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Effect of the activation procedure on the performance of Mo/H-MFI catalysts for the non-oxidative conversion of methane to aromatics

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Abstract

The effect of pre-treatment on the performance of Mo/H-MFI zeolite catalysts applied to the non-oxidative conversion of methane to aromatics has been investigated. It is demonstrated that catalyst performance depends on activation conditions. Activation of the Mo-oxide/H-MFI precursor with an *n*-butane/hydrogen mixture results in higher catalyst stability and benzene selectivity which are tentatively attributed to the formation of the α-MoC$_{1-x}$ carbide, with f.c.c. structure as revealed by XRD. © 2000 Published by Elsevier Science B.V.

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1. Introduction

In view of the large natural gas reserves, there is much to gain economically from the direct catalytic transformation of methane to higher hydrocarbons, including aromatic compounds. Extensive studies have been devoted in the past to the oxidative coupling and upgrading of methane using a variety of catalysts but such routes have appeared to offer no or little economical advantage relative to other routes leading to C$_2$ and higher products via multi-step processes.

Recently, the direct upgrading of methane to higher hydrocarbons (mostly aromatic in nature) under non-oxidative conditions, yielding hydrogen as a valuable by-product, has received increasing attention. So far, the most effective catalysts for this reaction derive from the molybdenum-modified H-MFI system first reported by Wang et al. [1] in 1993. Traditional methods for the preparation of Mo/H-MFI catalysts have focused on the dispersion of molybdenum onto H-MFI.

There is ample evidence that the performance of these catalysts depends on their in situ activation treatment in a reducing and carburising hydrocarbon atmosphere. It has been proposed that molybdenum species are transformed to Mo$_2$C by methane at 943 K [2]. Lunsford and coworkers [3] confirmed by XPS the formation of Mo$_2$C from MoO$_3$/H-MFI and suggested that this species was responsible for the activation of methane. Solymosi et al. [4] reported further that higher activity was obtained upon partial oxidation of Mo$_2$C/H-MFI and proposed that an additional oxygen-containing molybdenum phase was responsible for methane activation. More recent reports of Lunsford and coworkers [5] and Xu and

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coworkers [6] suggested that the induction period observed before reaction may be due to the deposition of carbon species on the carbide surface. They proposed that a coke-enriched molybdenum carbide plays an important role in methane activation.

A major problem in the non-oxidative aromatisation of methane using Mo/H-MFI catalysts is deactivation attributed to carbon deposition at the high temperature (HT), i.e., ca. 1000 K, at which reaction occurs in the absence of added hydrogen. Ichikawa and coworkers [7] showed that addition of CO or CO_2 to the methane feed promotes catalytic activity and stability. Ledoux and coworkers [8] observed that a carbon modified-MoO_3 catalyst showed excellent stability for the isomerisation of saturated hydrocarbons in the temperature range 623–723 K in their investigations of bulk carbides. Their molybdenum oxycarbide catalyst was obtained by reacting MoO_3 with a H_2/butane mixture at 623 K. Carburisation under these conditions was shown to yield the meta-stable carbide α-MoC_{1-x} (f.c.c. structure) [9,10].

We now report on the aromatisation of methane over Mo/H-MFI catalysts activated by different procedures. We show that the performance of a MoO_3/H-MFI precursor activated using a H_2/*n*-butane mixture at 623 K shows superior performance compared to a conventionally activated catalyst under similar reaction conditions. Loadings of 10 wt.% MoO_3 were used to follow the Mo-phase changes by XRD. The combustion of carbon was followed by TGA and the pore structure was analysed by N_2 and *n*-C_6 adsorption.

2. Experimental

2.1. Catalyst preparation

H-MFI was obtained by calcining NH_4-MFI (Zeolyst International, batch CBV 8014G, $SiO_2/Al_2O_3 = 80$) at 773 K for 4 h. A Mo/H-MFI precursor, containing 10 wt.% of MoO_3 (Mo-HMFI) was prepared by adding 10 g of H-MFI to 20 ml of distilled water and adding slowly to the slurry 20 ml of an aqueous solution containing the desired amount (2.1 g) of ammonium heptamolybdate ($(NH_4)_6$ $[Mo_7O_{24}]\cdot 4H_2O$, Aldrich, analytical grade). Water was evaporated whilst stirring at 353 K. The resulting solid was further dried in an oven at 393 K for 2 h and calcined at 823 K for 2 h. The calcined powder was pressed into tablets, crushed, and sieved to 250–425 μm particles (40–60 mesh).

