



The effects of boron and silver on the oxygen-free conversion of methane over Mo/H-ZSM-5 catalysts

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ABSTRACT

The effect of adding boron (0.05–0.2 wt.%) and silver (0.5 wt.%) on the performance of Mo/H-ZSM-5 catalysts has been investigated. The results indicate that at the levels studied, boron did not influence the conversion level but improved the selectivity for C₂ hydrocarbons with increasing boron content, while the selectivity for aromatics was decreased when the boron content was more than 0.05 wt.%. The selectivity for C₂ hydrocarbons was increased from 4.5 to 9.5% for a boron loading of 0.2 wt.%. The presence of silver in Mo/H-ZSM-5 catalysts increased the conversion as well as the selectivity for C₂ hydrocarbons and aromatics. The catalysts were characterised using TPR, NH₃-TPD, UV–vis DRS, FTIR and XPS.

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1. Introduction

It is believed that natural gas could serve as an alternative source of fuel and chemicals in the future when the crude oil reserves become insufficient. This has prompted a lot of research involving the conversion of methane, the main component of natural gas, into useful chemicals and easily transportable liquid fuels. At present, methane is an underutilized resource for chemicals and fuels. This is in part due to the fact that methane is the most stable among alkanes. The structure of methane molecule with its four C–H covalent bonds of high bond energies (435 kJ mol⁻¹), zero dipole moment, no multiple bonds or functional groups and no asymmetry, is responsible for extremely low methane reactivity [1]. Thermodynamically, methane is unstable only above 530 °C, becoming more unstable than benzene above 1030 °C.

Commercially, methane is currently converted via indirect routes involving reforming steps to produce syngas which can then be upgraded via Fischer-Tropsch synthesis or methanol synthesis [1–5]. However, considerable efforts have been made to directly convert methane to valuable products. For this purpose, processes such as the oxidative coupling of methane (OCM) and the partial oxidation of methane have been intensively studied [6]. However, these processes have not yet reached the commercial stage because of the low selectivity to hydrocarbons as a result of the oxidation reactions that occur in the presence of dioxygen. This problem

of non-selective oxidation can be alleviated by operating in the absence of oxygen. The non-oxidative conversion of methane has received considerable attention since the first report by Wang et al. [7] in 1993. The Mo/H-ZSM-5 catalyst is regarded as one of the most promising catalysts for this reaction, yielding aromatics, some lighter alkanes and dihydrogen. In principle the conversion is an excellent way in which to convert methane directly to higher hydrocarbons and the hydrogen is, of course an extremely valuable co-product. It has been demonstrated that the performance Mo/H-ZSM-5 can be improved by the addition of elements such as W, Ga, Ru, Cu Al, Co, Cu, Fe, Pt, Zn and Zr [8–12], while V, Li and P on the other hand tend to decrease the activity [8,11,12].

In this report the promotional effects of doping of boron or silver are demonstrated for what we believe is the first time. Elsewhere, in hydroprocessing catalysis, it has been realised that boron modifies the dispersion of Mo on the surface of alumina as well as the acidic properties of alumina [13,14]. Sayed et al. [15] have shown that introducing boron into the zeolite ZSM-5 by impregnation with HBO₃ decreased the acidity of the zeolite. Since it is accepted that acidity plays a significant role in the aromatization of methane [8], the effect of boron on this aspect of catalysis by Mo/H-ZSM-5 catalysts was also investigated. In other work it was 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 [16–18]. In addition, Miao et al. [18] studied the non-oxidative conversion of methane into C₂ hydrocarbons over Ag/ZSM-5 catalysts. These studies indicated that methane is activated by the Ag⁺ species and that heterolytic splitting of the C–H bond of the reactant takes place. In Mo/H-ZSM-5 catalysts, methane is considered

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to be activated by Mo₂C species, the latter being produced by reaction of molybdenum oxide entities with the methane in a carbiding step [8]. It was therefore, speculated that the introduction of Ag⁺ ions into the Mo/H-ZSM-5 catalysts might improve the catalytic performance for the non-oxidative conversion of methane.

2. Experimental

2.1. Catalyst preparation

The ZSM-5 zeolite, with a nominal SiO₂/Al₂O₃ ratio of 70, was synthesised and ion-exchanged as previously reported [19]. Mo/H-ZSM-5 catalysts were prepared by impregnating the H-ZSM-5 zeolite with an aqueous solution of ammonium heptamolybdate of appropriate concentration to obtain samples with a Mo loading of 2 wt.%. The resulting sample was dried at 120 °C overnight and then calcined in air at 500 °C for 6 h. In the case where boron was used as a dopant, the zeolite was impregnated with aqueous solutions of HBO₃ dried and calcined as above before to the introduction of molybdenum. The content of boron was varied from 0 to 0.2 wt.%. Silver was introduced into the already-prepared 2%Mo/H-ZSM-5 by impregnation with a solution of silver nitrate, with a resultant silver content of 0.5 wt.%. A sample of 2%Ag/H-ZSM-5 was also prepared as above for comparison purposes.

