31] and the work on the cracking of hexane [29] over H-ZSM-5-based catalysts. This decrease at higher %XRD crystallinities was attributed to the fact that the crystallite size of ZSM-5 increased with increasing crystallinity of the catalysts, and this imposed diffusion restriction on the products [29,30].

Table 6.8 The effect of the %XRD crystallinity of H-ZSM-5 on the catalytic performance of Mo/H-ZSM-5 catalysts for the nonoxidative conversion of methane at 750°C for a time on stream of 5 h

| Catalyst | %XRD crystallinity | %Conversion | %Selectivity | | | Ethene/Ethane ratio |
			C$_2$ hydrocarbons	Aromatics	Coke	
M1	5	4.1	6.9	20.0	73.0	∞
M2	17	7.4	8.9	9.9	81.3	7.1
M3	45	10.6	5.6	51.5	42.9	3.7
M4	47	12.0	4.5	80.3	15.1	4.6
M5	51	10.9	6.3	82.6	11.1	3.8
M6	52	12.4	4.1	49.5	46.3	3.1
M7	53	9.4	4.0	46.3	49.7	3.4
M8	57	13.2	4.8	54.2	41.0	3.4
M9	60	11.4	4.7	49.2	46.1	3.7
M10	60	12.3	4.9	64.4	30.7	3.5
M11	61	11.6	3.9	56.6	39.4	2.3
M12	61	9.7	4.1	40.8	55.1	2.7
M13	67	9.3	6.9	47.3	45.8	4.3
M14	70	11.2	5.5	63.2	31.2	3.2
M15	73	9.0	5.5	69.2	25.3	2.2
M16	85	9.2	5.1	63.0	31.9	2.0
M17	86	9.1	6.4	85.1	8.4	5.4
M18	97	5.4	14.1	64.1	21.9	9.1

In order to observe the effect of the percentage XRD crystallinity on the selectivity to various products, a comparison of the catalytic performance of different catalysts was done at a conversion of about 10%. The effect of the percentage XRD crystallinity on the product selectivity is shown in Figure 6.29, for a conversion of 10%. The selectivity for C$_2$ hydrocarbons did not change significantly with increasing percentage XRD crystallinity, as shown in Figure 6.29. There is a general increase in the selectivity to aromatics with increasing percentage XRD crystallinity of the catalysts, while on the other hand the selectivity for coke decreased. There is an inverse relation between the selectivity for aromatics and the selectivity for coke.
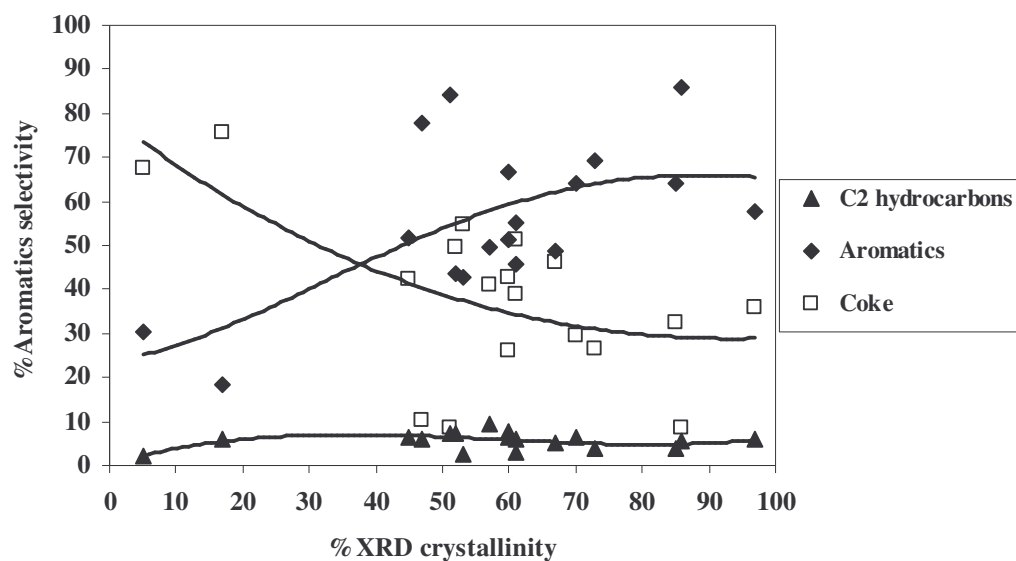
Figure 6.29 The effect of the %XRD crystallinity on the product selectivity from the conversion of methane at $750^{\circ}C$, for a conversion of about 10%.

The variation of the ethene/ethane ratio with the percentage XRD crystallinity of the catalysts is shown in Figure 6.30, for a conversion level of 10%.
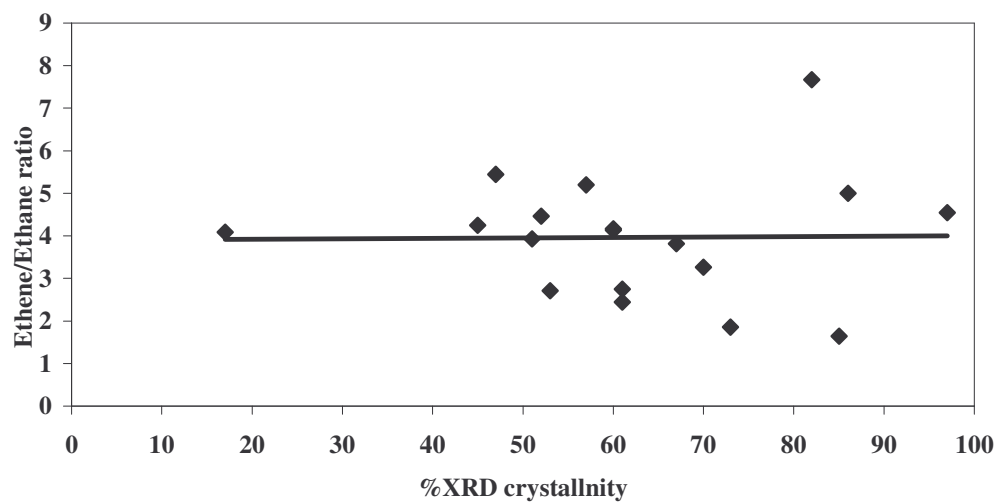

Figure 6.30 The effect of the %XRD crystallinity on the ethene/ethane ratio from the conversion of methane at $750^{\circ}C$, for a conversion of about 10%.

The results show that there is no discernable trend of the ethene/ethane ratios with an increase in the crystallinity of the catalysts, due to the observed scatter.

It was also interesting to note that some of the carbonaceous materials formed during the aromatisation of methane comprised of carbon nanotubes as shown in Figure 6.31. The formation of carbon nanotubes was also reported by other researchers [32] for 2%Mo/H-ZSM-5 pretreated by microwave heating.
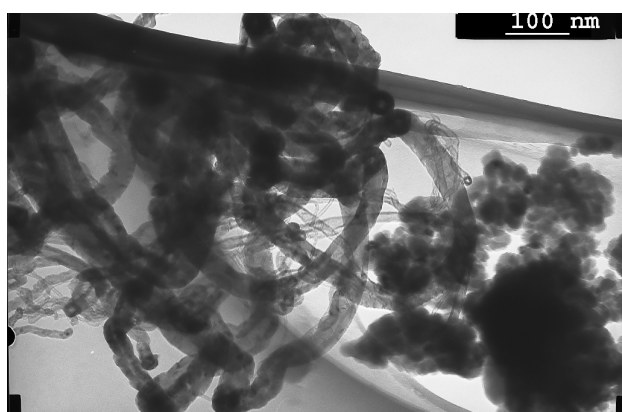

Figure 6.31 A TEM micrograph of the carbon nanotubes formed from the aromatisation of methane over Mo/H-ZSM-5 catalyst (with a crystallinity of 60%) at 750°C.

6.6 The effect of the SiO_2/Al_2O_3 ratio

It is known that the SiO_2/Al_2O_3 ratio of zeolites is related to their acidity [33,34]. On the other hand, Brønsted acidity is said to play a significant role in the aromatisation step during the nonoxidative conversion of methane [1]. Therefore, the effect of SiO_2/Al_2O_3 ratio of the H-ZSM-5 on the catalytic performance of Mo/H-ZSM-5 catalysts was also studied. H-ZSM-5 samples with

SiO$_2$/Al$_2$O$_3$ ratios ranging from 60 to 540 were used in the preparation of Mo/H-ZSM-5 catalysts.

The effect of the SiO$_2$/Al$_2$O$_3$ ratios on the acidity of the 2%Mo/H-ZSM-5 catalysts is shown in Figure 6.32.

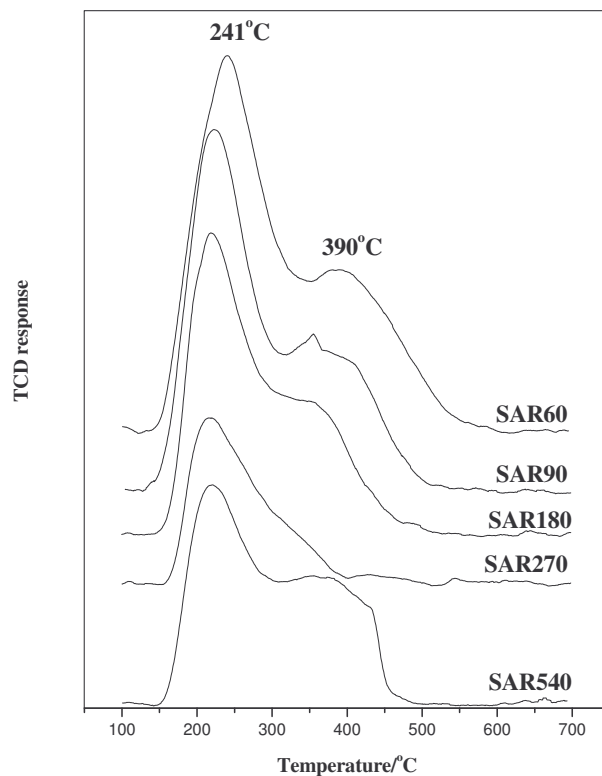**Figure 6.32**   TPD profiles of 2%Mo/H-ZSM-5 catalysts with different SiO$_2$/Al$_2$O$_3$ ratios.

Two peaks were observed in the NH$_3$-TPD profiles of the sample, one at a lower temperature (241°C) and one at a higher temperature (390°C). It should be noted that the SiO$_2$/Al$_2$O$_3$ ratios that are reported here were adopted from the ratios of the respective components used in the synthesis mixtures used in the preparation of these zeolites. There is a significant decrease in the intensity of the desorption

profiles for SiO_2/Al_2O_3 ratios above 180. This is due to the lower content of Al atoms in the framework of such samples.

The effect of the SiO_2/Al_2O_3 ratio on the physicochemical properties of Mo/H-ZSM-5 catalysts is shown in Table 6.9.

Table 6.9 A summary of the physicochemical properties of 2%Mo/H-ZSM-5 catalysts with different SiO_2/Al_2O_3 ratios

Sample	SiO_2/Al_2O_3	%XRD crystallinity	BET surface area (m^2/g)	Pore Volume (cm^3/g)	%Reducibility
SAR60	60	56	391	0.46	72
SAR90	90	61	396	0.26	93
SAR110	110	61	372	0.21	59
SAR180	180	77	389	0.21	45
SAR270	270	91	417	0.22	71
SAR540	540	94	420	0.22	54

The BET surface areas decreased with increasing SiO_2/Al_2O_3 ratio up to 110 and then increased with further increase in the SiO_2/Al_2O_3 ratio. Similarly the pore volumes decreased up to a ratio of 110 but remained almost unchanged when SiO_2/Al_2O_3 ratio was further increased. The reducibility of the Mo/H-ZSM-5 catalysts with different SiO_2/Al_2O_3 ratios was studied by means of TPR and the results are also summarised in Table 6.9 and the resulting TPR profiles are shown in Figure 6.33. The results show that the reducibility of the samples is affected by the SiO_2/Al_2O_3 ratio of the sample. The TPR profiles of the samples showed two reduction peaks, one at lower temperatures and one at higher temperatures and the position of these peaks was dependent on the SiO_2/Al_2O_3 ratio of the sample. As the SiO_2/Al_2O_3 ratio of the sample increased, the intensity of the molybdenum species that reduced at higher temperatures decreased, while that for the species that reduce at a lower temperature increased, and the peak became more symmetrical. It has also been shown that the coordination mode of the molybdenum species is also dependent on the SiO_2/Al_2O_3 ratio of the zeolite [35].
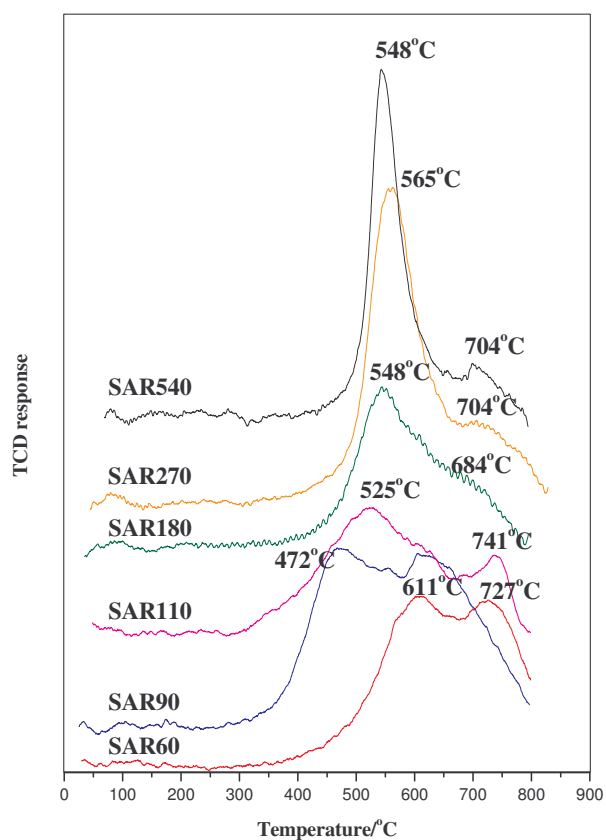
Figure 6.33 The TPR profile of 2%Mo/H-ZSM-5 catalysts with different molybdenum.

Therefore, it is possible that the change in the TPR profiles is due to the changing coordination mode of the molybdenum species.

The effect of the SiO_2/Al_2O_3 ratio on the catalytic conversion of methane over Mo/H-ZSM-5 catalysts was investigated and the results are discussed below. The variation of the percentage methane conversion with increasing time on stream is shown in Figure 6.34, for catalysts with different SiO_2/Al_2O_3 ratios.

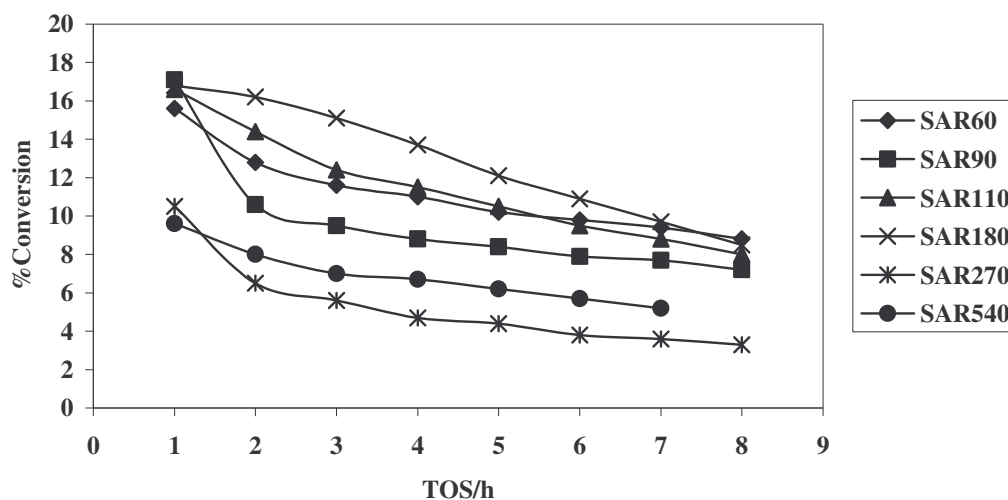**Figure 6.34** The effect of the SiO_2/Al_2O_3 on the catalytic conversion and stability of 2%Mo/H-ZSM-5 catalysts for the conversion of methane at $750^{\circ}C$.