2.2. Catalyts characterisations

Specific surface area and pore volume measurements were obtained from volumetric nitrogen adsorption using a Micromeritics ASAP-2010 instrument.

^{27}Al MAS NMR was used to detect the presence of non-framework aluminium species. ^{27}Al MAS NMR Bloch decay spectra were acquired on a Bruker Avance DSX-400 multinuclear NMR spectrometer operating at 104.27 MHz using 0.35 μs ($<10^\circ$) pulse lengths and 0.3 s recycle delays, with a spinning rate of ca. 4 kHz.

The nature and amount of coke deposits and carbidic species on the deactivated catalysts were determined using a Perkin Elmer TGA-7 thermogravimetric analyser. For this purpose, a ca. 20 mg sample of the used catalyst was heated from 303–1173 K in an air flow (20 ml/min), at a heating rate of 15 K/min.

The same TGA apparatus was adapted to study *n*-hexane adsorption by the fresh and used catalysts. The sample was heated, under N_2, from ambient temperature to 673 K, at a heating rate of 10 K/min, and then cooled to 363 K and held at this temperature for the *n*-hexane adsorption measurements, in order to avoid capillary condensation effects. The sample was then exposed to a flow of N_2 (20 ml/min) passing through a dual saturator containing *n*-hexane at ambient temperature ($p/p_0 = 0.20$). The rates of *n*-hexane adsorption were calculated using both the Cointot [11] and Barrer [12] models.

Powder X-ray diffraction patterns were obtained at room temperature using a Siemens D5005 diffractometer (Cu Kα radiation, step-size: 0.014°). Diffractograms were recorded for 2θ values ranging from 15 to 60° with a scanning rate of 0.02 s/step. The carbide region ($2\theta = 30$–50°) was further analysed at a scanning rate of 5 s/step.

2.3. Catalyst activation treatments

Several treatments were used to activate the catalyst precursor, Mo-HMFI. Pre-treatment gases included He, air, H_2 (UHP grade), *n*-butane, and methane (N2.0 grade). They were all supplied by BOC and were used without further purification. Activation was carried out in situ, i.e., by treating Mo-HMFI directly in the microreactor.

Calcination of Mo-HMFI was carried out in an air flow of 16.7 ml/min, the temperature was ramped at 5 K/min from 298 to 873 K and held for 1 h at the latter temperature. This sample is denoted Mo-HMFI-C.

Methane activated catalysts, denoted as Mo-HMFI-M, were obtained by subjecting the precursor, at all stages, to a gas flow of 16.7 ml/min. The catalyst was calcined as described above, then flushed with helium for 10 min before methane was introduced and the temperature was raised to 973 K at a heating rate of 5 K/min.

Butane activated catalysts, denoted as Mo-HMFI-B, were obtained by allowing the system to cool to 298 K after calcination. After 10 min of flushing in He, a 11:1 molar mixture of $H_2/n\text{-}C_4$ was introduced (total flow rate $= 63\,\text{ml/min}$) and the temperature was raised to 623 K at a heating rate of 16 K/min. This temperature was held at 623 K for 6 h before further heating to 823 K at 5 K/min, where the catalyst was flushed with He for 10 min. Methane (16.7 ml/min) was then introduced and the temperature was raised to 973 K at a heating rate of 5 K/min.