2.2. Characterisation

2.2.1. Hydrogen temperature programmed reduction (TPR)

Temperature programmed reduction was performed in a flow reactor system equipped with a thermal conductivity detector. Before reduction the sample (about 0.2 g) was pretreated at 700 °C for 1 h in nitrogen and then cooled to room temperature. Reduction was performed by using 5% H₂/Ar mixture at a flow rate of 30 ml/min, and a ramping rate of 7.5 °C/min.

2.2.2. Temperature programmed desorption of ammonia (NH₃-TPD)

Temperature programmed desorption of ammonia was performed in a similar flow reactor system, also fitted with a thermal conductivity detector. Before adsorption of ammonia took place, the sample (about 0.2 g) was pretreated by heating to 700 °C at rate of 10 °C/min and then cooled to 100 °C. A mixture of ammonia in helium (4 vol.% NH₃) was passed over the catalyst for 1 h at 100 °C and the flow was then switched to helium in order to remove the weakly adsorbed and physisorbed ammonia. Desorption was carried out in helium at a flow rate of 30 ml/min by heating the sample from room 100 °C to 700 °C at a heating rate of 10 °C/min.

2.2.3. Diffuse reflectance spectroscopy (DRS)

The DRS spectra of the samples were collected on a Varian Cary 500 Scan UV–vis–NIR spectrophotometer equipped with a diffuse reflectance accessory. The spectra were collected in the UV–vis region at a scanning rate of 120 nm/min in the range 200–600 nm.

2.2.4. FTIR spectroscopy

A Bruker Vector 22 spectrophotometer fitted with an AABSPEC #2000-A multi-mode system transmittance cell was used in this study. AABSPEC #2000-A is an all-metal high vacuum cell fitted with KBr windows. This cell is designed to operate at vacuum up to 10⁻⁸ Torr and temperatures of up to 900 °C. Opus Version 5.5 software from Bruker was used to operate the spectrophotometer. Resolution was 4 cm⁻¹ and 128 scans per spectrum were collected.

A self-supporting wafer was prepared using about 20 mg of a sample and a pressure of 3 tons from a hydraulic press. The wafer was then degassed at 500 °C under vacuum (2.3 × 10⁻⁵ Torr)

overnight. A background spectrum was collected prior to loading the sample in the cell. Pyridine dried using molecular sieve 3 Å was adsorbed at 100 °C and allowed to equilibrate for 12 min. Excess pyridine was evacuated at 100 °C for 1 h; this also allowed for the removal of the weakly physisorbed pyridine. The sample was then cooled to room temperature prior to collecting the IR spectrum.

2.2.5. X-ray photoelectron spectroscopy

X-ray photoelectron spectra were measured on a Kratos Axis Ultra DLD spectrometer using a monochromatic AlK_α X-ray source (75 W) and an analyzer pass energy of 160 eV (survey scans) or 40 eV (detailed scans). Samples were mounted using double-sided adhesive tape, and binding energies are referenced to the C(1s) binding energy of adventitious carbon contamination taken to be 284.7 eV. The data were quantified using Wagner's sensitivity factors and integrated peak intensities computed from the detailed regional scans using in-house software.

2.3. Catalytic aromatization tests

Methane conversion was studied at 750 °C and 0.075 MPa (the prevailing ambient pressure in Johannesburg) at a GHSV close to 800 h⁻¹, using a conventional quartz microreactor system. Analysis of products focused on the gas-phase components present in the exit-stream, which was heated in order to prevent condensation of products, with conversion levels being determined using argon as an internal standard (present at 10%) in the inlet methane. Products are quoted as C₂-hydrocarbons (ethene and ethane), aromatics (largely benzene with a little toluene) and C₈₊ (suspected to be mainly naphthalenes, with very little or no formation of C₈₊ mononuclear and polynuclear aromatics). The quoted C₈₊ selectivities also represent conversion to other carbonaceous products, such as polynuclear aromatics, coke and carbon. All selectivities are expressed on a %C basis. The conversion range studied is necessarily limited because the maximum thermodynamically permitted % conversion under the conditions used is approximately 12–15%, depending on the product selectivity. Within this range the selectivities do not change markedly except for very high space velocities (low conversions) when there is a tendency for C₂ selectivities to be increased somewhat, which is fully in line with their probable role as the reactive intermediate products. (We accept that there is still a need for detailed studies of selectivity/conversion trends in order to help elucidate the mechanism and the sequence of reactions involved, although selectivity disguise in zeolitic systems makes this work more difficult in practice.) Most selectivities are quoted for a conversion extent of 10%.