All the catalysts deactivated with increasing time on stream. The highest activities were observed for the sample with a SiO_2/Al_2O_3 ratio of 180 and the activities decreased when the SiO_2/Al_2O_3 ratio was increased above 180. This effect of the SiO_2/Al_2O_3 ratio is more clearly shown in Figure 6.35 and Table 6.10, for a time on stream of 5 h.

Table 6.10 The effect of the SiO_2/Al_2O_3 on the catalytic performance of 2%Mo/H-ZSM-5 catalysts for the conversion of methane at $750^{\circ}C$, after a time on stream of 5 h

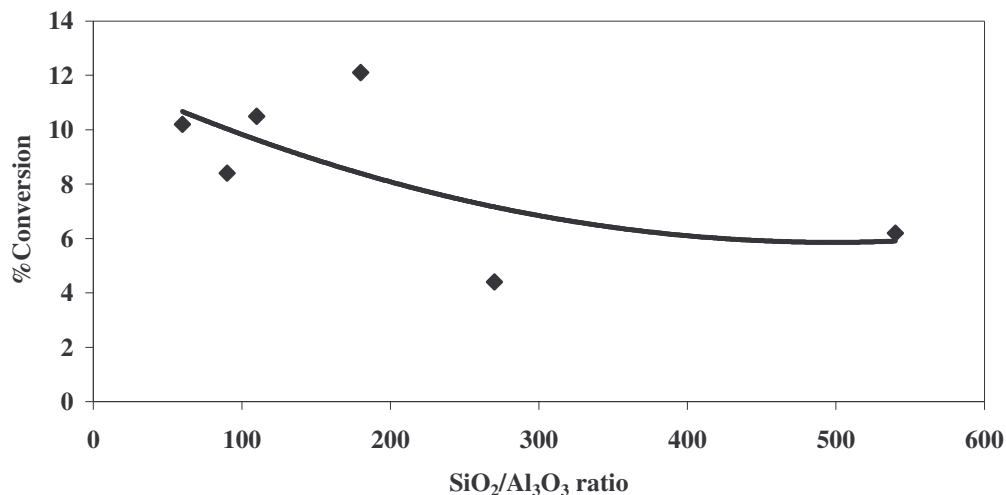| Sample | %XRD crystallinity | SiO_2/Al_2O_3 ratio | %Conversion | %Selectivity | | | Ethene/Ethane ratio |
				C_2 hydrocarbons	Aromatics	Coke	
SAR60	56	60	10.2	5.8	88.3	5.9	2.3
SAR90	60	90	8.4	6.2	66.5	27.2	1.9
SAR110	61	110	10.5	6.3	62.3	31.4	1.9
SAR180	77	180	12.1	6.1	74.9	19.0	4.1
SAR270	91	270	4.4	15.2	45.2	39.6	8.5
SAR540	94	540	6.2	11.2	62.4	26.4	5.2

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Figure 6.35 The effect of the SiO_2/Al_2O_3 ratio on the catalytic conversion of methane over 2%Mo/H-ZSM-5 catalysts at 750°C, after a time on stream of 5 h.

It should also be noted that the crystallinity of the samples was also varied (see Table 6.9) and as a result the observations cannot be attributed only to the SiO_2/Al_2O_3 ratio of the catalysts. The conversion of methane decreased with an increase in the SiO_2/Al_2O_3 ratio of the catalysts. The effect of the SiO_2/Al_2O_3 ratio on the product selectivity is shown in Figure 6.36. The selectivity for C_2 hydrocarbons was not affected by the SiO_2/Al_2O_3 ratio of the catalysts, while the selectivity for aromatics decreased as the SiO_2/Al_2O_3 ratio increased. The highest selectivity for aromatics was observed when the SiO_2/Al_2O_3 ratio of the sample was 60. Liu et al [36] reported that the highest benzene formation rates were obtained when the SiO_2/Al_2O_3 ratio of H-ZSM-5 was 40. The selectivity for coke, on the other hand, increased with increasing SiO_2/Al_2O_3 ratio of the catalysts. It is also noted that the ethene/ethane ratio changed as the SiO_2/Al_2O_3 ration of the catalysts increased. Higher ethene/ethane ratios were observed for catalysts with higher SiO_2/Al_2O_3 ratios, which is also an indication that less ethane is produced when the amount of Brønsted acid sites of the catalysts was lowered.
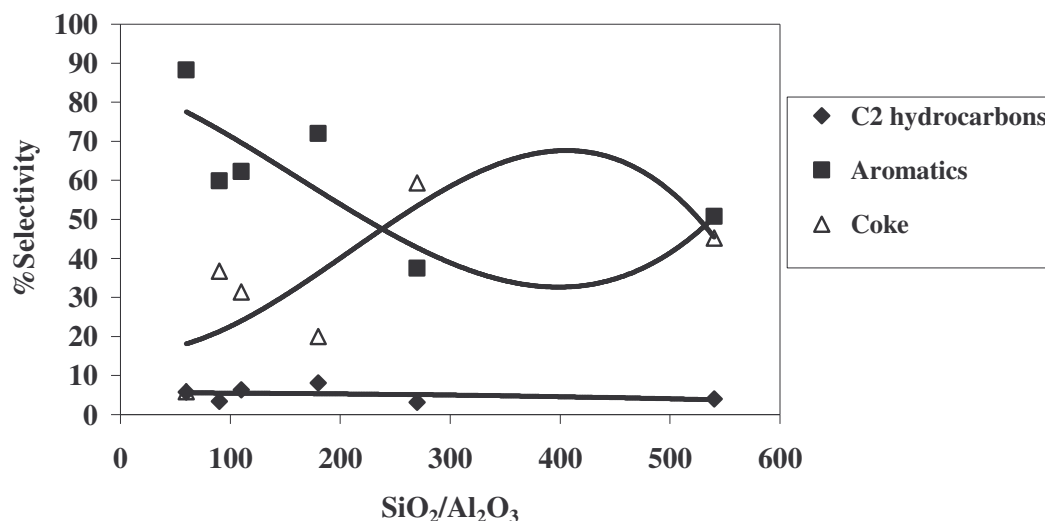
Figure 6.36 The effect of the SiO_2/Al_2O_3 ratio on the selectivity for C_2 hydrocarbons from the conversion of methane over 2%Mo/H-ZSM-5 catalysts, for a conversion of 10% at 750°C.

6.7 The effect of the molybdenum precursor

One of the most common methods or preparing Mo/H-ZSM-5 catalysts is via impregnation of the zeolite with solutions of molybdenum salts. The source of molybdenum which is commonly used by various researchers is ammonium heptamolybdate and other molybdenum sources are rarely employed. Therefore, the effect of the type of the molybdenum precursor used in the preparation of Mo/H-ZSM-5 catalysts on their catalytic properties was investigated in this study. Three molybdenum sources, namely, ammonium molybdate (AM), ammonium heptamolybdate (AHM) and dodecylmolybdo-phosphoric acid (DDMP), were used as molybdenum sources for the preparation of Mo/H-ZSM-5 catalysts. The %XRD crystallinity of the zeolite used in these preparations was 70.

The effect of the molybdenum source on the catalytic conversion of methane is shown in Figure 6.37. The results suggest that the molybdenum source has little

influence on the catalytic activity of Mo/H-ZSM-5 catalysts, although the catalyst prepared using DDMP was slightly less active. Burns et al. [37] recently reported that when the catalysts were prepared using DDMP the conversion was lowered. Therefore, the slightly lower activity observed for the catalyst prepared using DDMP may be attributed to the presence of phosphorous in the catalyst, which is co-introduced with molybdenum during the preparation.   Figure 6.37 also suggests that the molybdenum source did not influence the deactivation rate of the catalysts.
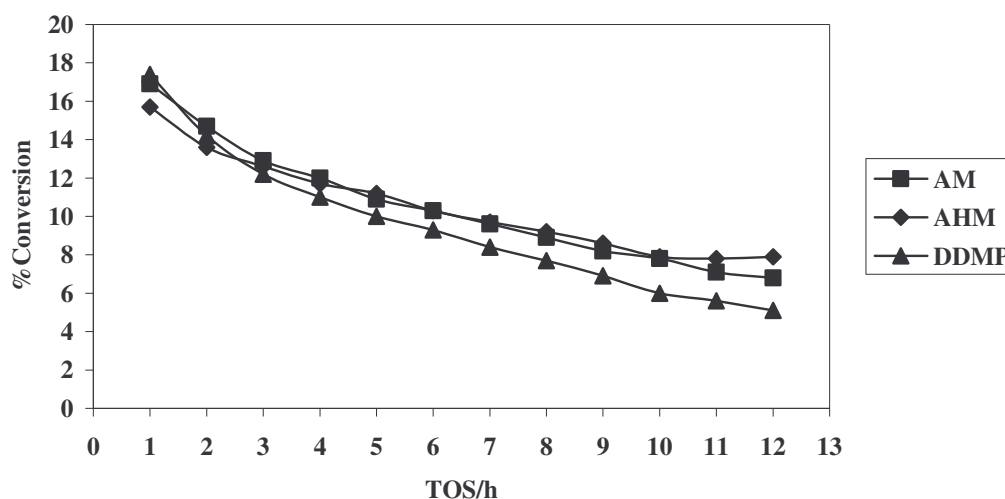

Figure 6.37   The effect of the molybdenum precursor on the conversion and stability of 2%Mo/ H-ZSM-5 catalysts for the conversion of methane at 750°C.

The catalytic product selectivities of the catalysts were compared at a conversion of about 10% in order to establish the influence of the molybdenum source and these results are shown in Figure 6.38.
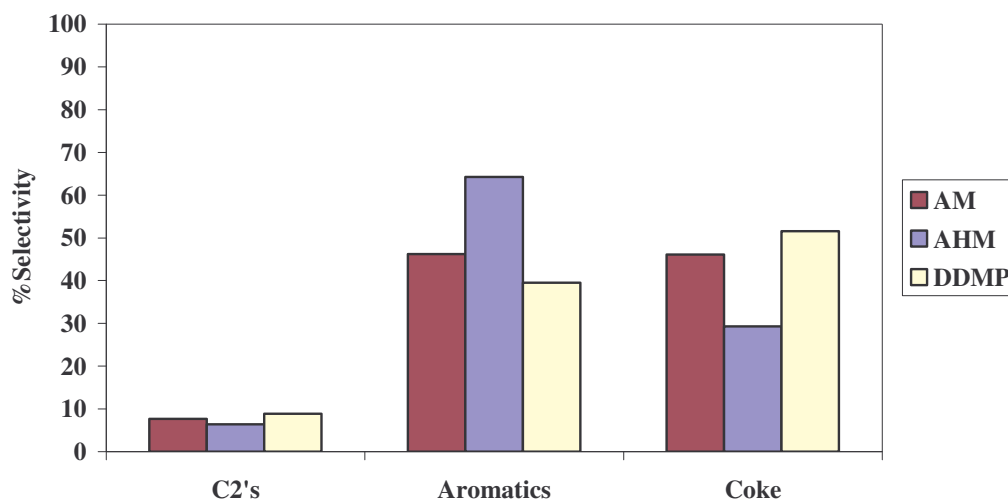
Figure 6.38 The effect of the precursor of molybdenum on the product selectivity of 2%Mo/H-ZSM-5 for the conversion of propane at 750°C, for a conversion of 10%.

Although the catalytic conversion of methane was not significantly influenced by the type of the molybdenum source used, the product selectivities were clearly different for each molybdenum source. Selectivities for aromatics decreased in the order, AHM > AM > DDMP, while the reverse trend was observed for the selectivity to coke and C_2 hydrocarbons.

6.8 The effect of the catalyst preparation method

Two methods of preparing the Mo/H-ZSM-5 catalysts have consistently been reported in the literature. One is impregnation of H-ZSM-5 with solutions of ammonium heptamolybdate while another one involves preparing homogeneous physical mixtures of MoO_3 and H-ZSM-5 and calcining the mixture at higher temperatures. The %XRD crystallinity of H-ZSM-5 zeolite used in these preparations was 54%. These methods were discussed in Section 3.2.1. Some

researchers have indicated that the method of physical mixing resulted in the preparation of superior catalysts [38], while some other studies suggest that the two methods give catalysts with similar catalytic performances [39]. A comparative study of these two methods was performed in order to establish the effect of the catalyst preparation procedure on the catalytic performance of the resulting catalysts. The results showing the effect of the preparation method on the activity and stability on the Mo/H-ZSM-5 are shown in Figure 6.39. The results suggest that the catalyst prepared by physical mixing was more active than the catalysts prepared by impregnation. This observation is in line with the observations of Chen et al. [38]. The deactivation profiles of the two catalysts were very similar.

The selectivities for various products were compared at a conversion of about 10% and the results obtained are shown in Figure 6.40. These results indicate that the catalyst prepared by physical mixing was more selective for aromatics than the catalyst prepared by impregnation.
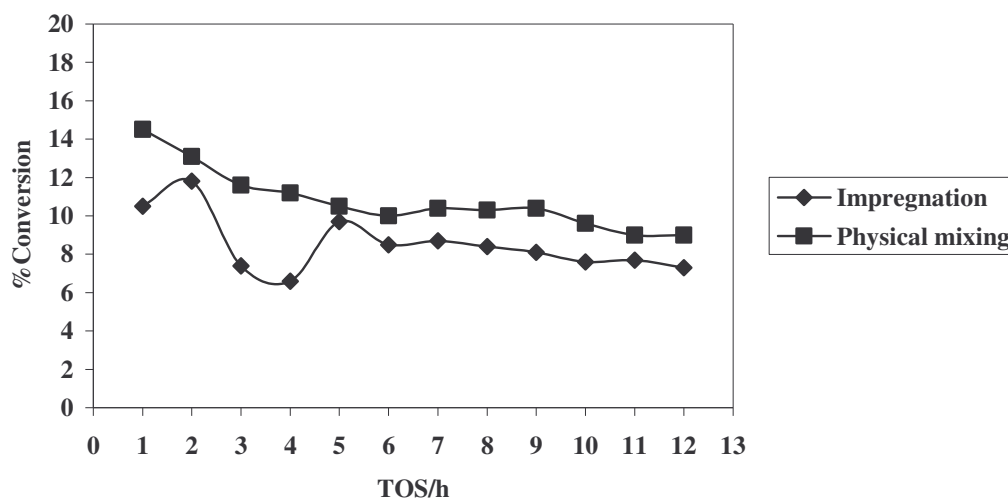

Figure 6.39 The effect of the method used for the preparation of 2%Mo/ H-ZSM-5 catalysts on the stability and conversion methane at 750°C.
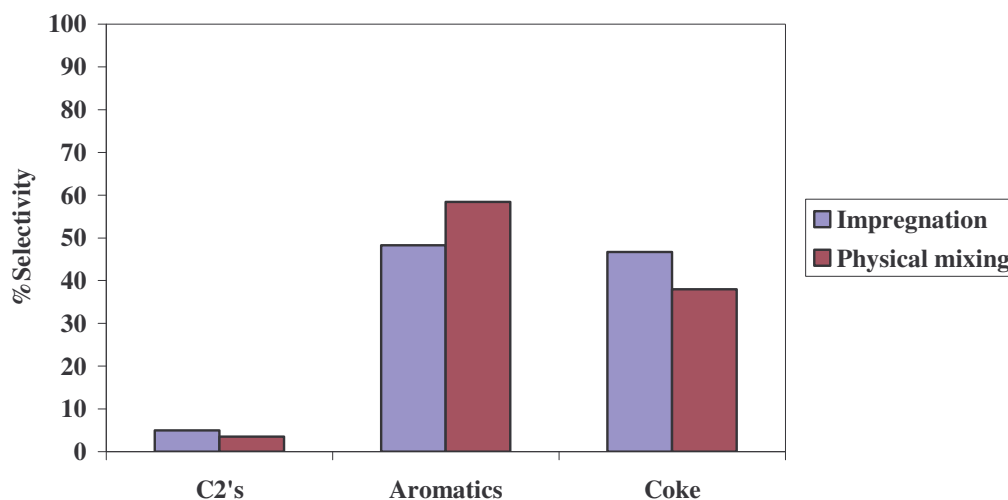
Figure 6.40 The effect of the catalysts preparation method on the product selectivity of 2%Mo/H-ZSM-5 for the conversion of propane at 750°C, for a conversion of 10%.