2.4. Catalytic testing

Testing was performed at atmospheric pressure using a fixed bed continuous plug-flow microreactor system consisting of an 11 mm i.d. 316 stainless steel reactor tube containing ca. 1 g of catalyst, plugged at both ends with quartz wool. The reaction temperature (973 K) was monitored using a K-type thermocouple positioned in the catalyst bed and gas flows were monitored and regulated with Brooks 5850S mass flow controllers (methane WHSV $= 0.714\,\text{h}^{-1}$). The outlet of the reactor was kept above 500 K to avoid condensation of heavy hydrocarbons. On-line analysis of the effluent was performed with a Varian Star 3400CX gas chromatograph using the Varian Star 4.5 data handling software. The aromatic products were separated using a capillary HP-1 column and quantified using an FID detector. Other products were separated using a Porapak Q column and detected using a TCD detector.

3. Results

3.1. Catalytic results

The performances of catalysts Mo-HMFI-M and Mo-HMFI-B for the aromatisation of methane are compared at 973 K and atmospheric pressure, respectively. Figs. 1 and 2 show the variations of methane conversion and selectivities to aromatics and C_2 hydrocarbons, with the products as a function of time-on-stream, without accounting for coke formation. Conversions and selectivities are expressed on a carbon basis.

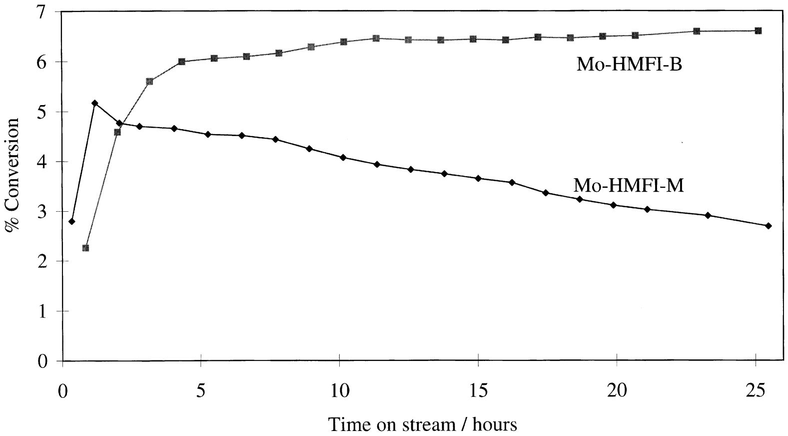

Fig. 1. Methane conversions, expressed on a carbon basis without accounting for coke formation. Reaction conditions: 973 K; 1 atm; feed = 100% CH_4.

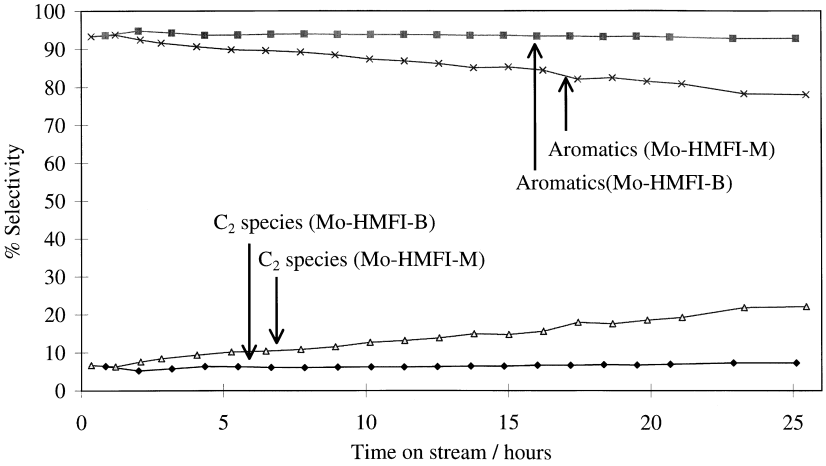

Fig. 2. Selectivity of C_2 and aromatic species. C_2 = ethane and ethylene. Aromatics = benzene, toluene, naphthalene and methyl-naphthalene. expressed on a carbon basis without accounting for coke formation. Reaction conditions: 973 K; 1 atm; feed = 100% CH_4.

Conversion using the Mo-HMFI-M catalyst reaches a maximum (ca. 5%) after 2 h on stream and decays progressively to ca. 2.5% at 25 h (Fig. 1). By contrast, the Mo-HMFI-B catalyst shows conversions comparable to those of Mo-HMFI-M up to 3 h, which increase further to about 7% after 7 h and remain constant afterwards up to 25 h (duration of the test) (Fig. 1).