3. Results and discussion

3.1. The effect of boron

The effect of boron on the conversion of methane over the 2%Mo/H-ZSM-5 catalysts is shown in Fig. 1. The catalytic conversion and stability of the Mo/H-ZSM-5 catalyst is not influenced by the presence of boron at the levels of boron studied. Usman et al. [13] observed that the hydrodesulfurization activity of MoS₂/B/Al₂O₃ remained constant up to a boron content of about 0.6 wt.%. The selectivity for C₂ hydrocarbons and the ethene/ethane ratio was, however, increased with increasing boron loading as shown in Fig. 2, for a conversion of about 10%. The selectivity to C₂ hydrocarbons increased from about 4.5% in the absence of boron to about 9.5% for a boron loading of 0.2 wt.%. Concomitantly, the ethene/ethane ratio increased from about 5 to about 9.5, suggesting that the hydrogenation/dehydrogenation characteristics of the catalyst was modified by boron, and we also note that the lack of

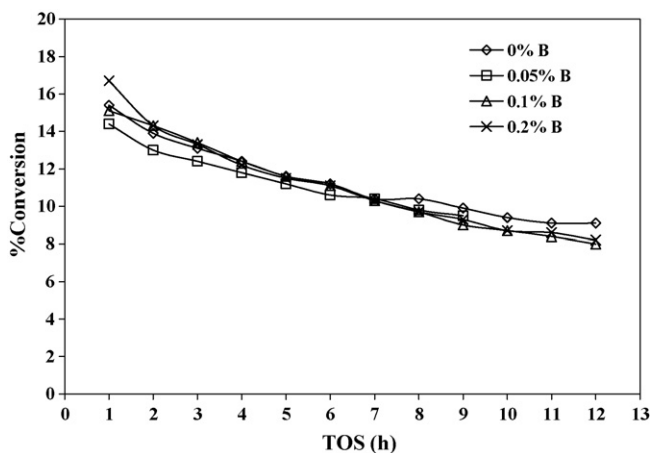


Fig. 1. The effect of boron on the catalytic and stability of and conversion of methane over Mo/H-ZSM-5 at 750 °C.

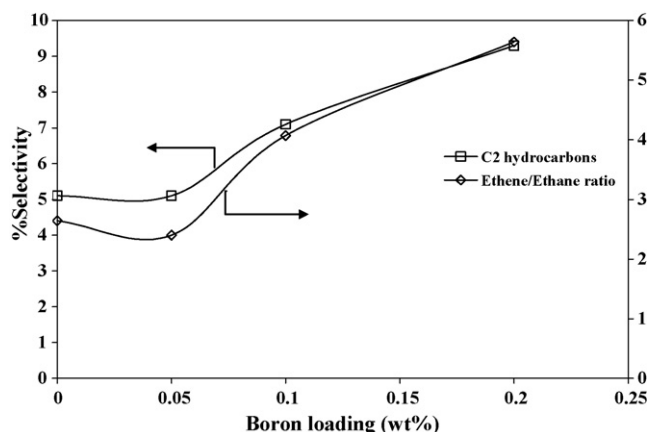


Fig. 2. The effect of boron content on the selectivity to C₂ hydrocarbons and the ethene/ethane ratio for conversion of 10% over Mo/H-ZSM-5 catalysts at 750 °C.

consistency in this ratio precludes the attainment of equilibrium between the ethene and ethane under all conditions studied. 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 further above 0.05 wt.% as shown in Fig. 3. On the other hand the selectivity to C₈₊ (also shown in Fig. 3) was increased when the boron loading was above 0.05 wt.%. The fact

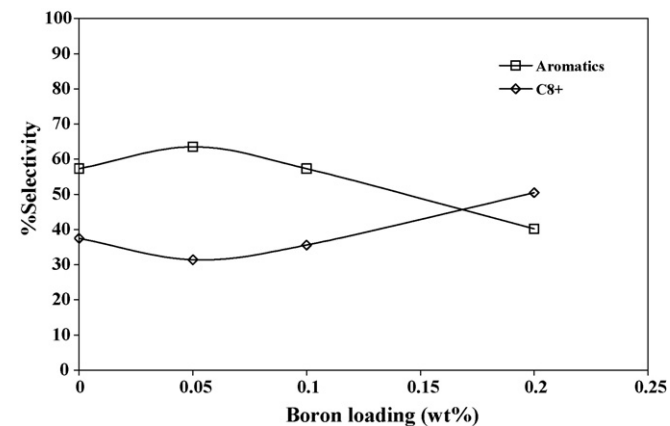


Fig. 3. The effect of boron content on the product selectivity for a conversion of 10% over Mo/H-ZSM-5 catalysts at 750 °C.

