

# Influence of the preparation method on the behaviour of Fe–Mo catalysts for the oxidation of methanol

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A series of Fe–Mo catalysts with different properties was prepared by modification of the synthesis variables. Their catalytic behaviour in the oxidation reaction of methanol to formaldehyde was determined. The differences in their textural, morphological, chemical and structural properties were determined using nitrogen adsorption, SEM–energy dispersive X-ray analysis, X-ray photoelectron spectroscopy, X-ray diffraction and Fourier transform-infrared analyses. We have attempted to establish relationships between these properties and their catalytic activity in the above reaction. We have found that their catalytic behaviour principally correlated with the atomic ratio of Mo:Fe. This ratio was sensibly higher than that required stoichiometrically for iron(III) molybdate.

## 1. Introduction

Catalysts of iron(III) molybdate are widely used industrially for the selective oxidation of methanol to formaldehyde. This reaction appears to occur through the adsorption of methanol on active centres of  $\text{Mo}^{6+}$  with the formation of  $\text{CH}_3\text{O}^-$  as an intermediate [1]. The active centres in the reduced state are later regenerated by oxidation with air through a little-understood mechanism. The desorption of the products, especially formaldehyde and water, appear to control the rate of the reaction [2].

Some preliminary studies [3] have demonstrated that the catalytic behaviour of different oxides in the oxidation of methanol, could be correlated with the enthalpy of transition of one oxidation state to another with greater or lesser ease of interchange of molecular oxygen with the surface. To make it possible appears to be the function of the iron in the iron(III) molybdate by comparison with molybdenum trioxide and other molybdates doped with different types and concentrations of other cations in various selective oxidation processes [4, 5].

Industrial catalysts always contain an excess of molybdenum in respect to that necessary stoichiometrically for the desired molybdate, perhaps, because early studies demonstrated that the catalytic activity was highest when the Mo:Fe atomic ratio was 1.7 [6]. This accounts for the fact that the reaction being so exothermic ( $\Delta H = -158 \text{ kJ mol}^{-1}$ ), an excess of molybdenum was necessary to compensate for its loss

through evaporation of  $\text{MoO}_3$  in the hot spots. This excess of molybdenum may well be incorporated in the structure of the molybdate, creating vacancies of  $\text{Fe}^{3+}$ , or may well segregate as a second phase rich in molybdenum,  $\text{MoO}_3$  for example. Only in the first case could the excess molybdenum have an effect on the catalytic activity, although some studies show that this excess could have a great effect on selectivity [7, 8]. Additionally, recent studies have demonstrated that the catalytic behaviour of these compounds, especially the selectivity, does not depend only on the crystallinity but also on the proportion of exposed crystalline faces, giving a structure-dependent oxidation reaction [9, 10].

When the catalyst is exposed to a methanol atmosphere, the reduction of the methanol generates structural defects shown by *in situ* electron microscopy [11]. Presumably, during the reaction, these defects should be stressed and cause the large structural changes which lead to the deactivation of the catalyst. Several studies have demonstrated that the surface of the deactivated catalyst is characterized by the presence of the reduced iron(II) molybdate [11–14]. However, the possible effects of these structural defects, produced during the reaction, have not been studied.

In order to contribute to the elucidation of this problem, taking into account that the preparation method determines the physical and chemical properties of the catalyst, a series of catalysts were synthesized under distinct preparation conditions se-

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lected by a statistical method. The object of the work consisted in determination of the preparation variables which caused the greatest influence on the final properties of the catalysts, and to find the possible correlations of these with their different behaviours in the catalytic oxidation of methanol to formaldehyde.