The initial selectivities to aromatics (benzene, toluene, and naphthalene) and C_2 hydrocarbons are similar for both catalysts. As conversions are also comparable, both systems thus appear to behave similarly in the early stage of the reaction. However, with increasing time-on-stream, major differences are observed. The selectivities to aromatics and C_2 hydrocarbons remain constant for Mo-HMFI-B catalyst, whereas the selectivities to aromatics and C_2 hydrocarbons decrease and increase, respectively, for the Mo-HMFI-M catalyst (Fig. 2).

Figs. 3 and 4 show the variation of the production rates (nmol/s, expressed on a carbon

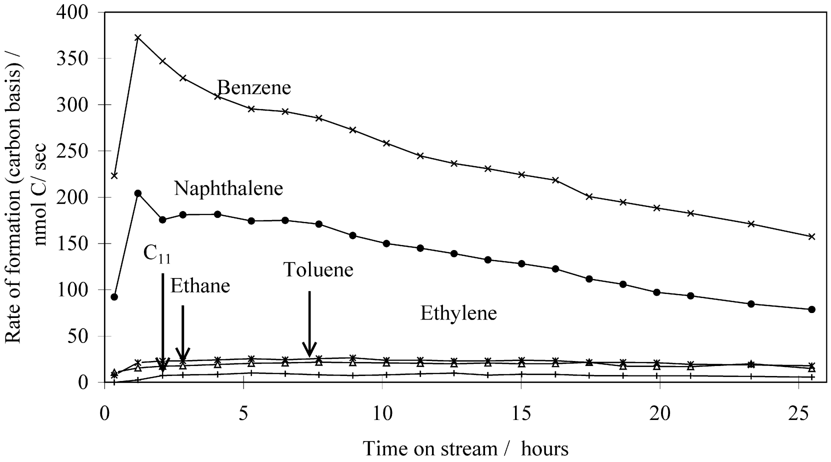

Fig. 3. Rate of product formation for Mo-HMFI-M, expressed on a carbon basis without accounting for coke formation. Reaction conditions: 973 K; 1 atm; feed = 100% CH_4.

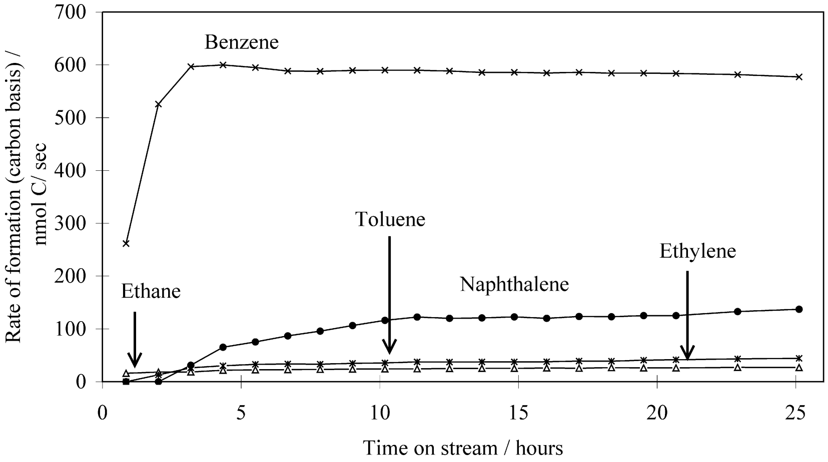

Fig. 4. Rate of product formation for Mo-HMFI-B, expressed on a carbon basis without accounting for coke formation. Reaction conditions: 973 K; 1 atm; feed = 100% CH_4.

basis) of ethylene, ethane, benzene, toluene, naphthalene, and methyl-naphthalene as a function of time-on-stream for the Mo-HMFI-M and Mo-HMFI-B catalysts, respectively. Besides variations in rates which parallel the variations in total conversions and selectivities mentioned above, the following features should be noted. The Mo-HMFI-M catalyst produced at a nearly constant rate (ca. 10 nmol/s) methyl-naphthalene after 3 h on stream (Fig. 3). Traces of C_3 hydrocarbons were also observed. These products were not observed using the Mo-HMFI-B catalyst. In the latter case, the production rate for the formation of benzene stabilises after ca. 5 h (ca. 600 nmol/s) and that for naphthalene production after ca. 10 h (ca. 100 nmol/s). Ethane also appears to be formed at a higher rate than ethylene at short reaction time (less than 2 h) (Fig. 4).