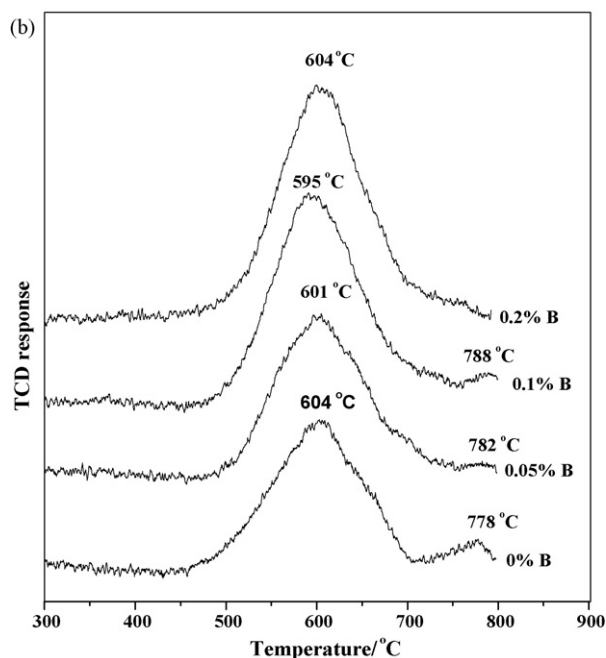
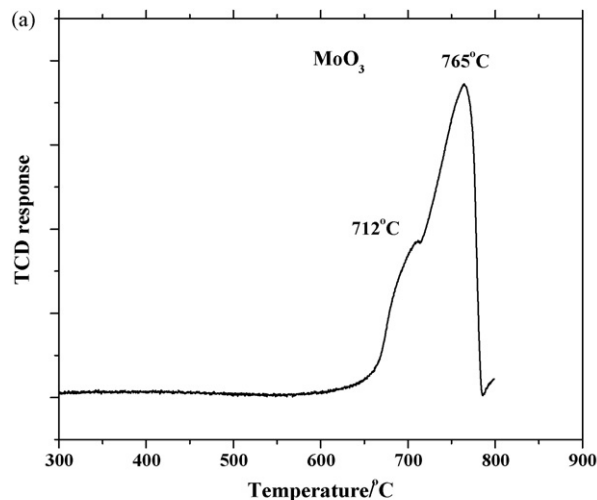


Fig. 4. H₂-TPR profiles of (a) MoO₃ and (b) 2%Mo/H-ZSM-5 catalyst with and without boron.

that the deactivation of the catalyst was independent of the boron content of the catalysts, while the selectivity to C₈₊ is increasing with boron loading may suggest that factors other than heavy aromatics formation might be responsible for the deactivation of the catalysts.

The effect of boron on the reducibility of molybdenum species in Mo/HZSM-5 catalysts is shown in Fig. 4. The TPR profile of MoO₃ showed a major reduction peak at a temperature of 765 °C and a shoulder at 712 °C. For the reduction of molybdenum trioxide to the dioxide,



An H₂ consumption/Mo contained ratio of 1.0 would be expected assuming that all MoO₃ entities were accessible. From the TPR profile of MoO₃, the calculated molar H₂/Mo consumption ratio was 0.8. This suggests that MoO₃ was only partly reduced to MoO₂, following Eq. (1), or that only part of the total Mo contained was reduced by dihydrogen. Part of the reason for a partial reduction may lie in the heterogeneous nature of the molybdenum

entities in these catalysts. Highly dispersed molybdenum entities are likely to be less easily reduced, for example [20]. Further, given that the size of the heptamolybdate ion [21] is consistent with effective radius of the oxide ion in the anion of approximately 148 pm the anion cannot enter the intrazeolitic voids of highly crystalline ZSM-5 samples. Indeed, it has been observed that the anion does not readily enter the voids of the even larger pore zeolites in USY samples [22]. The issue of molybdate anion modification taking place during or after impregnation has been discussed elsewhere [23–27]. The formation of monomeric Mo units has been proposed and again, Mo heterogeneity is invoked to cover internal and external-zeolite locations, and also to allow for the co-existence of monomolybdates and hexa- and hepta-entities. Of course, access by heptamolybdate units to intrazeolitic locations in defective or partially crystalline samples (studied in some of our other work [28] cannot be excluded.

The TPR profile of the Mo/H-ZSM-5 catalyst without boron exhibits two reduction peaks at 604 and 778 °C. The presence of two reduction peaks in the TPR profiles of Mo/H-ZSM-5 catalysts was reported by other researcher [29,9]. The peak intensity of the peak at higher reduction temperatures disappeared with increasing molybdenum loading. The reducibilities of the catalysts, calculated based on reaction (1) are summarised in Table 1. These results suggest that the reducibility of molybdenum was markedly improved in the presence of boron, and since boron or borate species are unlikely to act as hydrogen activators in a direct sense, we infer that some sort of direct chemical interaction between B and Mo may be taking place, or that the prior incorporation of boron modifies the manner in which molybdate entities, subsequently introduced, are dispersed within the zeolite.