6.9 The effect of dopants

The effect of introducing other elements into the Mo/H-ZSM-5 has been discussed in Section 3.3.4. In this study the effect of elements that received little or no attention such as boron, silver and alkali metals was investigated. The results obtained are discussed in the following subsections.

6.9.1 Boron

Studies have shown that boron modifies the dispersion of Mo on the surface of alumina as well as the acidic properties of alumina [40,41]. Sayed et al. [42] have shown that introducing boron into the zeolite ZSM-5 by impregnation with HBO$_3$ decreased the acidity of the zeolite. Since it is accepted that acidity plays a significant role in the aromatisation of methane [1], a study was undertaken to investigate the influence of boron in the Mo/H-ZSM-5 catalyst system. The

crystallinity of the H-ZSM-5 sample used for these studies was 61%. The effect of boron on the conversion and stability of 2%Mo/H-ZSM-5 catalysts for the conversion of methane is shown in Figure 5.41. The catalytic activity and stability of the Mo/H-ZSM-5 catalyst is not influenced by the presence of boron even when the boron loading is varied.

The effect of boron on the selectivity to C_2 hydrocarbons and the ethene/ethane ratio is shown in Figure 5.42, for a conversion of about 10%. The selectivity to C_2 hydrocarbons and the ethene/ethane ratio increased in the presence of boron and this increase was also a function of the boron loading. The selectivity to C_2 hydrocarbons increased from about 4.5% in the absence of boron to about 9.5% for a boron loading of 0.2 wt%. On the other hand the ethene/ethane ratio increased from about 5 to about 9.5. The effect of boron on the selectivity to aromatics and coke is shown in Figure 6.43
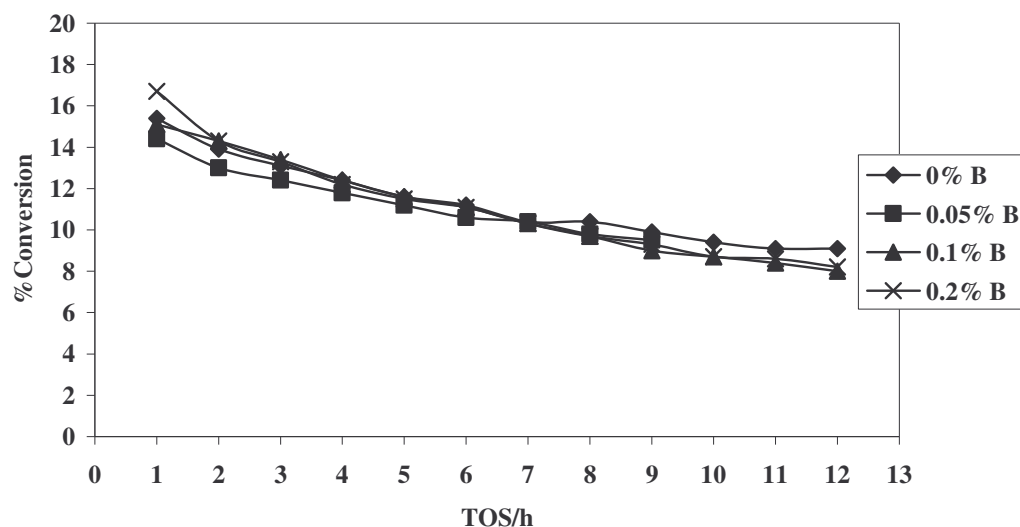
Figure 6.41 The effect of boron on the conversion and stability of Mo/H-ZSM-5 catalysts for the conversion of methane at 750°C.
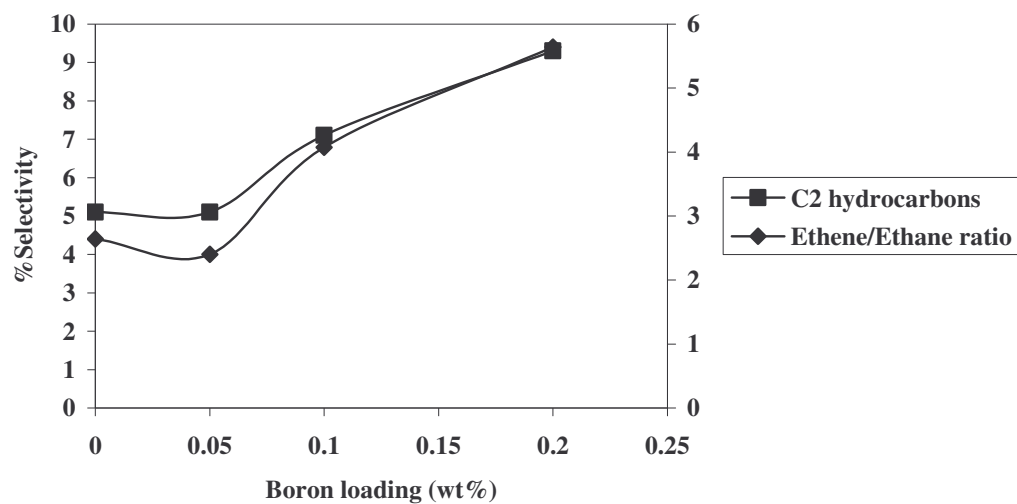
Figure 6.42 The effect of boron loading on the selectivity for C_2 hydrocarbons and the ethene/ethane ratio during the conversion of methane at $750^{\circ}C$ for a conversion of 10%.

Figure 6.43 The effect of boron loading on the selectivity for aromatics and coke during the conversion of methane at $750^{\circ}C$ for a conversion of 10%.

The selectivity to aromatics improved slightly from about 60% to 65% when the boron loading was 0.05 wt% but decreased when the boron content was

increased. On the other hand the selectivity to coke was increased when the boron loading was above 0.05 wt%.
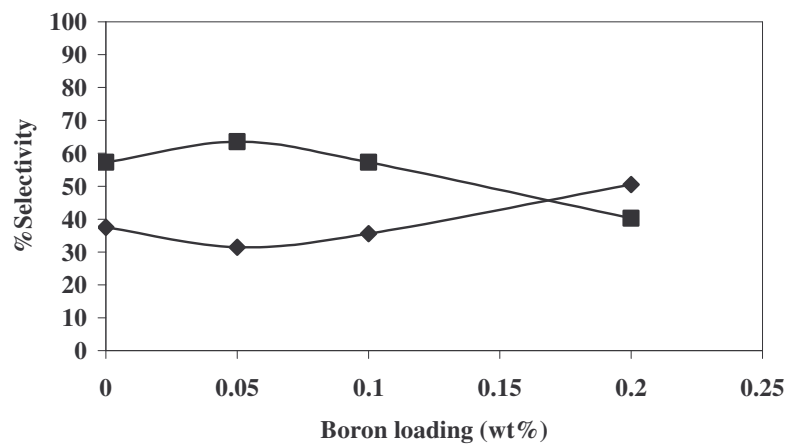
The effect of boron on the reducibility of molybdenum is shown in Figure 6.44. Two reduction peaks were observed at 604 and 778°C in the absence of boron. The intensity of the high-temperature peak decreased when boron was present and the peak was shifted to higher reduction temperatures. Furthermore the high-temperature peak was absent when the boron loading was 0.2 wt%. The TPR results are in agreement with the observed catalytic conversion results shown in Figure 6.44.
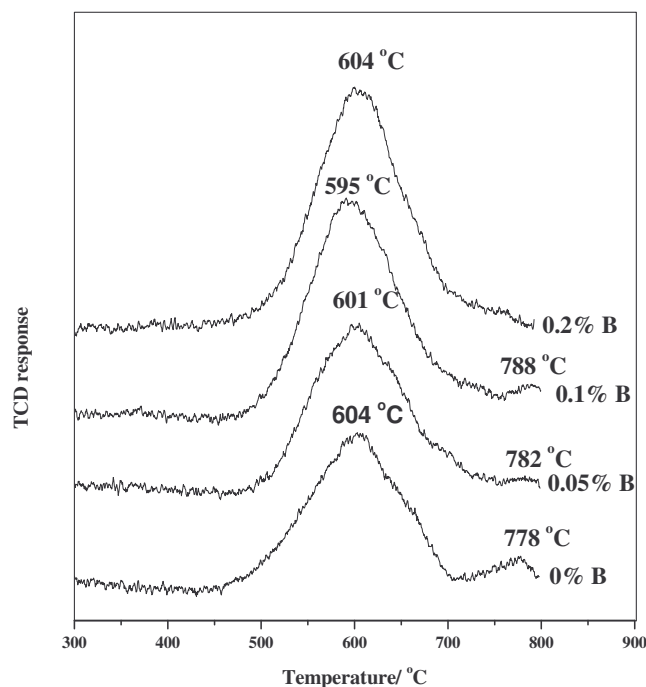
Figure 6.44 The TPR profiles for 2%Mo/H-ZSM-5 catalysts with different boron loadings.

The effect of boron on the acidity of the catalysts was investigated by means of temperature programmed desorption of ammonia. Figure 6.45 shows that the

intensity of the HT peak decreased upon addition of molybdenum, while the intensity of the LT peak remained unchanged. This observation indicates that the molybdenum species interacted with the Brønsted acid sites as previously reported by other researchers [1]. At the levels of boron used in this study the acidity of the Mo/HZSM-5 catalysts was not affected by the boron content, as shown in Figure 6.45.

Figure 6.45 NH$_3$-TPR profiles of 2%Mo/H-ZSM-5 catalyst with and without boron.

The DRS spectra of the catalysts doped with different amounts of boron are shown in Figure 6.46.
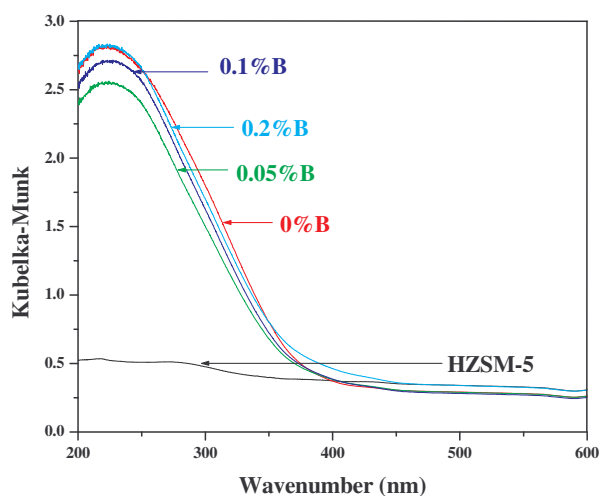
Figure 6.46 The UV-Vis diffuse reflectance spectra of 2%Mo/H-ZSM-5 catalysts with different boron loadings.

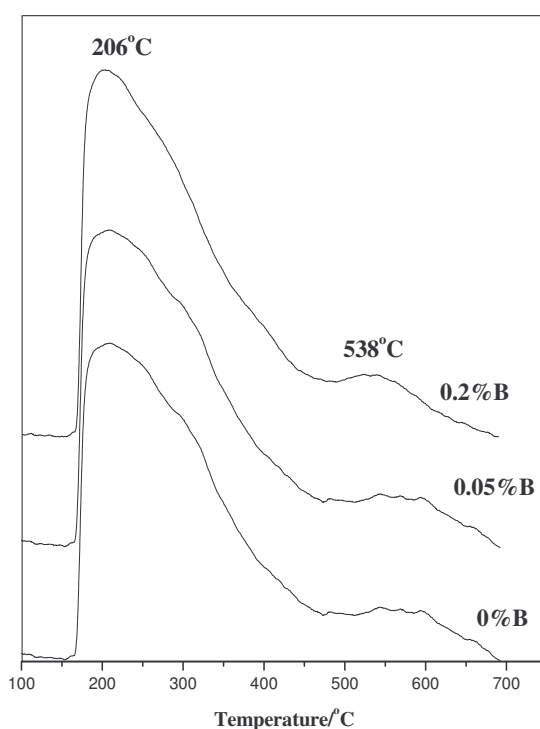The Mo/H-ZSM-5 catalysts with and without boron exhibits an absorption maximum at a wavelength of 225 nm, indicating the presence of tetrahedral molybdenum species. Therefore, at the concentrations reported in this study, boron does not influence the coordination mode of the molybdenum species.

As already indicated, the edge energy of the molybdenum species is related to their domain size. The variation of the edge energies with increasing boron loading is shown in Figure 6.47. The trend shown by the change in the edge energies with boron loading seems to correspond with the trends shown by the changes in the product selectivity with boron loading in Figures 6.42 and 6.43. Lower C_2 hydrocarbons and coke selectivities and higher aromatics selectivities were observed for the sample with the highest edge energy, in line with the trend in Figure 6.47. This suggests that boron modified the selectivity of the catalysts by influencing the electronic structure of the molybdenum species.
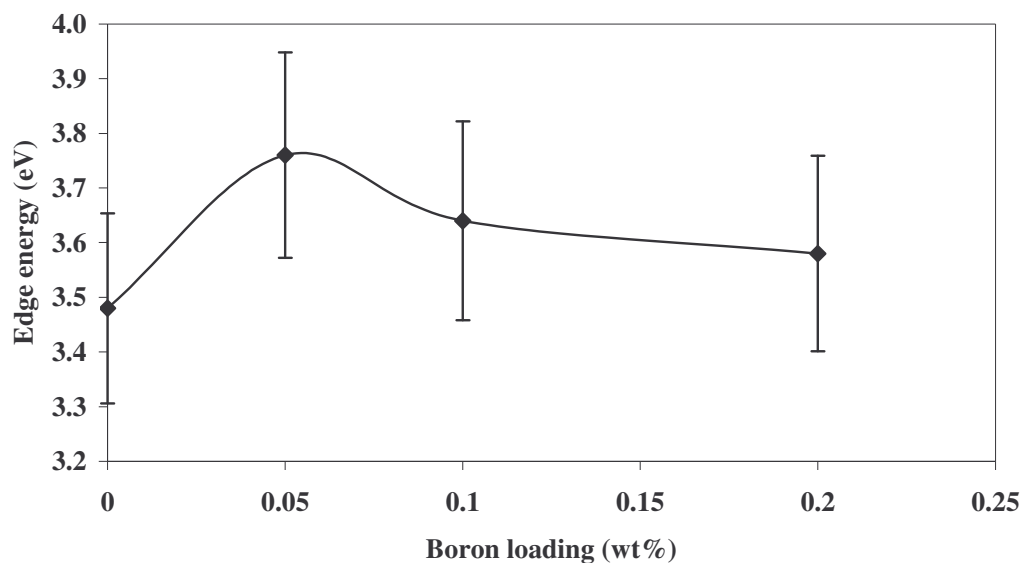
Figure 6.47 The variation of the absorption UV-vis absorption edge energies of Mo/H-ZSM-5 catalysts with the boron content.

6.9.2 Silver

It has been shown that the non-oxidative conversion of methane into higher hydrocarbons in the presence of ethylene can occur over Ag/Y and Ag/ZSM-5 catalysts [43,44]. On the other hand, Miao et al. [45] studied the non-oxidative activation of methane into C_2 hydrocarbons over Ag/ZSM-5 hydrocarbons. These studies indicated that methane is activated by the Ag^+ species by the heterolytic splitting of the C-H bond. On other hand, over the Mo/H-ZSM-5 catalysts methane is said to be activated by Mo_2C species. In this study the effect of the introduction of Ag^+ ions into the Mo/H-ZSM-5 catalysts was investigated. The effect of the presence of the silver ions on the catalytic activity of Mo/H-ZSM-5 catalysts is shown in Figure 6.48.
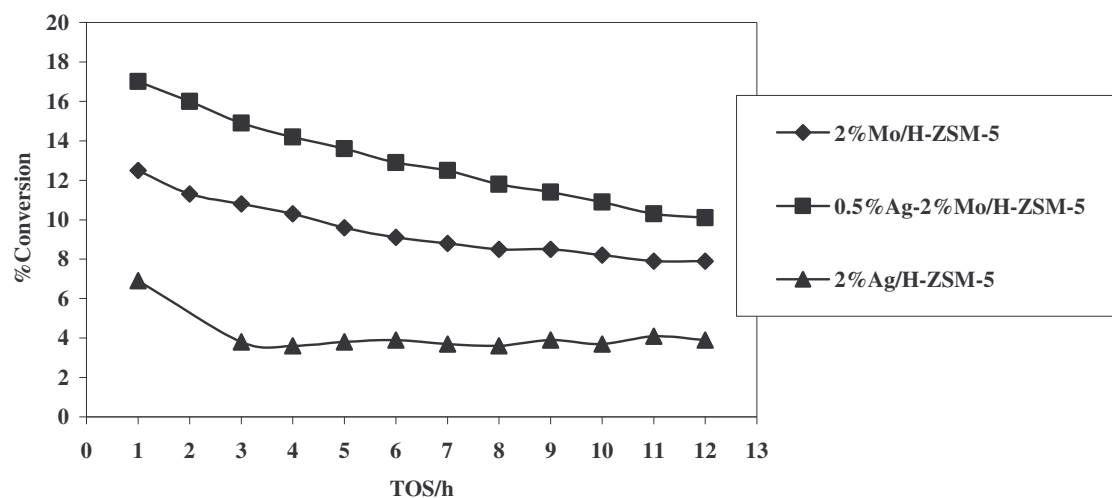
Figure 6.48 The effect of silver on the conversion and stability of Mo/H-ZSM-5 catalysts for the conversion of methane at 750°C.