It is also interesting to note that very little naphthalene is formed initially on the Mo-HMFI-B catalyst, the ratio of the benzene to naphthalene formation rates being ca. 2 and 4.5 for the Mo-HMFI-M and Mo-HMFI-B catalysts, respectively. The latter is thus not only more stable vs. time-on-stream but also more selective towards the production of benzene. These two observations are not unrelated as the formation of higher aromatic products is usually one of the steps leading to the formation of coke deposits.

4. Catalyst characterisations

4.1. ^{27}Al MAS NMR

^{27}Al MAS NMR was used to characterise all the catalysts before and after reaction. The MAS NMR spectra showed no evidence for extra-framework aluminium in all cases.

4.2. Surface area and pore volume characterisations

BET surface areas, BJH and *t*-plot pore volume determinations, *n*-hexane sorption capacities, and relative *n*-hexane sorption rates evaluated using both the Cointot [9] and Barrer [10] models are listed in Table 1 for the parent zeolite, the Mo-HMFI-C precursor, and the used Mo-HMFI-M and Mo-HMFI-B catalysts.

The nitrogen and *n*-hexane adsorption results correlate well with each other for all samples, which indicates that the variations observed are attributable to changes occurring in the accessible intracrystalline volume of the zeolite catalysts as no structural modifications of the zeolite material were detected by ^{27}Al MAS NMR.

Comparing the parent H-MFI zeolite to the Mo-HMFI-C precursor shows that the specific surface area and the accessible pore volume to both nitrogen and *n*-hexane are reduced by ca. 20% after addi-

Table 1
Pore volume data

Catalyst	BET surface area (m^2/g)	BJH pore volume[a] (cm^3/g)	t-plot[b] (cm^3/g)	n-C_6H_{14}[c] (wt.%)	Cointot rate[d] (%)	Barrer rate[d] (%)
H-MFI	393	0.151	0.111	9.88	100	100
Mo-MFI-C	278	0.116	0.088	7.16	100	106
Mo-MFI-M	245	0.087	0.074	6.73	107	124
Mo-MFI-B	248	0.103	0.080	7.00	93	103

[a] BJH pore volume relates to the cumulative pore volume.
[b] t-plot is the micropore volume calculated by the t-plot method.
[c] wt.% of n-hexane adsorbed with reference to the weight of calcined zeolite.
[d] The rates of n-hexane adsorption have been normalised to the parent H-MFI.

tion of molybdenum. The accessible pore volumes of the Mo-HMFI-M and Mo-HMFI-B used catalysts are smaller than that of their common precursor but this decrease is smaller for the Mo-HMFI-B catalyst relative to its Mo-HMFI-M counterpart, indicating less coke deposition in the former. The n-hexane adsorption rates determined using either the Cointot [9] or Barrer [10] model are nearly identical in all cases, showing that no significant pore mouth blockage has occurred neither due to Mo-species during modification nor to coke deposition during reaction.

4.3. Thermogravimetric analysis

The thermogravimetric analysis results are shown in Table 2. All catalysts show a small weight loss in the range 293–423 K due to desorption of water.

Mo-HMFI-C shows two additional weight losses in the region of molybdenum oxide sublimation. The first one (4.5 wt.%) at 1093 K corresponds to the weight loss observed when bulk MoO_3 is subjected to the same treatment. An additional weight loss (1.9 wt.%) is also observed in the 1123–1223 K region which may correspond to the sublimation of molybdenum oxide species interacting with the zeolite.