The NH₃-TPD profiles of zeolites generally show peaks in two regions, the low-temperature region (LT), and the high-temperature region (HT) [30]. The peak in the HT region has been ascribed to desorption of ammonia from strong Brønsted and Lewis acid sites [31], while assignment of the LT peak remains controversial. According to Katada et al. [31] the LT peak is due to weakly bound ammonia, probably hydrogen bonded. Lónyi and Valyon [30] 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 NH₄⁺ ions. The ammonia desorption profiles of the catalysts including that of the parent zeolite are shown in Fig. 5. Mo/H-ZSM-5 catalysts with and without boron exhibited two desorption peaks, one at about 206 °C in the LT region and another one at temperatures above 500 °C. 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 has been previously suggested [32,33]. At the levels of boron used in this study the acidity of the Mo/HZSM-5 catalysts was not greatly affected by the boron content, as shown in Fig. 5 though some modification does appear to take place.

The coordination sphere of the molybdenum species was characterised by diffuse reflectance spectroscopy. It is known that oxomolybdenum compounds give strong absorption bands in the UV–Vis region due to the charge transfer $O^{2-} \rightarrow Mo^{6+}$ [34].

Table 1

A summary of the effect of the B loading on the reducibility of the Mo/H-ZSM-5 catalysts in hydrogen.

B loading (wt.%)	Reduction temperature (°C)	%Reduction
0	604	33
0.05	601	31
0.1	595	42
0.2	604	43

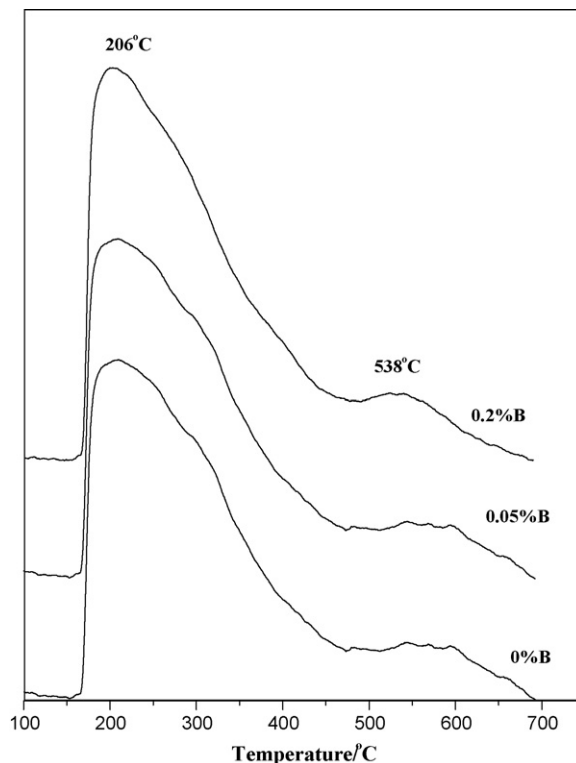


Fig. 5. NH₃-TPD profiles of 2%Mo/H-ZSM-5 catalyst with and without boron.

The position of this electronic transition depends on the ligand field symmetry surrounding the Mo centre. In general, three bands at 220–250, 280, and 320 nm are detected in the UV–visible diffuse reflectance spectrum of supported molybdate [35]. 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 established [35]. The DRS spectra of the catalysts doped with different amounts of boron are shown in Fig. 6, together with the spectra of sodium molybdate and ammonium heptamolybdate. It

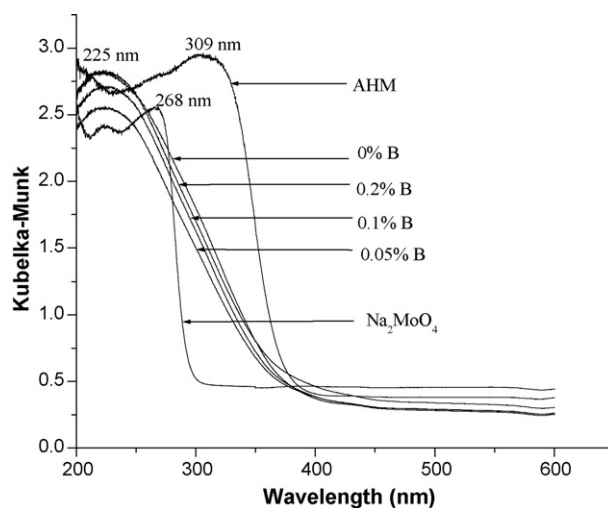


Fig. 6. DRS spectra of 2%Mo/H-ZSM-5 catalysts with and without boron, including the spectra of sodium molybdate (Na₂MoO₄) and ammonium heptamolybdate (AHM).