## 2. Experimental procedure

The following reactants were used for the preparation of the studied catalysts:  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{NH}_4\text{OH}$ ,  $\text{HNO}_3$  and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ . The method of preparation comprised the coprecipitation of iron and molybdenum oxides, which were then washed and heat treated at 603 K. The preparation variables studied were the precipitation temperature, pH of the molybdenum solution, precipitation pH, Mo:Fe atomic ratio, pH of the washing solution, length of calcination time at 603 K, and ageing. With the purpose of studying the effect of each of these variables with the minimum number of samples possible, the statistical method known as the Plackett–Burman matrix, was used [15]. In this method each variable is included four times at its highest and four times at its lowest levels, giving rise to a total of eight object samples of study (Table I). The possible effect of each preparation variable over a determined property can be obtained by averaging the results obtained at its highest level and comparing with the averaged results at its lowest level, in such form that when the calculation is made, the average of all the variables, except that which is being considered, are twice at their highest and twice at their lowest levels and their effects compensate each other approximately. Additionally, for comparative

purposes, apart from these eight samples a standard ferric molybdate (S) and a commercial one (I) employed in the industrial process, were also studied.

The characterization of the materials was made by a variety of physical techniques. The textural properties were determined by adsorption–desorption isotherms of nitrogen at 77 K in a conventional volumetric apparatus. The morphological study, chemical analysis, identification of chemical species and study of the homogeneity of the samples were determined with a scanning electron microscope (SEM) ISI DS-130 coupled to an Si/Li detector and a Kevex 8000-II processor for energy dispersive X-ray (EDX) analysis. X-ray photoelectron spectroscopy (XPS) was used for analysis of the chemical state of the surface using a Leybold–Heraeus LHS 10 provided with a magnesium source ( $\text{MgK}_\alpha = 1253.6 \text{ eV}$ ) operated at a potential of 12 kV and 10 mA. The residual pressure within the analysis chamber was maintained below  $7 \times 10^{-9}$  torr (1 torr = 133.322 Pa) and for the determination of the binding energies, the  $\text{C}_{1s}$  peak at 284.6 eV was taken as reference. Crystallinity studies were carried out by X-ray diffraction (XRD) in a Siemens Kristalloflex D-500 diffractometer using a  $\text{CuK}_\alpha$  source ( $\lambda = 1.5418 \text{ nm}$ ) at 40 kV and 25 mA and a nickel filter. Fourier transformed–infrared (FT–IR) measurements were made using a Nicolet 5ZDX spectrometer with a spectral range of 4000–400  $\text{cm}^{-1}$ , with a resolution of 4  $\text{cm}^{-1}$ .

The catalytic activity was determined in a fixed-bed reactor of 0.9 cm i.d. connected to a Hewlett-Packard 5840 A gas chromatograph with a TCD detector and a Chromosorb 101 column, for the analysis of reactants and products at the entrance and exit of the reactor,

TABLE I Variables used in the preparation of catalysts

Cat.	Precip. temp. (K)	Mo solution pH	Precipitation pH	Atomic ratio Mo/Fe	Ageing time (h)	Washing sol. pH	Calc. time at 603 K (h)
A	293	2.5	1.5	2.2	0.0	2.0	4.0
B	353	2.5	1.5	1.1	3.0	1.5	4.0
C	293	5.0	1.5	1.1	3.0	2.0	2.0
D	353	5.0	1.5	2.2	0.0	1.5	2.0
E	293	2.5	2.0	2.2	3.0	1.5	2.0
F	353	2.5	2.0	1.1	0.0	2.0	2.0
G	293	5.0	2.0	1.1	0.0	1.5	4.0
H	353	5.0	2.0	2.2	3.0	2.0	4.0

TABLE II Textural and surface properties of different catalysts

Cat.	$S_{\text{BET}}$ ( $\text{m}^2 \text{ g}^{-1}$ )	Density ( $\text{g ml}^{-1}$ )	Morphology	Mo/Fe		XRD crystallinity
				EDX	XPS	
A	2.3	2.4	Large particles	2.2	2.2	Amorphous
B	4.2	4.3	Globular	1.2	1.7	$(\text{Fe}_2(\text{MoO}_4)_3)_{\text{orth.}}$
C	6.8	3.1	Globular	1.0	0.8	$(\text{Fe}_2(\text{MoO}_4)_3)_{\text{orth.}}$
D	2.8	2.9	Small particles	2.1	1.7	Amorphous
E	4.0	3.3	Fair platelets	1.9	1.6	Scarce
F	2.8	2.3	Globular	1.2	1.3	$(\text{Fe}_2(\text{MoO}_4)_3)_{\text{orth.}}$
G	2.1	3.6	Large platelets	1.6	1.7	Scarce
H	6.2	5.2	Small platelets	1.9	1.8	Scarce
S	6.0	2.7	Globular	1.5	1.5	$(\text{Fe}_2(\text{MoO}_4)_3)_{\text{orth.}}$
I	4.0	3.5	Small platelets	2.2	1.5	$(\text{MoO}_3 + \text{Fe}_2(\text{MoO}_4)_3)_{\text{orth.}}$