The catalytic conversion of methane was increased by the presence of 0.5 wt.% Ag. It is also interesting to note that the Ag/H-ZSM-5 catalyst could activate methane, although with less effectiveness than the Mo/H-ZSM-5 catalyst. To study the effect of the presence of Ag species, on the product selectivity, the catalysts were compared at a conversion level of about 10% and the results are shown in Figure 6.49. The presence of silver species slightly improved the selectivity to aromatics. It is also interesting to note that the 2%Ag/H-ZSM-5 catalyst could only produce very small amounts of aromatics compared with the other catalysts even when the conversion was about 7%. The selectivity to coke over the 2%Mo/H-ZSM-5 was reduced when the Ag species were added to the catalyst, even though the selectivity for coke was high when 2%Ag/H-ZSM-5 was used.
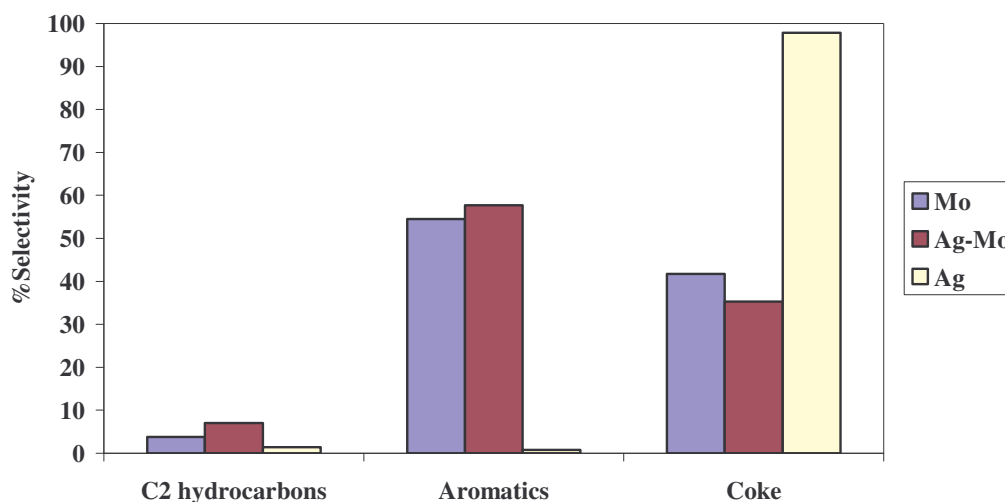
Figure 6.49 The effect of the silver ions on the product selectivity from the conversion of methane over Mo/H-ZSM-5 catalysts at 750°C, for a conversion of 10%.

The effect of the presence of silver on the acidity of Mo/H-ZSM-5 catalysts was studied by means of NH$_3$-TPD and the results are shown in Figure 6.50. The ammonia desorption profile of 2%Mo/H-ZSM-5 showed one peak at 232°C, and no peak at higher temperatures. This absence of the peak at higher temperatures indicates that the Brønsted acidity was effectively removed by the molybdenum species. However, upon addition of 0.5 wt% Ag into the Mo/H-ZSM-5, a peak at higher desorption temperature (446°C) was observed. It is also noted that the desorption profile of the 2%Ag/H-ZSM-5 sample showed two desorption peaks at 260 and 587°C. The results suggest that the silver ions enhanced the acidity of the Mo/H-ZSM-5 catalysts. Similar enhancement in acidity by dopants was reported for Cr [46]. Therefore, the observed improvement in the catalytic performance of 2%Mo/H-ZSM-5 catalysts upon addition of silver is likely due to the enhanced acidity of the catalyst.
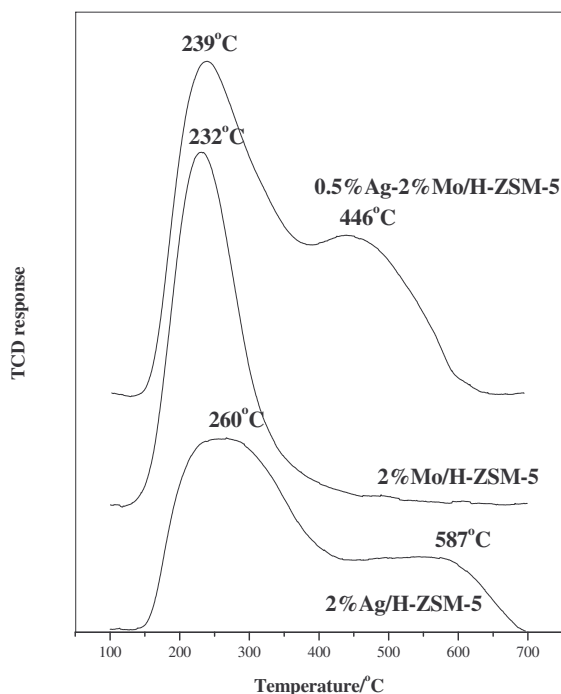
Figure 6.50 NH₃-TPD profiles of 2%Mo/H-ZSM-5 catalyst with and without silver ions.

The nature of the acid sites has been determined by pyridine adsorption using FT-IR spectroscopy, and the results are shown in Figure 6.51. The absorption bands associated with the adsorption of pyridine on H-ZSM-5 were observed at 1547 cm^{-1}, 1490 cm^{-1} and 1452 cm^{-1}. The pyridine adsorption band at 1547 cm^{-1} has been assigned to pyridine adsorbed on Brønsted acid site and the band at 1452 cm^{-1} is associated with pyridine adsorbed on Lewis acid sites [36]. On the other hand, the adsorption band at 1490 cm^{-1} has been attributed to the adsorption of pyridine on both the Brønsted and Lewis acid sites. Figure 6.51 shows that the intensity of these three bands was decreased when the metal additives were present, indicating decreased acidity due to the interaction of the acid sites with the Mo and/or Ag species. However, comparing the spectra of the 2%Mo/H-ZSM-5 with that of 0.5%Ag-2%Mo/H-ZSM-5 shows that the presence of Ag in Mo/H-ZSM-5 enhanced the acidity of the catalysts. This observation is in agreement with the results of NH₃-TPD and the catalytic results in Figure 6.50.

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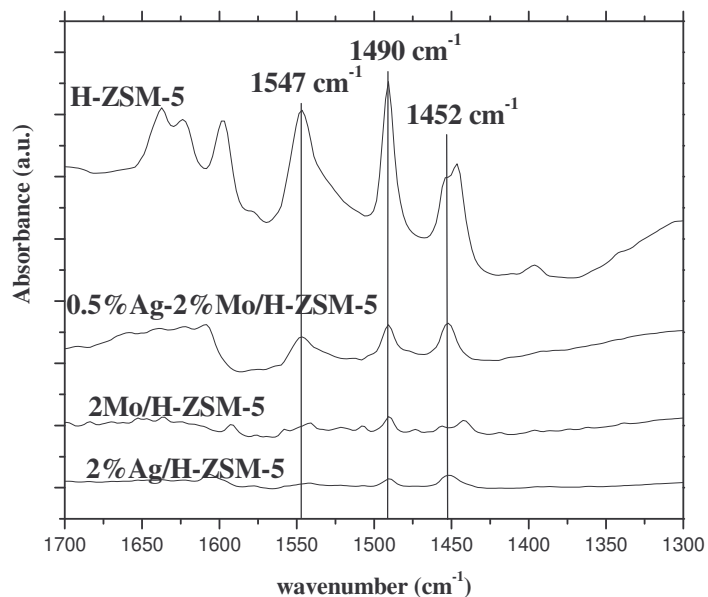
Figure 6.51 The IR spectra of adsorbed pyridine on H-ZSM-5 catalysts with and without metal additives.

6.9.3 Alkali metal ions

Since it is generally accepted that the Brønsted acidity of the zeolite plays a role in the aromatisation of methane, the effect of introducing alkali metal ions was also studied to evaluate their influence on the overall catalytic performance of Mo/H-ZSM-5 catalysts. The %XRD crystallinity of the H-ZSM-5 sample used in these studies was 57%. The effect of doping the Mo/H-ZSM-5 catalyst with Mo/H-ZSM-5 catalysts with the alkali metal ions is shown in Figure 6.52. The alkali metals were added in such a way as to keep a molar quantities equivalent to the molar alkali metal content in alkali molybdates (M_2MoO_4). As shown in Figure 6.52, the catalytic conversion of methane was lower in the presence of dopants. However, it was also noted that the reduction in activity of the catalysts was not severe in the presence of the alkali metal ions. There is no direct relation

between the influence of the alkali metal ions and their chemical properties derived from the periodic table of elements. The data are summarised in Table 6.11 for a time on stream of 5 h.
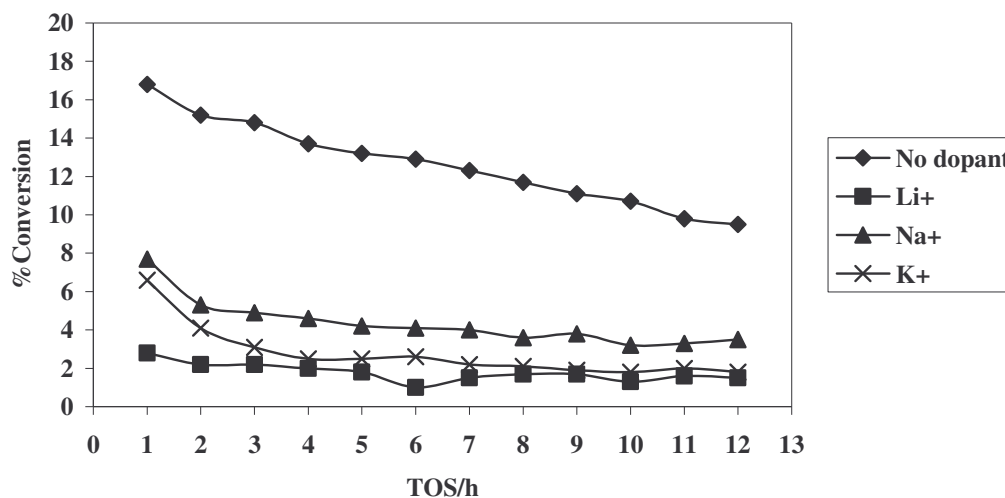
Figure 6.52 The effect of alkali metal ions on the conversion and stability of Mo/H-ZSM-5 catalysts for the conversion of methane at 750°C.

Table 6.11 The effect of alkali metal ions on the catalytic performance of 2%Mo/H-ZSM-5 catalysts for the conversion of methane at 750°C after a time on stream of 5 h

Dopant	%Conversion	%Selectivity		
		C$_2$ hydrocarbons	Aromatics	Coke
none	13.2	4.8	54.2	41.0
Li$^+$	1.8	10.1	0.0	89.9
Na$^+$	4.2	14.1	11.1	74.8
K$^+$	2.5	13.7	13.6	72.6

The lithium and potassium ions have a greater effect on the conversion than does sodium. While the conversion was lowered by the presence of the alkali metal

ions, the selectivity to C_2 hydrocarbons was increased and that of aromatic products was lowered. There was no ethane production in the presence of alkali metal ions. This could concur with the fact that once the active molybdenum species are formed ethylene became the primary product in the hydrocarbon stream and also is in line with ethane formation being influenced by the acidity of the zeolite.

In order to rationalise some of the observations made in the presence of alkali metal ions, the catalysts were characterised by various methods which are discussed below. The DRS spectra of the catalysts with and without the alkali metal ions are shown in Figure 6.53 including the spectrum of the parent H-ZSM-5.

Figure 6.53 UV-vis diffuse reflectance spectra of 2%Mo/H-ZSM-5 catalysts with and without alkali metal ion dopants.
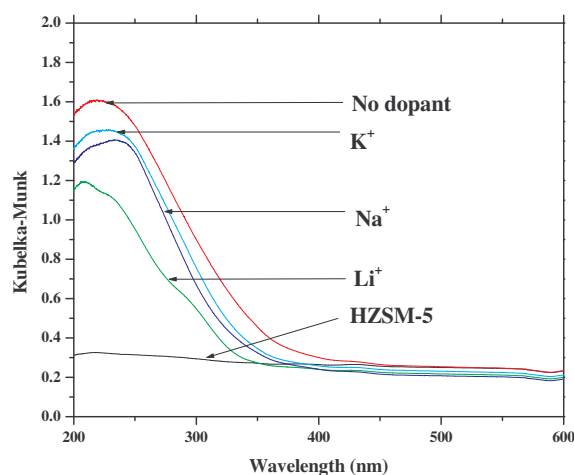
The results in Figure 6.53 show that there is an insignificant absorption due to H-ZSM-5, while the impregnation of the zeolite with Mo gave rise to a strong absorption band at a wavelength of about 215 nm. Hence, this absorption band may be assigned to the $Mo(T_d)$ species. A similar band was observed when the

Mo/H-ZSM-5 was doped with the alkali metal ions, suggesting that the Mo(T_d) species were present in the systems. However, in the case of doping with the lithium ions, an extra absorption band appeared as shoulder at a wavelength of about 288 nm. As already mentioned, the assignment of this band is not known, but it could be due to polymerised molybdenum species. The presence of these molybdenum species may be related to the low catalytic activities observed over the Li-doped catalysts   The edge energies of the catalysts were found to be at 4.10, 3.95 and 3.85 eV for the catalysts doped with Li^+, Na^+ and K^+ ions respectively, while that for the undoped catalyst was 3.81 eV. The catalyst doped with lithium contained predominantly the mononuclear molybdenum species as in Na_2MoO_4 while the undoped and the sample doped with sodium and potassium ions contained polynuclear species.

The effect of the alkali metal ions on the reducibility of the catalysts is shown in Figure 6.54.   The reduction profiles of the 2%Mo/H-ZSM-5 catalysts were influenced by the presence of alkali metal ions.   This observation is more apparent in the case of lithium ions. The reduction peaks of the sample doped with K^+ were of lower intensity and appeared at lower reduction temperatures than the others, while the reduction peaks were more intense in the presence of Na^+ ions. The profiles of the Mo/HZSM-5 doped with K^+ and Na^+ were similar to that for the undoped sample. The reduction profile was significantly modified in the presence of Li^+ ions. These observations could account for the lower activity observed in the presence of Li^+ as seen in Figure 6.52.

The character of coke deposited on the catalysts with and without the alkali metal ions was studied by means of TPO and the results obtained are shown in Figure 6.55. The TPO profile of the sample without alkali metal ions showed two oxidation peaks at 643 and 739°C. These peaks are due to the carbidic carbon and the carbonaceous species deposited on the Brønsted acid sites, respectively.