The spent Mo-HMFI-M catalyst shows a small, 0.3 wt.%, weight gain in the region 733–803 K, probably due to oxidation of the molybdenum carbide that was formed during methane pre-treatment and reaction. The oxidative removal of carbonaceous deposits (low temperature (LT) coke, 1.4 wt.% loss) and coke deposits (HT coke, 1.5 wt.% loss) occur in the temperature range 803–873 and 873–1003 K, respectively. A subsequent weight loss (4.1 wt.%) between 1013 and 1173 K is attributed to the sublimation of Mo-oxide.

Table 2
Thermogravimetric data

Catalyst	Temperature range (K)	Peak maximum (K)	wt.%	Assignment
H-MFI	303–523	373	−2.6	Water loss
Mo-MFI-C	303–523	373	−3.0	Water loss
	973–1123	1083	−4.5	MoO_3 sublimation
	1123–1173	1153	−1.9	Mo-oxide sublimation
Mo-MFI-M (spent)	303–523	373	−1.5	Water loss
	733–503	783	+0.3	Mo-carbide oxidation
	803–873	843	−1.4	LT coke combustion
	873–1003	893	−1.5	HT coke combustion
	1013–1173	1123	−4.1	Mo-oxide sublimation
Mo-MFI-B (spent)	303–523	373	−1.4	Water loss
	713–873	783	−7.6	LT coke combustion
	873–973	923	−0.5	HT coke combustion
	983–1173	1103	−5.3	Mo-oxide sublimation
MoO_3	993–1123	1063		MoO_3 sublimation

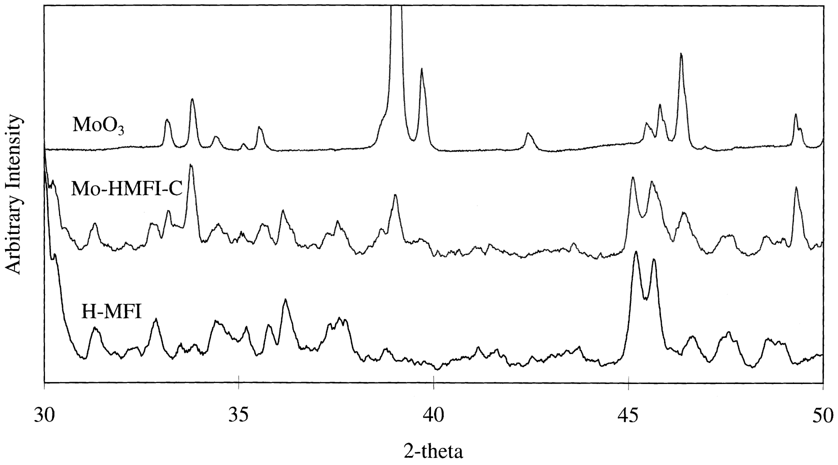

Fig. 5. XRD characterisation of fresh catalysts.

By contrast, the used Mo-HMFI-B catalyst shows a weight loss of 7.6 wt.% in the LT coke temperature range, a second one of only 0.5 wt.% in the HT coke temperature range (873–973 K), and eventually a 5.3 wt.% loss due to the sublimation of molybdenum oxide (973–1173 K). Carbide oxidation in Mo-HMFI-B is probably obscured by the large LT coke weight loss. The above results show that the used Mo-HMFI-B catalyst contains more LT coke (carbonaceous species) than the used Mo-HMFI-M catalyst, and vice versa for the HT coke.

4.4. X-ray powder diffraction

Fig. 5 compares the diffraction patterns of MoO$_3$, the parent H-MFI zeolite, and the Mo-HMFI-C precursor. The diffraction pattern of the Mo-HMFI-C is a composite of the MoO$_3$ and H-MFI diffraction patterns, indicating that molybdenum was present as MoO$_3$ (diffraction peaks at $2\theta = 33.2, 33.8, 39.0$ and $49.3°$)

Fig. 6 compares the diffractograms of the two spent catalysts, Mo-HMFI-M and Mo-HMFI-B in the 2θ