respectively. For the reaction, 1 g catalyst was used; before the reaction, it was subjected to a current of dry air ( $50 \text{ cm}^3 \text{ min}^{-1}$ ) for 12 h at 573 K. The reaction took place in a flow of  $50 \text{ cm}^3 \text{ min}^{-1}$  of a mixture of methanol and dry air (1/10) at atmospheric pressure with the catalyst maintained between 453 and 473 K.

### 3. Results and discussion

#### 3.1. Characterization of the catalysts

The textural, morphological, chemical and structural properties of the catalysts are presented in Table II. In general terms, the materials have low surface areas,

with a generally laminar appearance with distinct grades of aggregation. Through the application of the statistical method of Plackett–Burman, one can deduce that the  $S_{\text{BET}}$  of the final product was principally affected by the pH of the molybdenum solution, the pH of the washing solution and, overall, by the ageing time. The density was mostly affected by the ageing and calcination time.

The morphological aspect of the catalysts (Fig. 1) appeared to be mainly affected by the pH of the solution, the initial Mo:Fe atomic ratio in the solution and the ageing period. Low values of the first two and high values of the third favour the formation of

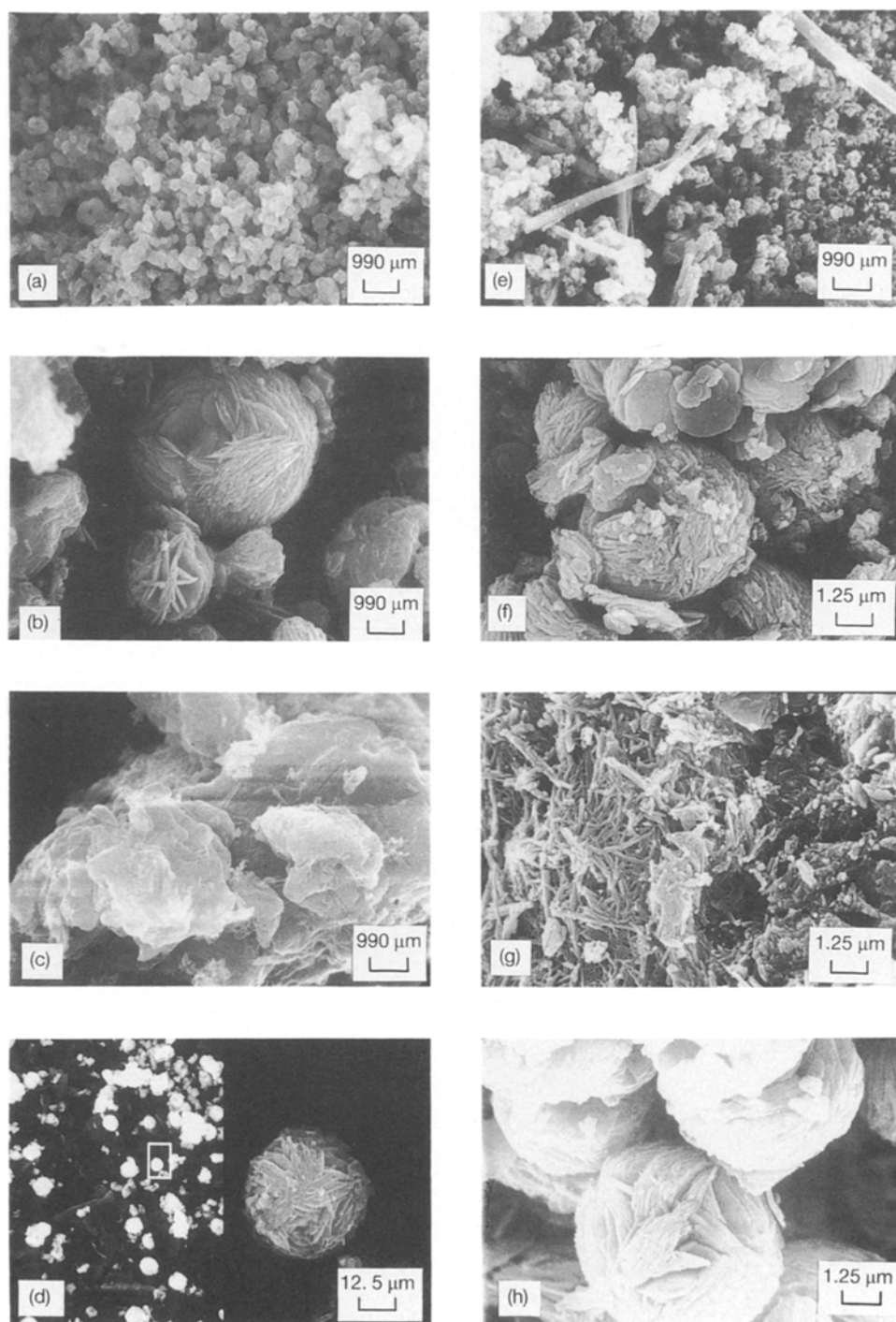


Figure 1 Scanning electron micrographs of several molybdate catalysts. (a–d) fresh catalysts (A, C, G, S, respectively). (e–h) Used catalysts (A\*, C\*, G\*, S\*, respectively).

ordered associations of lamellae in globular form of relatively high surface area (catalysts C and S). Contrarily, when the pH and the Mo:Fe ratios were high the resulting lamellae appeared small and disordered. In intermediate situations, when the Mo:Fe ratio in the solution was high and the pH of the solution low without ageing, the morphological appearance was of particles more or less developed (catalyst A), which under certain circumstances coexisted with disordered platelet forms (catalyst G). These various morphological changes are correlated with the surface area (Table II). The highest surface areas corresponded to samples formed by associated ordered lamellae, while small surface areas were related to disordered plates or particles.