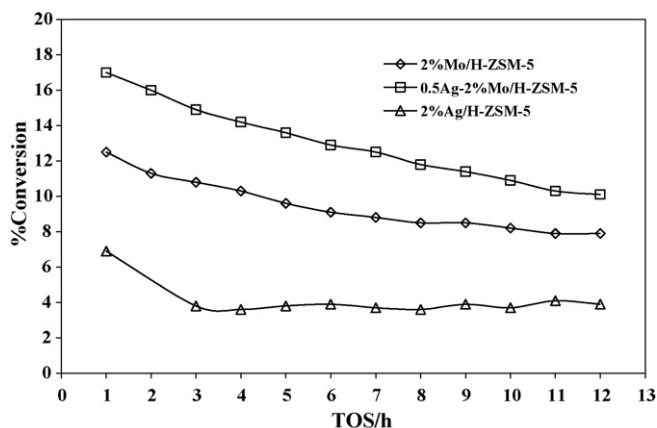


Fig. 7. The effect of silver on the conversion and stability of Mo/H-ZSM-5 catalysts for the conversion of methane at 750 °C.

is known that molybdenum species in sodium molybdate are in the tetrahedral coordination while ammonium heptamolybdate are in octahedral coordination [36]. This is also seen in the spectra of these compounds in Fig. 6, with sodium molybdate absorbing at a wavelength of 225 and 268 nm while AHM absorbs at a wavelength of 309 nm. The Mo/H-ZSM-5 catalysts with and without boron absorb at a wavelength of 225 nm, indicating the presence of tetrahedral molybdenum species. Therefore, boron does not influence the coordination sphere of the molybdenum at the concentrations reported in this study. These are heterogeneous catalysts and it is therefore likely that we have a range of Mo-entities. The location of the Mo is almost certainly not uniform, and there is a likelihood that we have oxidic, oxycarbide and carbide units co-existing. Our main issue argument is that the dominant Mo species present in the bulk of these catalysts remains largely unaffected by the composition of the solids.

3.2. The effect of silver

The results obtained from the catalytic conversion of methane over Mo/H-ZSM-5 catalysts with and without silver ions are shown in Fig. 6, together with those of 2%Ag/H-ZSM-5. The addition of silver ions into the Mo/H-ZSM-5 catalyst system significantly improved the percentage conversion of methane. It is also interesting to note that the 2%Ag/H-ZSM-5 catalyst could activate methane, although with less effectiveness than the 2%Mo/H-ZSM-5 catalyst. It can further be noted that the 2%Ag/H-ZSM-5 was more stable than the molybdenum based catalysts for a times on stream above 3 h. The effect of the addition of Ag⁺ ions, on the product selectivity at a conversion level of about 10% is shown in Fig. 7. The presence of silver ions slightly improved the selectivity to aromatics. The selectivity to C₈₊ over the Mo/H-ZSM-5 was reduced when the Ag⁺ ions were added to the catalyst. The 2%Ag/H-ZSM-5 catalyst produced very small amounts of aromatics as compared to the other catalysts even when the conversion was about 7%. Increased aromatization activity of similar catalysts promoted with silver has also recently been seen in other laboratories [37].

The effect of the silver ions on the acidity of the Mo/H-ZSM-5 catalysts is shown in Fig. 8. The NH₃-TPD profile the parent H-ZSM-5 shows the LT peak as well as the HT peak, while in case of the 2%Mo/H-ZSM-5 catalyst only the LT peak was observed. As discussed above, this indicates that the molybdenum species interacted with the Brønsted acid sites. When the 2%Mo/H-ZSM-5 catalyst was doped with about 0.5 wt.% Ag, the HT peak due to the Brønsted acid sites appeared suggesting that the silver ions acted by enhancing the acidity of the catalyst. The enhancement