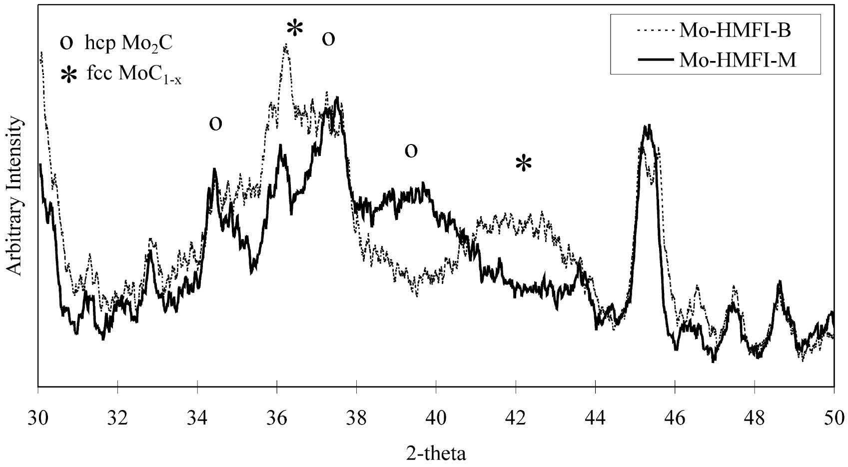

Fig. 6. XRD characterisation of spent catalysts.

range 30–50° to identify possible Mo-carbide species. The diffraction peak at ca. $2\theta = 45°$ arises from the zeolite framework. This peak, which is a doublet for the parent zeolite, the Mo-HMFI-C precursor, and the Mo-HMFI-B spent catalyst, appears as a singlet for Mo-HMFI-M. It indicates that the three former zeolite materials have a framework possessing monoclinic symmetry, whereas the latter, Mo-HMFI-M, has orthorhombic symmetry. As it is known that a reversible, displaceable transformation from orthorhombic to monoclinic symmetry of the MFI framework, with no change of framework topology, occurs when occluded organic material is removed for MFI materials with Si/Al ratio greater than ca. 85, [13,14] this observation may indicate that the used Mo-HMFI-M catalyst contains more extraneous material in its channels than the used Mo-HMFI-B one, and obviously more than the parent zeolite and the Mo-HMFI-C precursor which are fresh materials. This proposal agrees with the adsorption measurements.

Catalyst Mo-HMFI-M shows diffraction lines in the range $2\theta = 33–42°$ that match closely the position of peaks expected for the h.c.p. Mo carbide, β-Mo_2C. This observation is in agreement with earlier proposals indicating that formation of β-Mo_2C occurs under reaction conditions [3,5,6]. These features are less apparent in the diffraction pattern of catalyst Mo-HMFI-B which, by contrast, shows two more intense and broad peaks at ca. $2\theta = 37$ and 42°. These peaks positions correspond to those that are characteristic of the f.c.c. Mo carbide, α-MoC_{1-x}, which is formed when MoO_3 is reduced and carburised in conditions similar to those used to obtain Mo-HMFI-B [8–10].

5. Discussion

The Mo-HMFI-B catalyst shows superior performance in terms of activity, stability and selectivity (less C_2 hydrocarbons and higher benzene yields), compared to the Mo-HMFI-M catalyst. In particular, we observed that:

1. The Mo-HMFI-B catalyst has stable activity and selectivity to aromatics over at least 25 h of operation, whereas the activity of catalyst Mo-HMFI-M decreases by about 50%, with a simultaneous decrease in its selectivity to aromatics and an increase in the selectivity to C_2 hydrocarbons.
2. The ratio of the benzene/naphthalene formation rates (expressed on a carbon basis) for Mo-HMFI-B is twice that observed for Mo-HMFI-M.
3. The intracrystalline pore volume of the Mo-HMFI-B catalyst is less affected by coke deposition than that of the Mo-HMFI-M catalyst. More LT coke (carbonaceous deposits) is deposited at the external surface of the former. No evidence of pore mouth blockage is observed in both cases (pore volume and *n*-hexane adsorption rate measurements).
4. No extra-framework Al-species are formed during activation or reaction (^{27}Al MAS NMR). Symmetry differences of the MFI framework, orthorhombic for Mo-HMFI-M and monoclinic for Mo-HMFI-B catalysts, probably arise from a higher occupancy of the zeolite channels by extraneous species in the former case.
5. β-Mo_2C is the carbidic species present in used Mo-HMFI-M, whereas both Mo_2C (minor species) and α-MoC_{1-x} (major species) are present in used Mo-HMFI-B (XRD).