Similar peaks were observed in the presence of Na$^+$ ions, but with a lower intensity, suggesting the lower coke content in the presence of Na$^+$ ions.
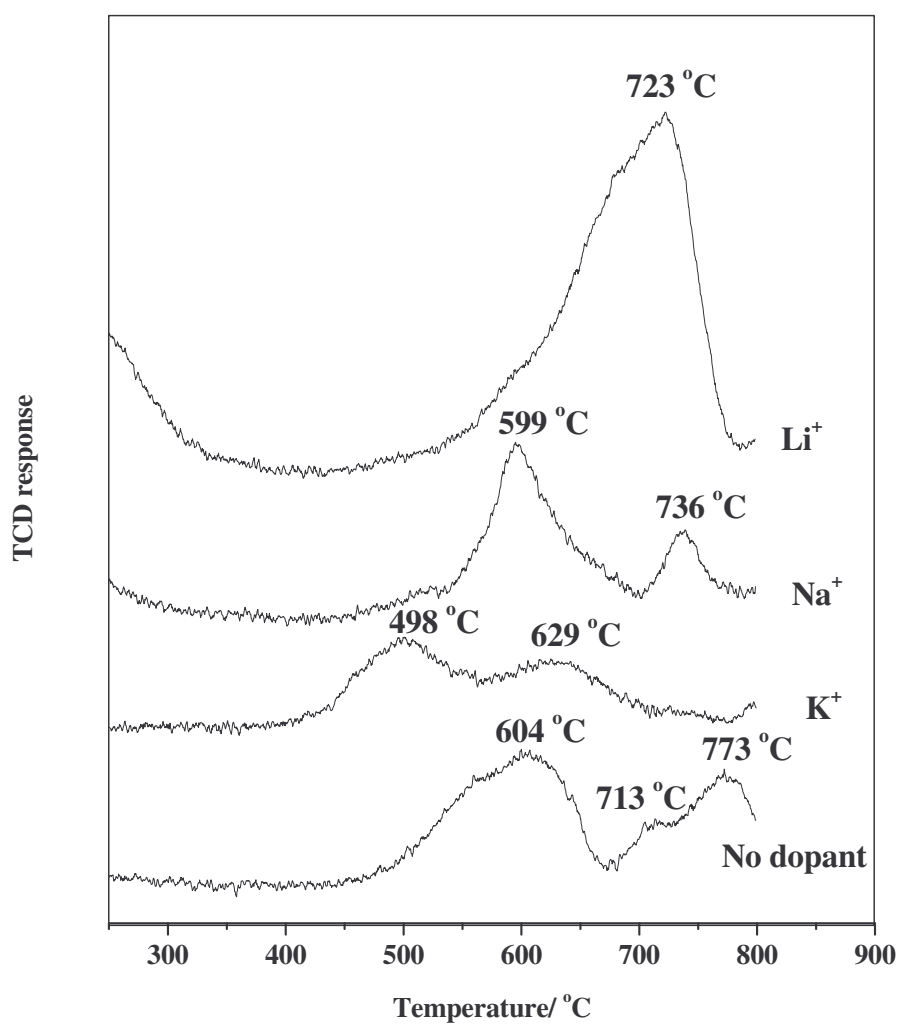
Figure 6.54 TPR profiles of 2%Mo/H-ZSM-5 catalysts with and without alkali metal ion dopants.
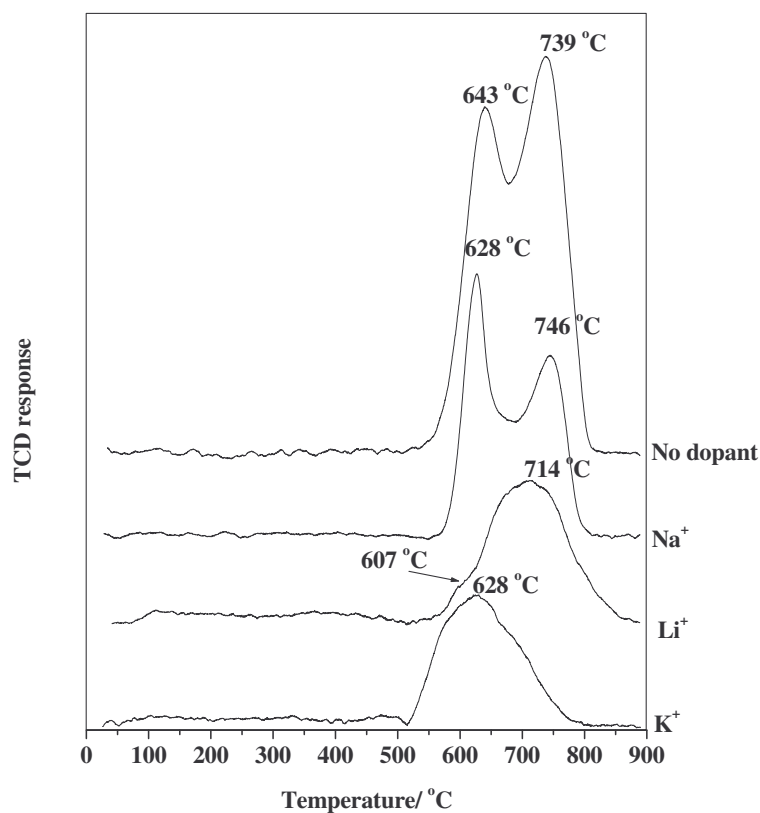
Figure 6.55 The TPO profiles of Mo/H-ZSM-5 catalysts with and without alkali metal ions used in the conversion of methane at 750°C.

In the presence of Li^+ ions the peak at high oxidation temperatures was more prominent while the peak due to the carbidic carbon was less intense. This means in the presence of Li^+ the formation of the carbide was inhibited, and as a result lower catalytic conversions were observed. In the case of the K^+, the major peak was the carbidic carbon. The lower activity for the sample doped with K^+ is probably due to the effectiveness of K^+ in neutralising the Brønsted acid sites. It is however, noted that the trends of coke selectivities in Table 6.11 are in agreements with the TPO observations. This discrepancy may be due to the fact that coke in this work means all the products that could not be detected by the

FID analysis. Since TPO detects the oxidation of carbonaceous species deposited on the catalysts, the trends observed in Figure 6.55 are more reliable.

The influence of the alkali metal ion on the acidity of the Mo/H-ZSM-5 catalysts is shown in Figure 6.56.
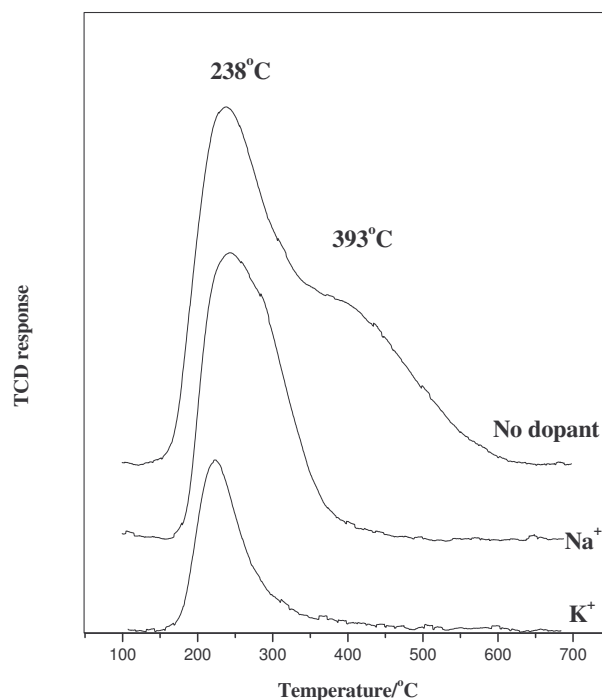
Figure 6.56 The NH_3-TPD profiles of 2%Mo/H-ZSM-5 catalysts with and without alkali metal ions.

The ammonia desorption profile of the undoped sample of the 2%Mo/H-ZSM-5 showed two peaks at 238 and 393°C. The peak at 393°C is due to desorption of ammonia from strong acid sites, while the peak at 238°C is due to desorption of ammonia from weak acid sites. In the presence of alkali metal ions, the peak at a higher temperature was eliminated. What is of interest is the fact that in the presence of K^+ ions the low-temperature peak had a significantly lower intensity, indicating that K^+ is more poisonous to acid sites than Na^+.

6.10 The effect of silanation

Zeolites are known to be shape-selective catalysts and this selectivity is realised partially because of their unique channel system. However, the external surface of these materials also contributes to the non-shape-selective reactions. These external surface sites can be selectively poisoned using bulky organosilicon compounds that cannot penetrate the channels of the zeolite [47-50]. This is usually done using the method of chemical vapour deposition or liquid deposition. The influence of the silanation of the zeolite on the catalytic activity of Mo/H-ZSM-5 catalysts was studied and is shown in Figure 6.57
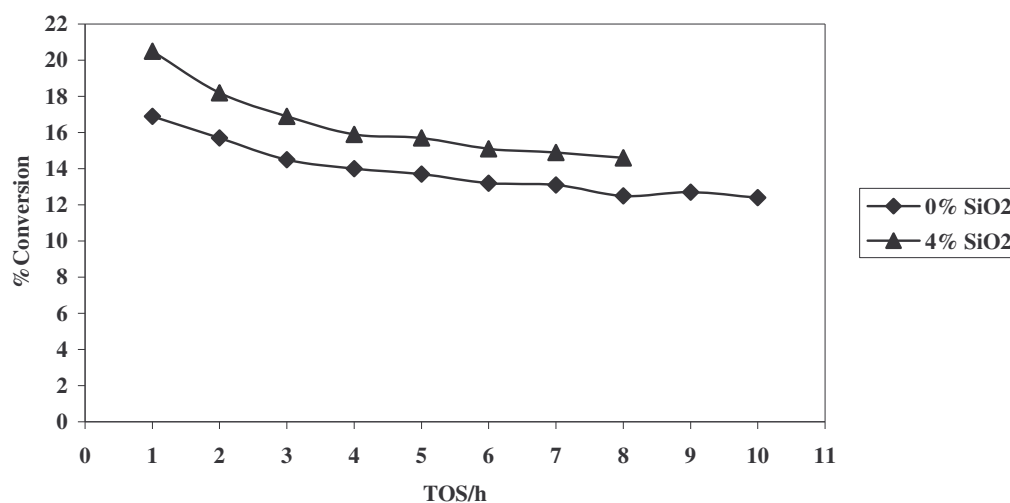
Figure 6.57 the effect of silanation on the catalytic performance of Mo/H-ZSM-5 catalysts for the conversion of methane at 750°C.

All the catalysts deactivated with increasing time on stream and the non-silanated was slightly more stable than the silanated catalysts. When the catalysts was

silanated with 4 wt.% SiO_2, the percentage conversion was higher than the non-silanated Mo/H-ZSM-5. The effect of silanation on the product selectivity is shown in Figure 6.58 a for conversion level of about 10%.
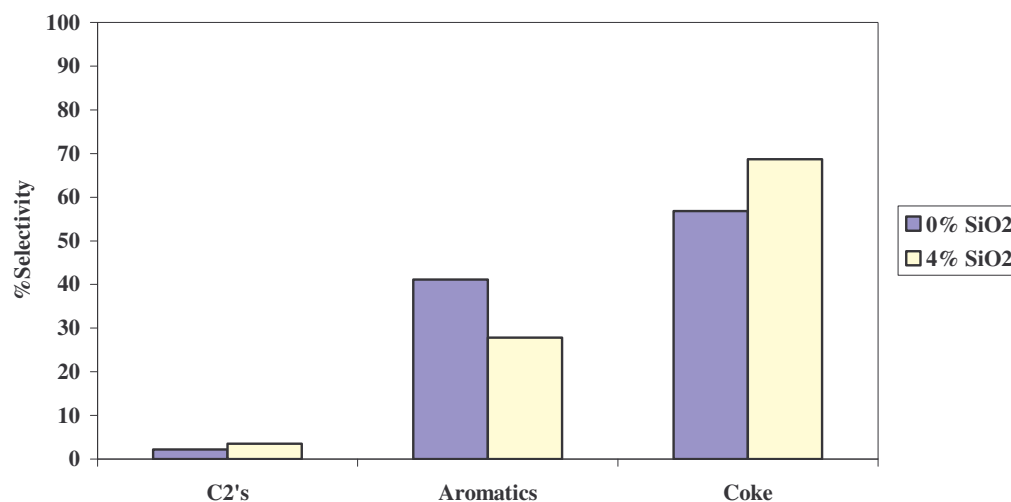
Figure 6.58 The effect of silanation of the product selectivity of 2%Mo/H-ZSM-5 catalysts from the conversion of methane at $750^{\circ}C$.

Silanation decreased the selectivity to benzene and led to higher levels of coke production. This is contrary to the observations of Ding et al. [48], who observed improved aromatics selectivities when H-ZSM-5 was silanated.

6.11 Regenerability of Mo/H-ZSM-5 catalysts

One of the important characteristics of a catalyst is its potential to be regenerated after it has deactivated to unacceptable activity levels. When the deactivation is due to the deposition of coke the catalyst can be regenerated by burning off the carbonaceous species in air at reasonable temperatures, selected such that the catalyst is not structurally modified. The regenerability of Mo/H-ZSM-5

catalysts was studied and the results are discussed below. The %XRD crystallinity of the H-ZSM-5 used in these studies was 54.

The catalysts were regenerated by lowering the reaction temperature to 600°C under nitrogen and switching from nitrogen to air flow (30 ml/min). After 1 hour the gas was switched to nitrogen and the temperature was increased to 750°C and held there under nitrogen for an hour before introducing methane. The effect of regeneration on the subsequent conversion of methane is shown in Figure 6.59.
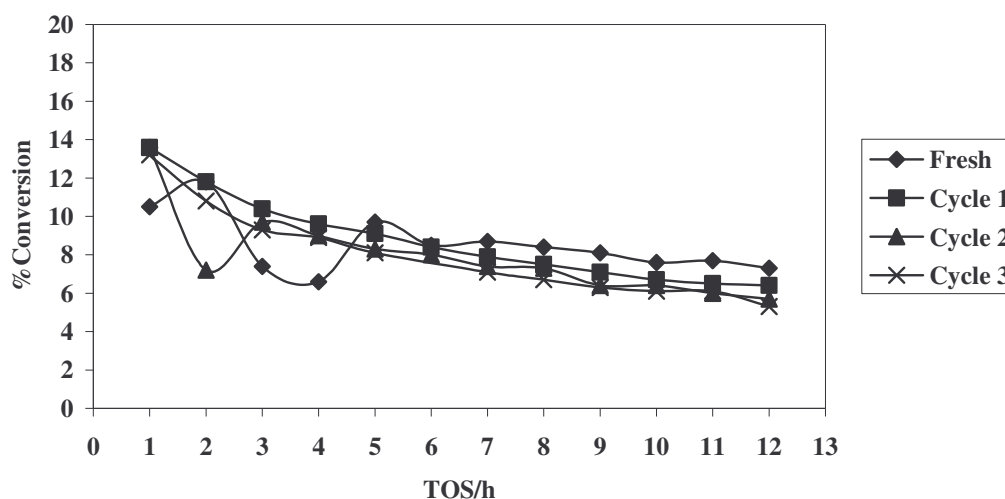
Figure 6.59 The effect of regeneration on the conversion of methane over the 2%Mo/H-ZSM-5 catalyst at 750°C.

Although there were some initial fluctuations in the conversions during the first hours on stream, for the first and the second regeneration cycles, it can be seen that the catalyst can be regenerated to an appreciable extent. This is contrary to the observations by Skutil and Taniewski [51] who reported that the Mo/H-ZSM-5 could not be effectively regenerated. However, it is noted that there was a slight decrease in the conversion with increasing number of regeneration cycles, as seen in Figure 6.59.