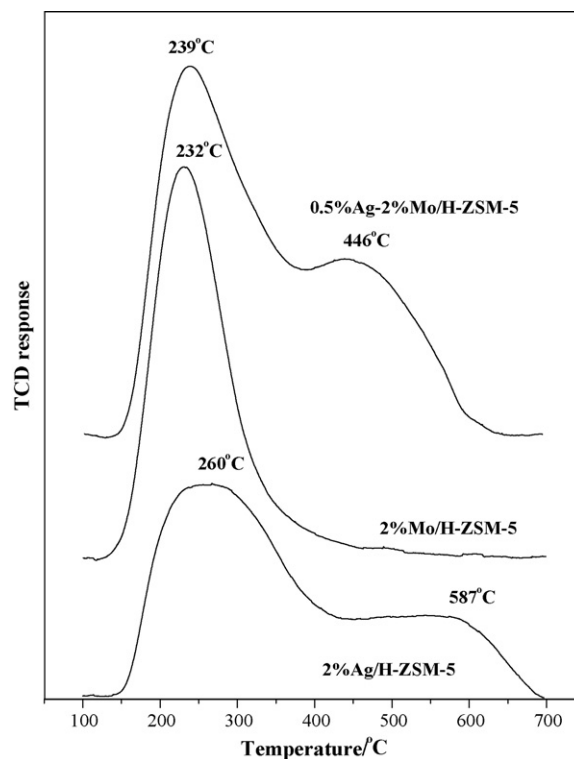


Fig. 8. NH₃-TPR profiles of 2%Mo/H-ZSM-5 catalyst with and without silver ions.

of the acidity of the Mo/H-ZSM-5 catalysts was reported for Cr-containing samples [38]. The nature of the acid sites has been determined by pyridine adsorption using FTIR spectroscopy, and the results are shown in Fig. 9. 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 [39]. On the hand the adsorption band at 1490 cm⁻¹ has been attributed to the adsorption of pyridine on both the Brønsted and Lewis acid sites. Fig. 9 shows that the intensity of these bands was decreased when the

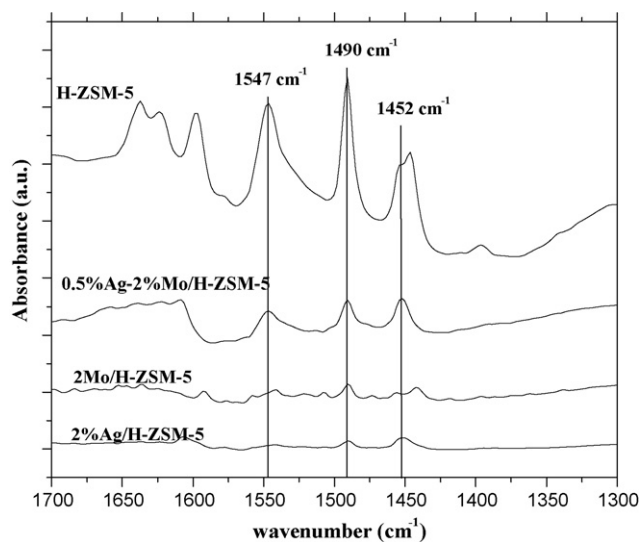


Fig. 9. The IR spectra of adsorbed pyridine on H-ZSM-5 catalysts with and without metal additives.

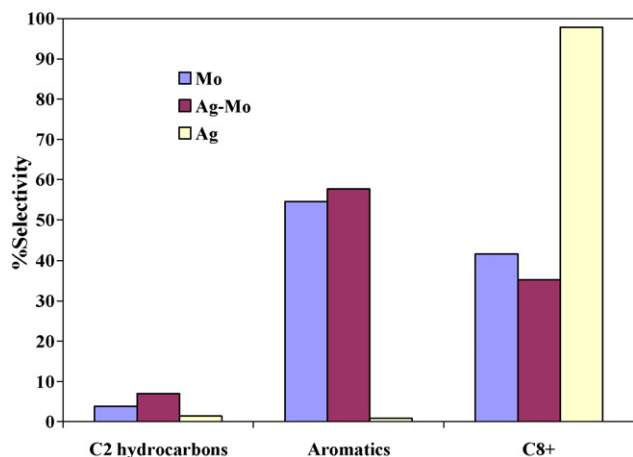


Fig. 10. The effect of silver ions on the product selectivity during the non-oxidative conversion of methane over Mo/H-ZSM-5 catalysts at 750 °C, for conversion of 10%.

metal additives were present, indicating decreased acidity due to the interaction of the acid sites with the Mo and/or Ag species. (The IR data are not claimed to be fully quantitative. No “internal” standard was used, and our main aim was to collect qualitative data. Nevertheless, practical considerations of optical transmission requirements and the need for mechanical integrity of wafers dictate that wafer thicknesses do not change very much, probably not more than 20% and so a self-imposed standardisation in terms of zeolite sample thickness exists.)