Observations 4 and 5 mentioned above are consistent and indicate that more coke species are deposited in the intracrystalline volume of the zeolite for the Mo-HMFI-M catalyst, compared to its Mo-HMFI-B counterpart. Observation 5 also proves that zeolite dealumination is not responsible for catalyst deactivation.

The following discussion focuses on features possibly explaining the difference in catalytic performances observed for Mo-HMFI-M and Mo-HMFI-B.

Lee et al. [2] showed that carburisation of MoO_3 using pure methane is thermodynamically expected to form graphitic carbon. The thermogravimetric analysis results for the spent Mo-HMFI-M catalyst show that it contains about equivalent amounts of LT and HT coke, the latter being graphitic carbon. Thus, we propose that the rapid deactivation of Mo-HMFI-M is due to the deposition of graphitic carbon. The above proposal agrees with the observation that the used Mo-HMFI-B catalyst contains less h.c.p. Mo_2C (f.c.c. MoC_{1-x} is the major phase) and that deposition of graphitic carbon in the latter case is only about 30% compared to that for used Mo-HMFI-M.

Lee et al. [2] also showed that addition of hydrogen to methane enabled the obtention of clean carbide surface. The same effect should be observed when carburising MoO_3 with a hydrogen/*n*-butane mixture and if the Mo-carbide surface is modified by chemisorbed hydrogen, one may indeed expect the formation of a higher amount of ethane, relative to ethylene, at short time-on-stream as observed by us for the Mo-HMFI-B catalyst.

The small amount of C_3 species observed for the Mo-HMFI-M catalyst suggests that methane reacts with ethylene, but this is only a speculation at this time.

Considering that the LT coke deposits are mostly present at the external surface of the Mo-HMFI-B catalyst and that the HT coke deposits are more abundant in the intracrystalline volume of the Mo-HMFI-M catalyst, as shown by adsorption and TG results, it is most likely that the HT coke deposits also poison or prevent the access to the acidic sites of the zeolite. Although we have no direct proof for this effect at the moment, it should be recalled that the non-oxidative aromatisation of methane is thought to be a bifunctional process, whereby a Mo carbidic species provides the dehydrogenation function and the zeolite acidity is responsible for the oligomerisation and dehydrocylisation of the intermediates and products.

The lower formation of intracrystalline coke deposits in Mo-HMFI-B, probably associated to the lower rate of naphthalene formation probably explains its higher stability vs. time-on-stream.

The major difference between the Mo-HMFI-M and Mo-HMFI-B catalysts is the nature of the Mo carbidic phase which is dominant, h.c.p. Mo_2C in Mo-HMFI-M and f.c.c. MoC_{1-x} in Mo-HMFI-B, confirming the importance of the catalyst activation pre-treatment. These two carbidic phases may have different catalytic properties [15]. It is also interesting to note that the meta-stable nature of the f.c.c. MoC_{1-x} phase, possibly more reactive, could explain the effects of O_2 [4], CO, and CO_2 [7], previously reported.

6. Conclusions

Pre-treatment conditions play a major role in determining the catalyst activity and selectivity of Mo-modified HMFI catalyst active for the non-oxidative aromatisation of methane to aromatic hydrocarbons.

Activation of a Mo-modified HMFI zeolite by a H_2/*n*-butane mixture, under conditions leading to the formation of the f.c.c. α-MoC_{1-x} carbide, leads to a catalyst with higher activity and selectivity, in particular to benzene, and longer lifetime.

Graphitic coke, deposited on Mo-HMFI catalysts, prepared and operated using conventional procedures appears to be the determining factor responsible for catalyst deactivation.

Acknowledgements

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