The effect of regeneration on the selectivity for various products is shown in Figures 6.60 to 6.62.
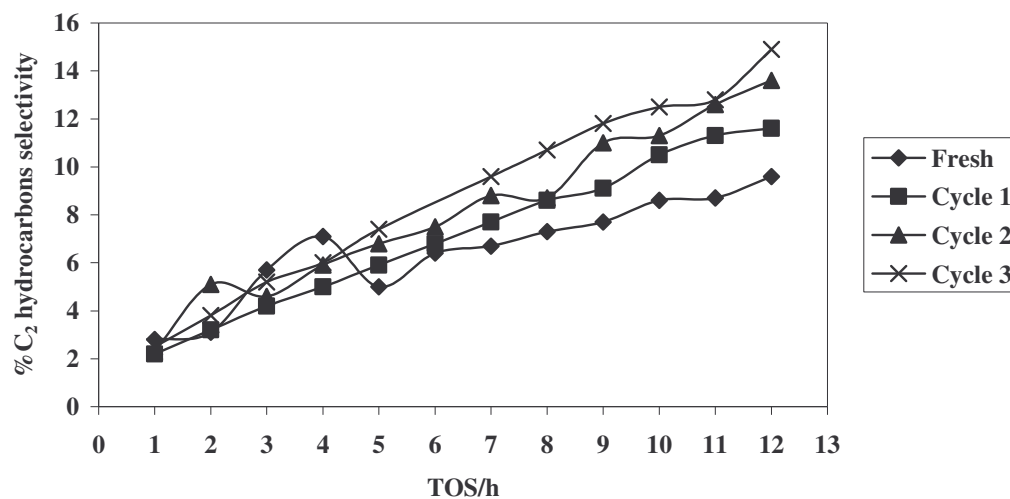
Figure 6.60 The effect of regeneration on the selectivity for C_2 hydrocarbons from the conversion of methane over the 2%Mo/H-ZSM-5 catalyst at 750°C.
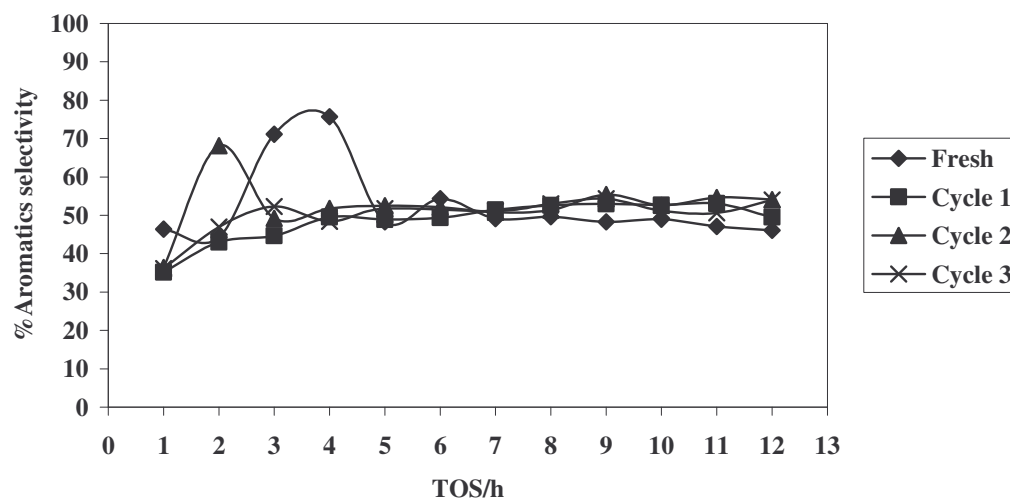
Figure 6.61 The effect of regeneration on the selectivity for aromatics from the conversion of methane over the 2%Mo/H-ZSM-5 catalyst at 750°C.
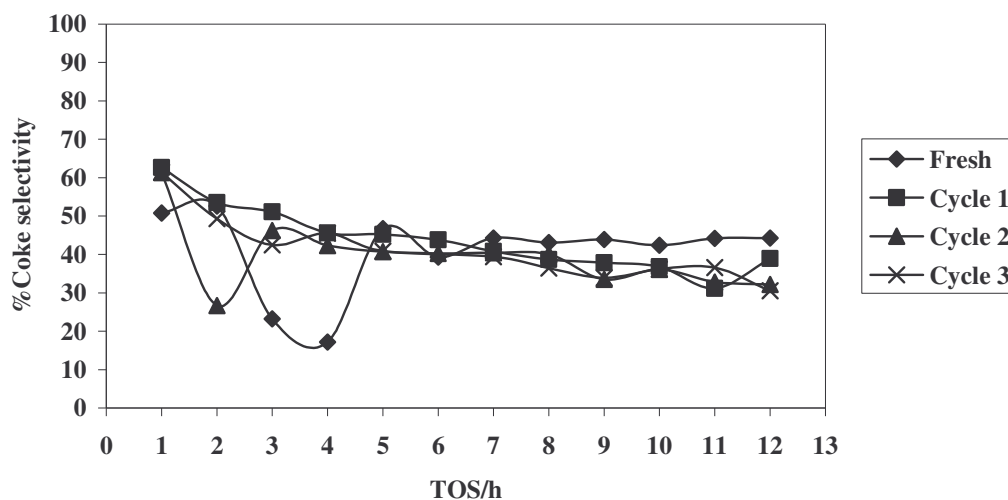
Figure 6.62 The effect of regeneration on the selectivity for coke from the conversion of methane over the 2%Mo/H-ZSM-5 catalyst at 750°C.

The selectivity for C_2 hydrocarbons showed a significant increase with increasing regeneration cycles, while the selectivity for aromatics and coke did not show such significant changes. The results generally suggest that that the catalytic performance of the catalysts could be regenerated to an appreciable extent, though some changes seem to be irreversible for the "upward drift" in C_2 selectivity.

6.12 On the use of tungsten as replacement for molybdenum in Mo/H-ZSM-5 catalysts

A discussion in Section 3.8 has indicated that tungsten is thermally more stable at high temperatures than molybdenum. This factor, combined with better benzene formation yields predicted by thermodynamics at higher temperatures, make tungsten a potential substitute for molybdenum as a catalyst component. As a result, this study also evaluated the effect of crystallinity on some W/H-ZSM-5

catalysts. For easier comparison with the 2%Mo/H-ZSM-5 catalysts, tungsten was introduced at an equivalent molar basis to that used for molybdenum.

The effect of the percentage crystallinity of H-ZSM-5 on the catalytic stability of the W/H-ZSM-5 catalysts is shown in Figure 6.63. Except for the 5% crystalline sample which was the least active, all the catalysts deactivated with increasing time on stream.
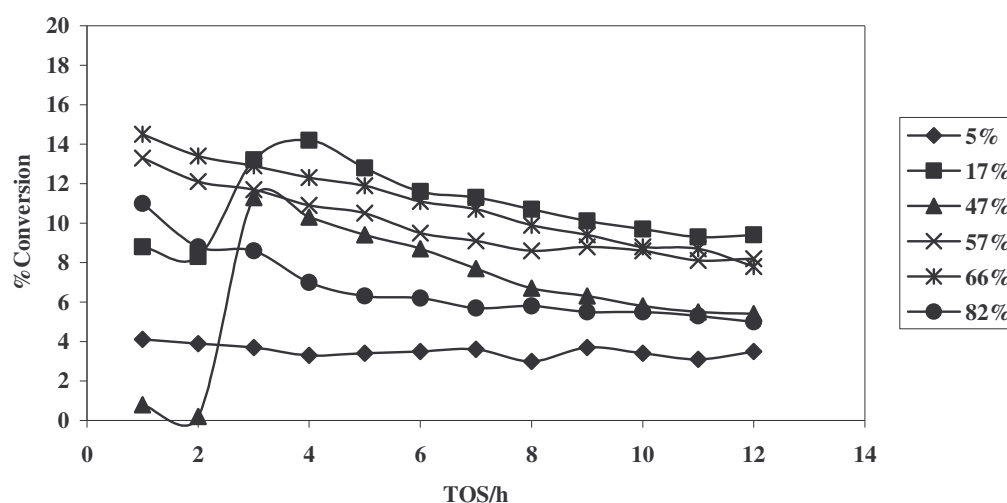
Figure 6.63 The effect of %XRD crystallinity on the stability of W/H-ZSM-5 catalysts during the conversion of methane at 750°C.

The effect of the percentage XRD crystallinity on the conversion of methane over W/H-ZSM-5 catalysts is shown in Figure 6.64, and compared with that for 2%Mo/H-ZSM-5 catalysts. As in the case of the Mo/H-ZSM-5 catalysts, the conversion of methane over W/H-ZSM-5 catalysts increased with increasing %XRD crystallinity reached a maximum for crystallinities between 50 and 70%. The catalytic activity of the W-based systems is slightly lower than that for the Mo/H-ZSM-5 catalysts.
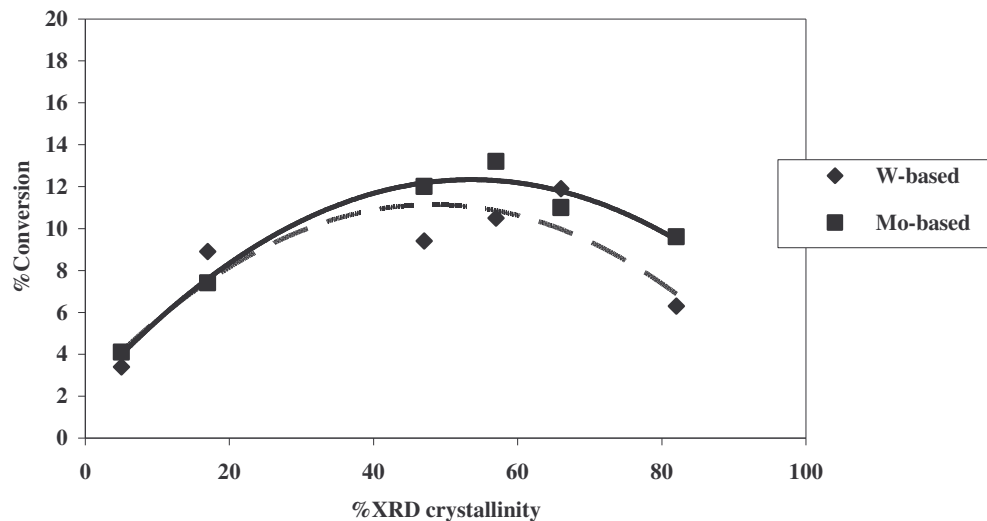
Figure 6.64 The effect of %XRD crystallinity on the performance of W/H-ZSM-5 catalysts during the conversion of methane at 750°C, compared with that for 2%Mo/H-ZSM-5 catalysts.

A comparison of the product selectivity of the W/H-ZSM-5 and 2%Mo/H-ZSM-5 catalysts during the conversion of methane at comparable percentage conversions is shown in Table 6.12.

Table 6.12 A comparison of the product selectivity of W/H-ZSM-5 and 2%Mo/H-ZSM-5 catalysts during the conversion of methane at 750°C

| Active metal | %XRD crystallinity | %Conversion | %Selectivity | | | Ethene/ Ethane ratio |
			C_2 hydrocarbons	Aromatics	Coke	
W	5	4.1	1.5	0.0	98.5	0.9
Mo	5	4.1	6.9	20.0	73.0	∞
W	47	10.3	3.3	31.4	65.3	1.8
Mo	47	10.5	5.8	77.9	10.3	5.4
W	82	8.6	5.9	24.9	69.2	3.9
Mo	82	8.8	5.7	20.3	74.0	10.4

The results show that the Mo-based catalysts gave higher selectivities for aromatics and C_2 hydrocarbons compared with the W-based catalysts. Furthermore, the Mo-based catalysts gave higher ethene/ethane ratios and lower selectivities for coke compared with the W-based catalysts. These observations confirm that Mo/H-ZSM-5 catalysts are among the most active catalysts for the nonoxidative conversion of methane.

6.14 Conclusions

From the study of the nonoxidative conversion of methane at 750°C the following conclusions can be drawn.

The study of supported molybdenum catalysts confirmed that the zeolite H-ZSM-5 is a good support, giving reasonable aromatic selectivities and stabilities.

The optimum molybdenum loading for the most active catalysts is somewhere between 2 and 4 wt%. However, higher molybdenum loadings lead to rapid deactivation as a result of the loss of the zeolitic structure at a reaction temperature of 750°C.

The conversion of methane increased in a near-linear manner with an increase in temperature from 700 to 850°C. The apparent activation energy of the reaction was found to be 64.5 kJ/mol. Although it is expected that the aromatisation activity will increase with an increase in the reaction temperature, this investigation showed that for temperatures above 800°C, the selectivity for aromatics decreased, probably due to the high coking rate favoured at high reaction temperature.

The primary hydrocarbon product is ethene, while ethane is probably formed either as a primary product or as a secondary product of the hydrogenation of

ethene. The Brønsted acid sites seem to play a role in the formation of ethane. The aromatisation of ethene is probably a very rapid reaction.

The percentage XRD crystallinity of H-ZSM-5 has been shown to be an important parameter for the activity of Mo/H-ZSM-5. Higher conversions were observed when the percentage XRD crystallinity was between 50 and 60%. The selectivity for aromatics increased with increasing crystallinity of the zeolite, while the selectivity for coke was lowered. The formation of carbon nanostructures has been shown to be feasible under the reaction conditions used in this study. The study also showed that good catalytic performance could be obtained when the SiO_2/Al_2O_3 ratio of the catalyst was below 90. The nature of the molybdenum species also changed with a change in the SiO_2/Al_2O_3 ratio of the catalyst.

The type of the molybdenum precursor used in the preparation of Mo/H-ZSM-5 catalysts did not affect the catalytic conversion of the resulting catalysts. However, the selectivity for aromatics was higher when ammonium heptamolybdate was used as a source of molybdenum. Similarly the preparation method did not have a significant effect on the conversion of methane, though slightly higher selectivities for aromatics were obtained when Mo/H-ZSM-5 were prepared by the method of physical mixing of MoO_3 and H-ZSM-5.

The addition of boron (0.05-0.2 wt%) in Mo/H-ZSM-5 did not have an affect on the conversion of methane, while the selectivity for C_2 hydrocarbons was increased. Boron acted by influencing the electronic structure of the catalysts. In the presence of 0.5 wt% Ag, the selectivity conversion of methane was significantly improved. Further, the selectivities for C_2 hydrocarbons and aromatics were also improved. The improved catalytic activity of Mo/H-ZSM-5 doped with Ag ions was related to the improved acidity of the catalyst when Ag ions are present. The addition of alkali metal ions led to decreased conversions, probably due to the decreased acidities of the catalysts.

Silanation of the catalysts led to improved catalytic conversion, but the selectivity for aromatics was decreased at the expense of coke formation. The stability of the catalysts was also slightly decreased.

By treating the catalysts in air at 600°C, the catalytic performance of deactivated 2%Mo/H-ZSM-5 was recovered to an appreciable extent. Comparisons of the effect of crystallinity on the performance of Mo/H-ZSM-5 and W/H-ZSM-5 catalysts with equal molar contents of each metal has shown that molybdenum-based catalysts are more active than tungsten-based samples

6.15 References

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Chapter 7

The aromatisation of propane over Mo/H-ZSM-5 catalysts

The aromatisation of propane has been extensively studied using Ga and Zn-loaded ZSM-5 zeolite catalysts. Not much attention was paid to the aromatisation of propane over Mo/H-ZSM-5 catalysts. In this chapter the some preliminary results obtained from the aromatisation of propane over Mo/H-ZSM-5 catalysts are presented and discussed. This work covered the effects of the molybdenum content, the reaction temperature and the percentage XRD crystallinity of the zeolite. The preparation and catalytic evaluation of the catalyst was described in Chapter 5.

7.1 The effect of the molybdenum loading

In the study of the effect of the molybdenum loading on the aromatisation of propane over H-ZSM-5 catalysts, molybdenum contents from 2 to 15 wt% were investigated. The addition of molybdenum to H-ZSM-5 led to a decrease in the catalytic conversion and stability of the H-ZSM-5 zeolite as shown in Figure 7.1.
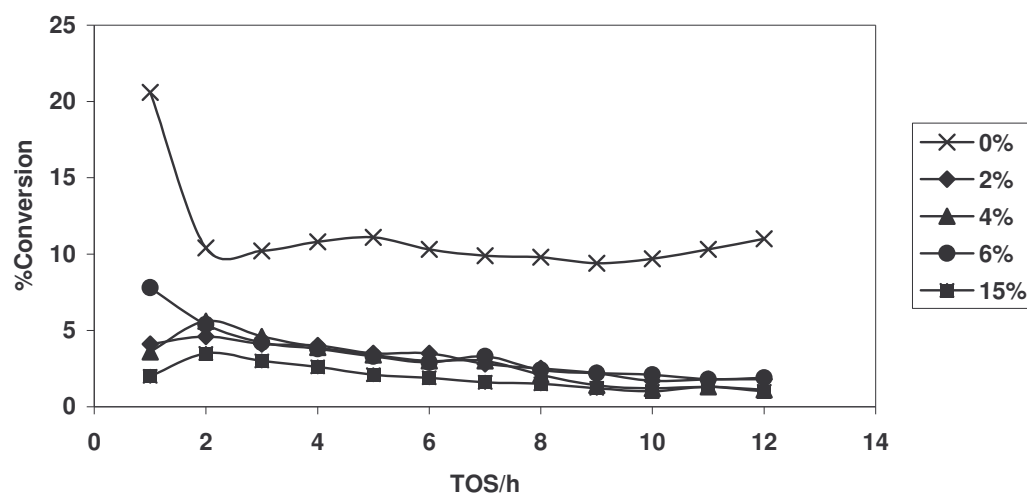
Figure 7.1 The catalytic conversion of propane as a function of time on stream over Mo/H-ZSM-5 catalysts of different molybdenum loading at 530°C.