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 observations depicted in Fig. 10. The UV–vis DRS spectra of Mo/H-ZSM-5 catalysts with and without silver are shown in Fig. 11, including the spectrum of Ag/H-ZSM-5 for comparison. The results show that the molybdenum species are in the tetrahedral coordination form even when doped with silver, since the samples show an absorption band centred around 228 nm. The Ag/H-ZSM-5 sample also shows an absorption band at centred around 238 nm. This band may be attributed to the presence of an Ag_n^{δ+} cluster [18]. The silver ions

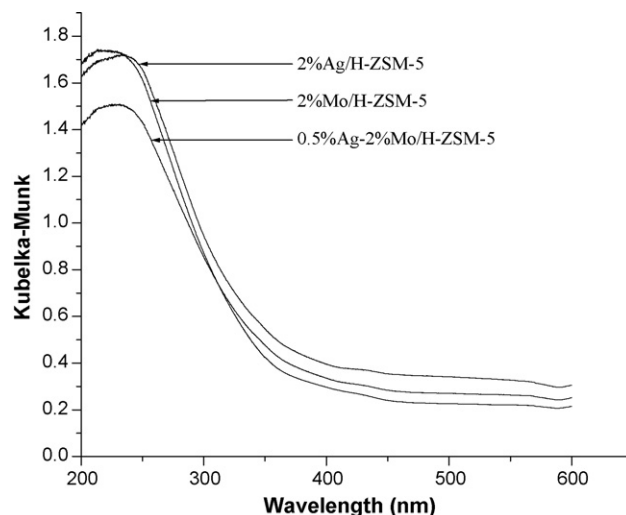


Fig. 11. DRS spectra of 2%Mo/H-ZSM-5 catalysts with and without silver, together with that of 2% Ag/H-ZSM-5.

did not exert an influence on the electronic spectra of the Mo species in the Mo/H-ZSM-5 catalyst.

The XPS data (Fig. 12) clearly indicate that the Mo species are retained in the +6 oxidation state during methane treatment at 750 °C, with only a small fraction of reduced Mo appearing at relatively long times. Significant carbon build-up occurs during methane treatment, as expected for conditions associated with the formation of molybdenum carbide phases, which are generally considered to be responsible for methane aromatization. If the bulk of the Mo that is visible to XPS were fully carbided then we might expect to see a lower binding energy for some of the other samples. It may be that Mo becomes carbided more readily within the zeolitic structure rather than on the surface, but we are in a position only to speculate, and, in any event the impact on catalysis is not yet clear, though this interpretation is consistent with the heterogeneity of the Mo as mentioned above. The lower binding energy peak is consistent with XPS data obtained elsewhere for molybdenum carbide synthesis [40].

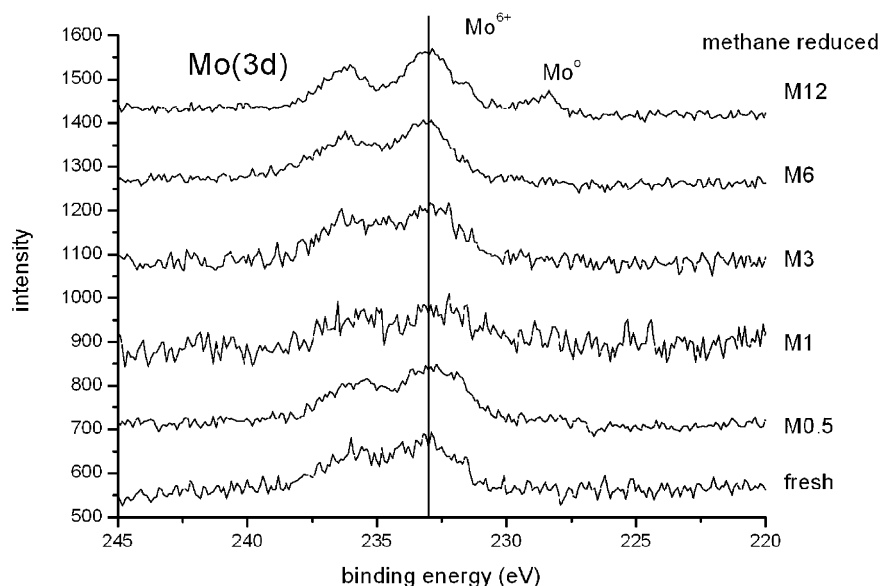


Fig. 12. XPS spectra (Mo 3d) of Mo/ZSM-5 samples treated in methane at 750 °C. M1 denotes a treatment duration of 1 h, etc.

4. Conclusions

This study has shown that the presence of boron in Mo/H-ZSM-5 catalysts did not affect the conversion of methane but noticeably changed the selectivity to various products. At the levels of boron used in this study, the physical and chemical properties of the Mo/H-ZSM-5 were not greatly changed by the presence of boron, though some acidity modification is apparent. On the other hand, the addition of Ag in Mo/H-ZSM-5 improved the conversion of methane as well as the selectivity for higher hydrocarbon products. This may have been due the fact that silver also improved the acidity of the catalyst. The Ag/H-ZSM-5 catalyst on its own can activate methane but with a low selectivity to desirable hydrocarbon products. The production of C₈₊ products is the main feature seen with Ag/H-ZSM-5.

It is expected that the use of these promoter elements may prove of use in helping to develop the higher activity catalysts that are required if methane aromatization using Mo/H-ZSM-5 is to become of commercial significance in the future.

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