The Mo:Fe atomic ratios of all the samples are presented in Table II. Apparently the Mo:Fe atomic ratio used in the solution, along with the final pH, were the most influential factors. Low acidity levels led to samples with atomic ratios inferior or superior to the design (1.1 and 2.2, respectively) close to the stoichiometric value of 1.5, which corresponded to iron(III) molybdate, considered in many works as the unique active species in the methanol oxidation reaction [1, 16]. Contrarily, higher levels gave rise to samples very similar to the design.

The Mo:Fe atomic ratio at the surface, obtained by XPS, was not very different from that obtained by SEM-EDX in most of the catalysts, which appeared to indicate the absence of segregation of phases when the ratio was different to the stoichiometric one. Following Forzatti and Villa [5], the accommodation of molybdenum ions within the iron molybdate structure, was made possible by the openness and apparent flexibility of the matrix. Possibly an excess of interstitial molybdenum could be compatible with atomic ratios higher than 1.5. Chen [17] explained this situation stating that the  $\text{Fe}_2(\text{MoO}_4)_3$  structure was related to a distorted  $\text{A}_3\text{B}_2(\text{SiO}_4)_3$  garnet structure with the A sites unoccupied. These unoccupied sites are ordered and can form channels for the transport of molybdenum toward, or away from the catalysts surface, which could explain the different surface molybdenum content detected. The prepared solids are homogeneous and only in the industrial sample (catalyst I), could evidence be found of two different phases, one of iron(III) molybdate, which appeared to exist in all of the samples, and the other molybdenum trioxide (found from XRD results).