Since it is known that Brønsted acid sites are involved in the first step of propane dehydrogenation over Ga/H-ZSM-5 catalysts, it is likely that the decrease in the catalytic performance is due to the decrease in the Brønsted acidity of the catalysts upon addition of molybdenum H-ZSM-5 as was discussed in Chapter 6. This is also suggested by the observation that the catalyst without molybdenum was more active than the molybdenum impregnated H-ZSM-5. A more clear illustration of the effect of the molybdenum loading on the catalytic conversion of propane is given in Table 7.1 and Figure 7.2 for a time on stream of 5 h. Since the conversion of the molybdenum-free H-ZSM-5 was higher than for the Mo/H-ZSM-5 catalysts it was not possible to tell if the presence of molybdenum improved the selectivity of the catalysts or not. It is noted, however, that Wang et al. [1] observed an increase in the aromatics selectivity upon introduction of molybdenum into H-ZSM-5, while Fu et al. [2] reported a decrease.

Table 7.1 The effect of molybdenum loading on the catalytic aromatisation of propane over Mo/H-ZSM-5 catalysts at 530°C after a time on stream of 5 h and with a flow rate of propane = 20ml/min

Mo loading (wt%)	%Conversion	%Selectivity		%Yield		A/C ratio
		C_1+C_2	Aromatics	C_1+C_2	Aromatics	
0%	11.1	42.4	58.0	4.7	6.4	1.4
2%	3.5	33.1	64.5	1.2	2.3	1.9
4%	3.4	43.1	61.4	1.5	2.1	1.4
6%	3.3	32.8	59.7	1.1	2.0	1.8
15%	1.3	36.9	63.2	0.9	1.0	1.2
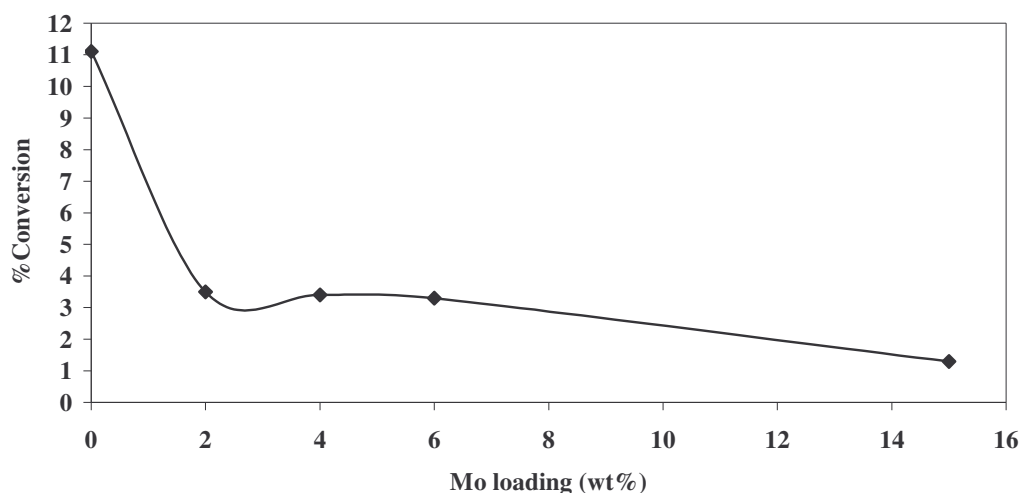
Figure 7.2 The effect of molybdenum content on the catalytic conversion of propane at 530°C at a TOS of 5 h and propane flow rate of 20 ml/min.

By comparing the product selectivities of the catalysts with molybdenum loadings of 2, 4 and 6 wt%, whose conversions are similar, it can be seen that the selectivity for C_1+C_2 hydrocarbons decreased with increasing molybdenum loading up to 6 wt% and increased when the molybdenum loading was 15 wt% (probably due to the low conversion level), while on the other hand the selectivity for aromatics increased with increasing molybdenum loading. The selectivity for aromatics also decreased with increasing molybdenum loading. Since it is known

that the selectivity for different products depends on the percentage conversion of methane [3,4], the effect of molybdenum content on the selectivity and yield at a conversion of about 2% are summarised in Table 7.2.

Table 7.2 The effect of molybdenum loading on the selectivity and yield of aromatics and cracking products at a conversion of about 2% and a reaction temperature of 530°C

Mo loading (wt.%)	%Selectivity		%Yield		A/C ratio
	C_1+C_2	Aromatics	C_1+C_2	Aromatics	
2	38.9	66	0.9	1.5	1.7
4	38.8	62.8	1.2	1.3	1.1
6	41.8	56.2	0.9	1.2	1.3
15	41.4	59.5	0.9	1.6	1.8

As shown in Table 7.2, the yield to aromatics (benzene, toluene, and xylenes) generally decreased with increasing molybdenum loading, while the yield for C_1+C_2 was virtually unchanged at 0.9%. It should however be noted that the yield for aromatics was high when the molybdenum content was 15 wt%. At this stage, it is not clear what could be the reason for this observation. The aromatisation/cracking (A/C) ratio, calculated by dividing the yield of aromatics with C_1+C_2 hydrocarbons, also decreased until a molybdenum loading of 6 wt%, indicating that cracking was favoured when molybdenum was present.

7.2 The effect of the reaction temperature

The effect of the reaction temperature on the aromatisation of propane was studied over Mo/H-ZSM-5 with a molybdenum loading of 2 wt%, with temperatures ranging from 400 to 700°C. Figure 7.3 illustrates the stability of the

Mo/H-ZSM-5 catalysts for the conversion of propane at different reaction temperatures. The highest conversion of about 54% was obtained at a reaction temperature of 700°C for a time on stream of 1 h. However, due to the high reaction temperature, the catalysts deactivated more rapidly than when the reaction temperatures were lower than 700°C, as shown in Figure 7.3.
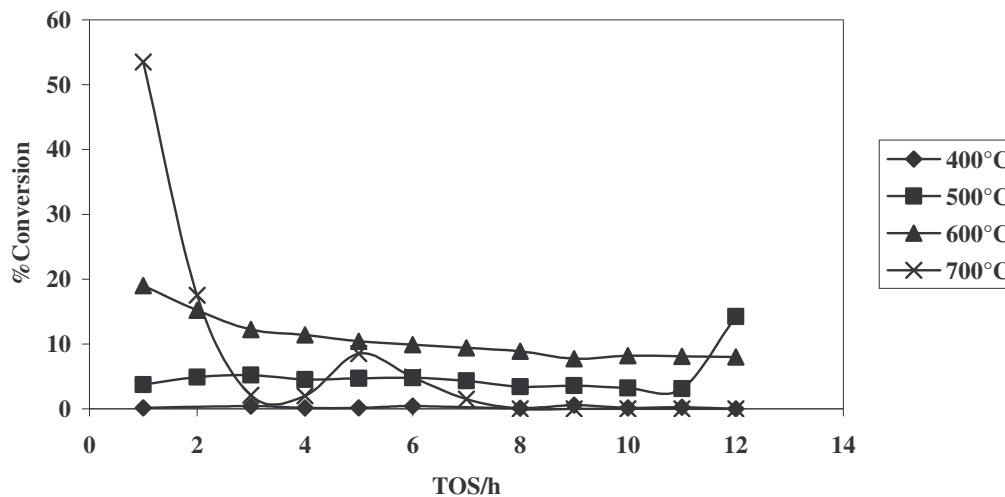
Figure 7.3 The catalytic conversion of propane as the function of time on stream over 2%Mo/HZSM-5 catalysts at different temperatures.

There was virtually no conversion observed when the reaction temperature was 400°C. The effect of temperature on the catalytic performance is clearly shown in Figure 7.4 for times on stream of 1, 5 and 10 h. For a time on stream of 1 h, there is an exponential increase in conversion with increasing reaction temperature. However, as the time on stream increased the trend changed from an exponential increase to a situation where a maximum conversion was observed at a temperature of 600°C because the catalyst deactivated rapidly at a reaction temperature of 700°C and reached a conversion of zero in 8 h as shown in Figure 7.2. It should also be noted that deactivation was observed at a reaction temperature of 600°C as illustrated by the decrease in the maximum conversion

when the time on stream was at 5 and 10 h, and this is also shown in Figure 7.4. At a reaction temperature of 500°C the deactivation of the catalyst was minimal.
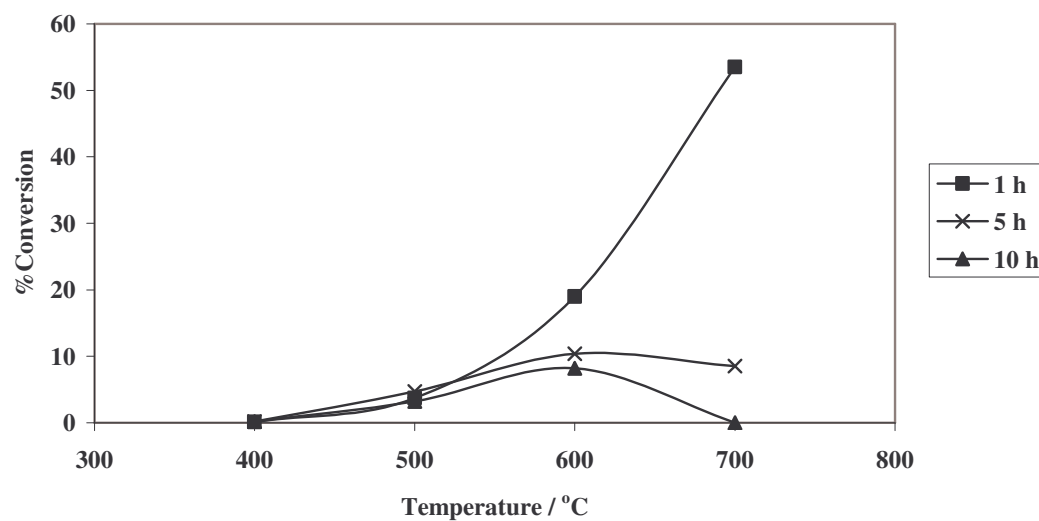
Figure 7.4 The catalytic conversion as the function of temperature over the 2%Mo/HZSM-5 catalysts at time of stream of 1, 5 and 10 h.

A summary of the results showing the effect of reaction temperature on the catalytic performance of 2%Mo/H-ZSM-5 catalysts is shown in Table 7.3 for a time on stream of 1 h.

Table 7.3 The effect of the reaction temperature on the catalytic performance of 2%Mo/H-ZSM-5 catalysts for the aromatisation of propane at 530°C and propane flow rate of 20 ml/min

Temperature (°C)	%Conversion	%Selectivity		%Yield		A/C ratio
		C_1+C_2	Aromatics	C_1+C_2	Aromatics	
400	0.1	34.2	0.0	0.0	0.0	0.05
500	3.7	58.6	29.9	2.2	1.2	0.5
600	19.0	43.8	48.6	8.3	9.2	1.1
700	53.5	10.9	71.7	5.8	38.4	6.6

The results show that the yield of the aromatics increased with increasing reaction temperature, while the yield for C_1+C_2 decreased. Furthermore, the A/C ratio increased showing the aromatisation was favoured by an increase in temperature when the time on stream was 1 hour. The highest yield of aromatics of 38.4% was observed at a reaction temperature of 700^oC. Since, it is known that Mo/H-ZSM-5 catalysts are able to catalyse the aromatisation of methane at a reaction temperature of 700^oC [5], the active species involved in such transformations are the Mo_2C species which are formed by reduction of MoO_3 species in the presence of methane at high temperatures. It was also shown that molybdenum carbide species could only be formed at temperatures above 580^oC, when butane was reacted over Mo/H-ZSM-5 catalysts [6]. Therefore the high activity observed at a reaction temperature of 700^oC after 1 hour on-stream may be attributed to the fact that the molybdenum species were in the form of the carbide at this temperature. However, a temperature of 700^oC favoured deactivation of the catalyst. It is also interesting to note that no aromatisation was observed when the reaction temperature was 400^oC, indicating that aromatisation is favoured at higher temperatures. Since the conversions were different at various reaction temperatures used in this study it was not possible to establish the effect of the reaction temperature on the product selectivity of Mo/H-ZSM-5 catalysts.

7.3 The effect of the %XRD crystallinity of H-ZSM-5

The effect of crystallinity on conversion of propane was studied on 2%Mo/H-ZSM-5 catalysts of various crystallinities (ranging from 5 to 86%) at 530°C, and the result are shown in Figure 7.5. The highest catalytic conversion was observed over the sample with a crystallinity of 61%, which gave conversions ranging from 20 to 26%. The 61% crystalline sample also exhibited better stability than the other catalysts.
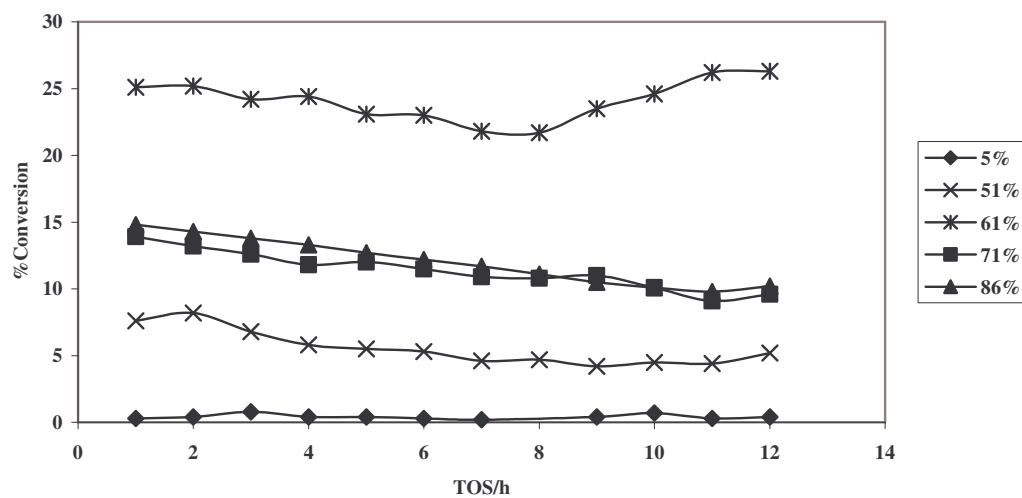
Figure 7.5 The catalytic conversion of propane as a function of time-on-stream over the 2%Mo/H-ZSM-5 catalysts of various %XRD crystallinities.

The effect of the percentage XRD crystallinity on the catalytic conversion of propane is shown in Figure 7.6 and Table 7.4, for a time on stream of 5 h. Figure 7.6 shows that there is an increase in the conversion of propane with increasing %XRD crystallinity reaching a maximum for a sample with a crystallinity of 61%. A maximum conversion of propane was previously observed for Ga/H-ZSM-5 and Zn/H-ZSM-5 catalysts with crystallinities between 50 and 60% [7,8]. Similar results

Figure 7.6 The effect of the percentage XRD crystallinity of H-ZSM-5 on the catalytic conversion of propane at 530°C over 2%Mo/H-ZSM-5 catalysts at TOS of 5 hours.

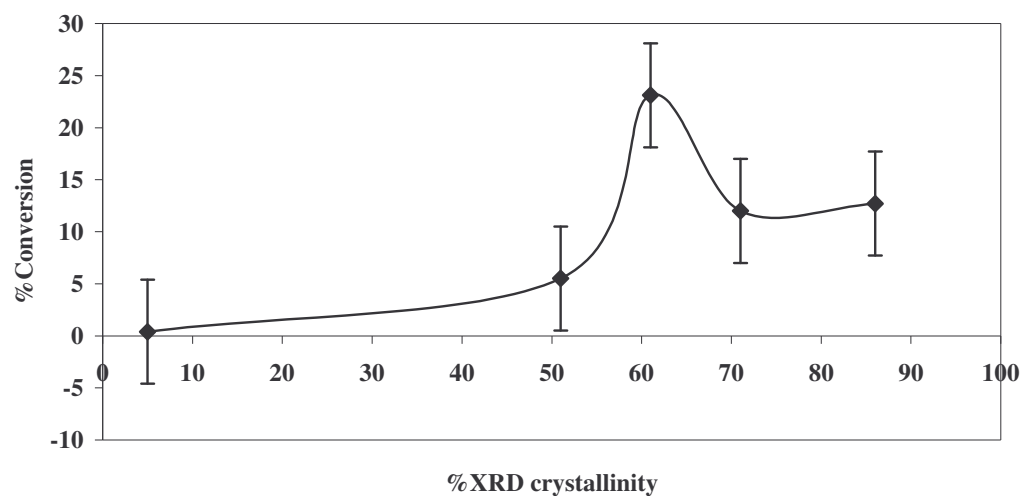**Table 7.4** The effect of %XRD crystallinity of H-ZSM-5 on the catalytic performance of 2%Mo/H-ZSM-5 catalysts for the aromatisation of propane at 530°C and propane flow rate of 20 ml/min

%XRD crystallinity	%Conversion	%Selectivity		%Yield		A/C ratio
		C_1+C_2	Aromatics	C_1+C_2	Aromatics	
5	0.4	97.6	45.1	0.4	0.2	0.5
51	5.5	51.4	52.1	2.8	2.9	1.0
61	23.1	34.6	47.9	8.0	11.1	1.4
71	12.0	32.1	51.8	3.9	6.2	1.6
86	12.7	33.2	56.3	4.2	7.2	1.7

were also observed for the nonoxidative conversion of propane over Mo/H-ZSM-5 catalysts as discussed in Section 6.6, for samples with crystallinities between 50 and 60%. The effect of the percentage XRD crystallinity on the yield of aromatic products follows the same trend the effect of crystallinity on the percentage

conversion as shown in Figure 7.6. The results in Table 7.4 also show that the aromatisation/cracking (A/C) ratio increased with an increase in the crystallinity.
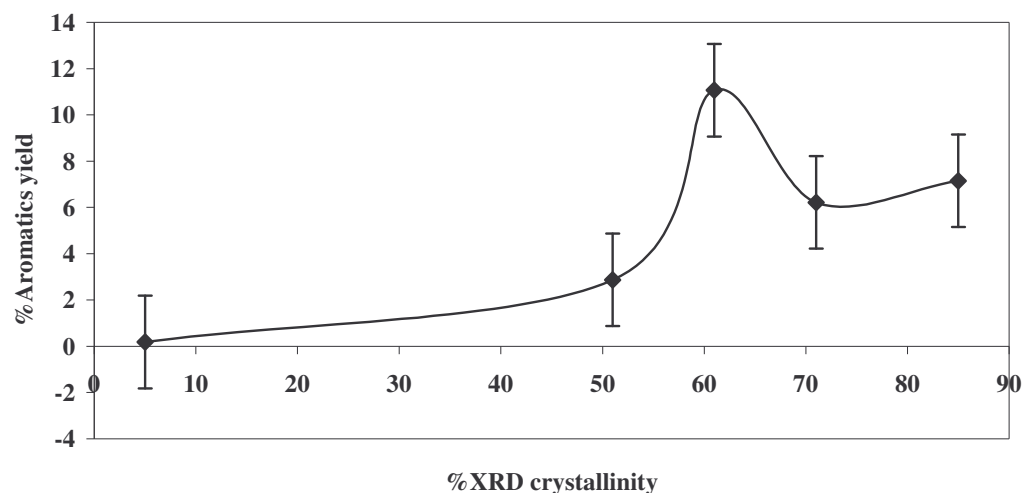

Figure 7.7 The effect of the crystallinity on the yield of aromatic products from the aromatisation of propane over 2%Mo/H-ZSM-5 catalyst at 530°C and a time on stream of 5 h.

It should be remembered that the product selectivities and theretofore, the A/C ratios also depend on the percentage conversion. The proper effect of the crystallinity on the product selectivity should be determined at similar conversion levels. In the current study this comparison could only made for samples with crystallinities of 51, 71 and 86%, at a conversion close to 10%, as given in Figure 7.8. The results indicate that the selectivity for aromatics at iso-conversion increased steadily from 47 to 53% with increasing percentage crystallinity, while the selectivity for the cracked products decreased from 41 to 38%. The A/C ratio increased from 1.1 to 1.4 with increasing percentage XRD crystallinity of the catalysts.
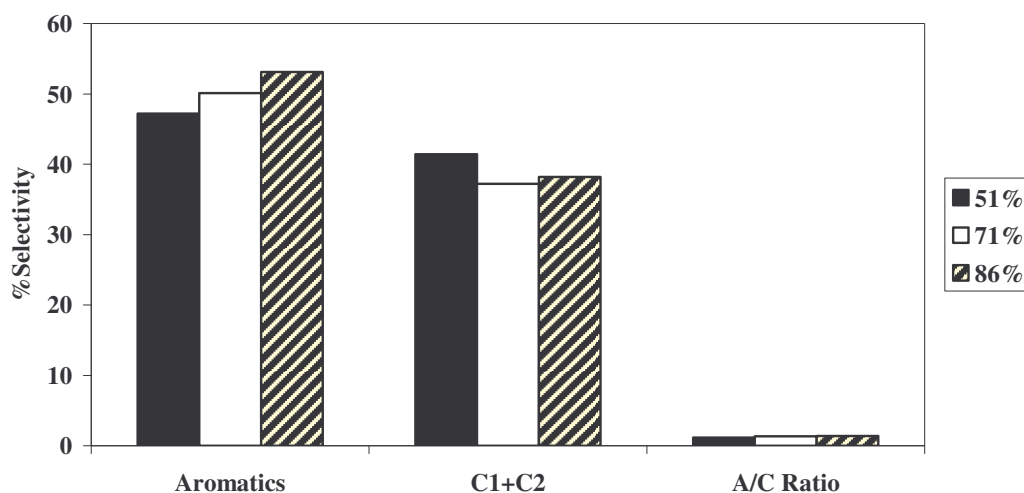
Figure 7.8 The effect of %XRD crystallinity on the product selectivity during the aromatisation of propane over 2%Mo/H-ZSM-5 at 530°C at a conversion of about 10%.

From the above observation this study has established that the addition of molybdenum into H-ZSM-5 lowered the catalytic conversion, probably due to decreased acidity. High conversions of propane can be realised over Mo/H-ZSM-5 catalyst at higher temperatures which are favourable for the formation of molybdenum carbide species. However, deactivation remains an obstacle when high reaction temperatures are used. The percentage crystallinity of the zeolite has a significant impact on the catalytic activity of H-ZSM-5- based catalysts.

7.4 References

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Chapter 8

Conclusions

8.1 The aromatisation of methane

The study of the nonoxidative conversion of methane was carried out at 750°C over Mo/H-ZSM-5 catalysts. Mo/H-ZSM-5 catalysts were prepared by the method of incipient wetness impregnation using solutions of ammonium heptamolybdate. The effects of parameters such as the support, the molybdenum loading, the reaction temperature, the flow rate of the feed, the crystallinity and the SiO_2/Al_2O_3 ratio of H-ZSM-5, the molybdenum precursor, the preparation method, the addition of dopants and silanation of H-ZSM-5 on the catalytic performance of Mo/H-ZSM-5 catalysts, were investigated. The regenerability of Mo/H-ZSM-5 catalysts and the possible replacement of Mo with W were also evaluated.

From the results obtained in this study it has been shown that the catalyst prepared using H-ZSM-5 as a support was more stable and selective to aromatics than the other supports used in this study. This has been attributed to the unique pore structure of ZSM-5, which has a two-dimensional pore system with diameters close to the kinetic diameter of benzene as already noted in Chapter 3. Good catalytic activities could be obtained when the amount of molybdenum loading in the Mo/H-ZSM-5 catalysts was between 2 and 4 wt%. The lower methane conversion levels observed when the molybdenum loading was above 4wt% has been attributed to the partial blockage of the zeolite pores by agglomerated molybdenum oxide species. The formation of MoO_3 crystallites in Mo/H-ZSM-5 was also evidenced by X-ray diffraction studies for catalysts with molybdenum loadings higher than 4 wt%. Diffuse reflectance spectroscopy also

showed that the domain sizes of the molybdenum oxide species increased with increasing molybdenum species. The deactivation of the catalysts with high molybdenum loadings this was mainly due to the collapse of the zeolite structure, while for lower loadings was mainly due to the deposition of carbonaceous coke. It has been shown that with increasing Mo loading higher than the monolayer coverage, the interaction between the framework aluminium becomes so strong that the framework aluminium is extracted by Mo to form $Al_2(MoO_4)_3$, as discussed in Chapter 3. This extraction of aluminium atoms from the zeolite framework can lead to the collapse of the zeolite structure.

The study also showed that the conversion of methane increased linearly with an increase in temperature from 700 to 850^oC and the apparent activation energy of the reaction was found to be 64.5 kJ/mol. Although it is expected that the aromatisation activity will increase with an increase in the reaction temperature, this investigation showed that for temperatures above 800^oC, the selectivity for aromatics decreased, probably due to the high coking rate favoured at high reaction temperature. The results of temperature programmed oxidation showed that the amount of coke deposited on the catalysts increased with increasing reaction temperature.

The effect of the percentage XRD crystallinity was investigated for crystallinities ranging from 5 to 97%. The conversion of methane increased with increasing percentage XRD crystallinity of the catalysts increased reaching maximum levels when the crystallinity was between 50 and 70%. Further increment of the crystallinity of the catalysts above 70% led to a decrease in the conversion. The lower conversion observed for samples with lower %XRD crystallinities may be attributed to the lower acidities exhibited by such samples while the lower conversions at higher crystallinities may be due to the growth of the zeolite crystallites, which imposed diffusion constraints on the products. The selectivity for C_2 hydrocarbons was not significantly affected by the %XRD crystallinity of

the H-ZSM-5, while the selectivity for aromatics increased with increasing crystallinity until reaching a plateau. These results showed that the %XRD crystallinity of ZSM-5 used in the preparation of the catalysts impacts on their resultant catalytic performance.

The study also showed that the conversion of methane also decreased with increasing SiO_2/Al_2O_3 ratio of the catalyst. The selectivity for aromatics also decreased with decreasing SiO_2/Al_2O_3 ratio, and the highest selectivity was observed when the SiO_2/Al_2O_3 ratio was 60. The selectivity for C_2 hydrocarbons was not affected by the SiO_2/Al_2O_3 ratio of the catalyst. There is a general inverse relationship between the selectivity for coke and the selectivity for aromatics. The results also showed that ethene is a primary product of methane conversion. The formation of ethane, as a primary product, probably occurs via the hydrogenation of ethene as well as the direct reaction of methane. The formation of ethane appeared to require the presence of Brønsted acid sites, which probably acted in synergy with the molybdenum species. The formation of benzene from ethene occurs very rapidly and as a result benzene is observed in significant amounts even at high space velocities. The formation of carbon nanotubes under the reaction conditions used for the conversion of methane in this study has also been observed.

The study of the effect of the molybdenum precursor showed that the catalytic conversion of methane was not significantly affected by the type of molybdenum precursor used in the preparation of Mo/H-ZSM-5 catalysts. However, the selectivity for aromatics was higher when ammonium heptamolybdate was used as a source of molybdenum. A comparative study of the catalysts prepared by impregnation and those prepared by physical mixing showed that the catalyst prepared by physical mixing were more active than the catalyst prepared by impregnation. The selectivity for aromatics was also higher for the catalyst prepared by physical mixing. The silanation of H-ZSM-5 before impregnation with molybdenum improved the conversion of methane but lowered the selectivity for aromatics.

The addition of small amounts of boron (0.05 to 0.2 wt%) in 2%Mo/H-ZSM-5 did not affect the conversion of methane. The selectivity for C_2 hydrocarbons increased with increasing boron loading while the selectivity for aromatics decreased when the boron loading was more than 0.05 wt%. Boron influenced the selectivity properties of the catalysts by affecting the electronic structure of the molybdenum species. The addition of 0.5 wt% Ag in 2%Mo/H-ZSM-5 catalysts improved the conversion of methane but the selectivity for aromatics was slightly improved. The Ag/H-ZSM-5 catalyst on the other hand was more selective for coke, with little aromatics produced. Silver promoted the catalytic performance of Mo/H-ZSM-5 by enhancing the acidity of the catalyst. Addition of alkali metal ions in Mo/H-ZSM-5 resulted in a significant decrease in the conversion of methane. Lithium was more poisonous for methane conversion when compared with sodium and potassium ions. This observation was in line with the results of TPR and UV-vis spectroscopy, studies which showed the molybdenum species in the catalyst doped with lithium were in a different state from those in the other samples in the series. The nature of the carbonaceous species was modified by the presence of alkali metal ions. Lithium ions hindered the formation of carbon associated with the molybdenum species, but promoted the formation of carbon associated with acid sites, which is in agreement with the catalytic results.

The study also showed that at equivalent molar contents, the molybdenum-based catalysts were more active than the tungsten-based catalyst for the conversion of methane, and selectivity for aromatics. However, it was noted that the two catalyst systems showed similar trends of conversion versus %XRD crystallinity, with higher conversions observed when the selectivity was between 50 and 70%. The catalytic performance of Mo/H-ZSM-5 catalysts could be regenerated with high efficiency by treating the catalysts in air at $600^{\circ}C$.

8.2 The aromatisation of propane

Some preliminary studies were done to establish if Mo/H-ZSM-5 catalysts could be used for the aromatisation of propane. These studies involved focused on the effect of the molybdenum content, reaction temperature and the crystallinity of H-ZSM-5 on the catalytic aromatisation of propane. The results obtained showed that in the presence of molybdenum the catalytic conversion was decreased. This decrease could be attributed to the possible decrease in the acidity of the catalysts upon impregnation with molybdenum. It was however, noted that the selectivity for C_1+C_2 hydrocarbons decreased with increasing molybdenum loading from 2 to 6 wt%, but increased when the molybdenum loading was increased to 15 wt%. For a constant conversion of 2%, the yield for aromatics and C_1+C_2 hydrocarbons were virtually unaffected by the molybdenum loading.

The conversion of propane increased exponentially with reaction temperature (from 400 to 700°C) for a time on stream of 1 h. However, the catalysts deactivated more rapidly when the reaction temperature was 700°C. This rapid decrease was probably because of the higher rate of coke formation at this high reaction temperature. The yield for aromatics also increased with increasing reaction temperature for a time on stream of 1 h. The high activity at 700°C was attributed to the formation of molybdenum carbide species which are also known to able to catalyse the conversion of the more stable methane.

8.3 The contributions made by this study

This study has confirmed previously reported results as well as contributed new results in the field of nonoxidative methane dehydroaromatisation. Contributions which confirmed what was previously reported in the literature are:

- The effect of the support material on the activity of molybdenum-based catalysts for the aromatisation of methane.

- The effect of the molybdenum loading on the catalytic activities of Mo/H-ZSM-5 in methane aromatisation reactions.
- The effect of the reaction temperature.
- The effect of the SiO_2/Al_2O_3 ratio of the zeolite.
- The effect of the molybdenum precursor
- The effect of the catalyst preparation method.
- The effect of silanation of ZSM-5 on the catalytic performance of Mo/H-ZSM-5 catalysts.
- The study of the regenerability of the deactivated Mo/H-ZSM-5 catalysts.

Some of the contributions which, to the best of our knowledge, were not previously reported but are illustrated in this study include:

- The effect of the percentage crystallinity of ZSM-5 on the nonoxidative methane dehydroaromatisation.
- A comparison of molybdenum and tungsten-based catalysts at different levels of the zeolite crystallinity.
- The effect of boron and silver on the catalytic performance of Mo/H-ZSM-5 catalyst for the nonoxidative methane aromatisation.
- The effect of the percentage crystallinity of ZSM-5 on the aromatisation of propane.

8.4 Proposed future research

Some of the future work that could be pursued in line with this work could involve the following:

- The study of the effects of the percentage XRD crystallinity of MCM-22-based materials on the nonoxidative methane dehydroaromatisation. This would follow from the fact that studies elsewhere have shown that these

materials are more stable and are more selective to naphthalene when compared with the ZSM-5-based materials (see Chapter 3).

- More extensive characterization of the Mo species present in the active catalyst.

- An extension of these studies to higher hydrocarbons like butane, pentane, etc.

- A more detailed study on the conditions under which the carbon nanotubes could be maximized together with the aromatics.

- A more detailed study on the nature carbon of the nanotubes that are formed during the dehydroaromatisation of methane.