The oxidation states at the surface from XPS, presented in Fig. 2, indicated that the oxidation state of molybdenum was identical in all of the fresh samples, with  $\text{Mo}^{6+}$  as the only detected species.  $\text{Fe}^{3+}$  was the only iron species in all the samples and the same occurs with the  $\text{O}_{1s}$  peak which was located at the natural bonding energy of 530.8 eV. The XPS results indicated the presence in all of the samples of the chemical species corresponding to iron(III) molybdate; however, other compounds with similar bonding energies cannot be discounted.

In Fig. 3 some representative X-ray diffractograms of the samples are presented, which are summarized in Table II. There were three well-defined series: series 1

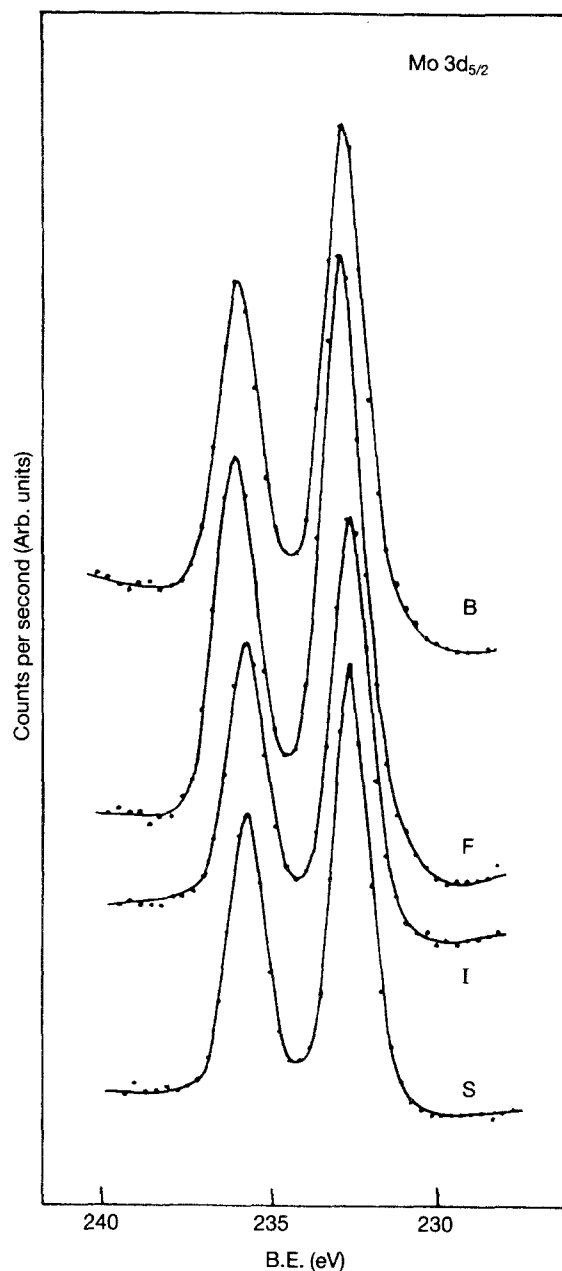


Figure 2 XPS spectra of fresh catalysts: B, F, I, S.

(catalysts B, C and F) which corresponded to materials of high crystallinity, series 2 (catalysts A and D) constituted by amorphous particles and series 3 (catalysts E, G and H) which has an intermediate crystallinity with a laminar morphology and a short-range order. In general terms, the highest crystallinity was given by low initial Mo:Fe atomic ratios, whereas final ratios higher than 2 gave rise to totally amorphous particles. The assignment of peaks on the diffractograms confirmed the results detected by SEM-EDX, showing the orthorhombic ferric molybdate as the only detectable crystalline phase in all of the samples, except for the industrial one (sample I), in which additionally  $\text{MoO}_3$  appeared. The weight of this evidence does not totally reject the existence of  $\text{MoO}_3$  in the other samples because recent studies [18] have demonstrated that the  $\text{MoO}_3$  is only detectable by XRD when found in quantities greater than 7%; below these proportions the material is amorphous or microcrystalline. Equally it could be present in

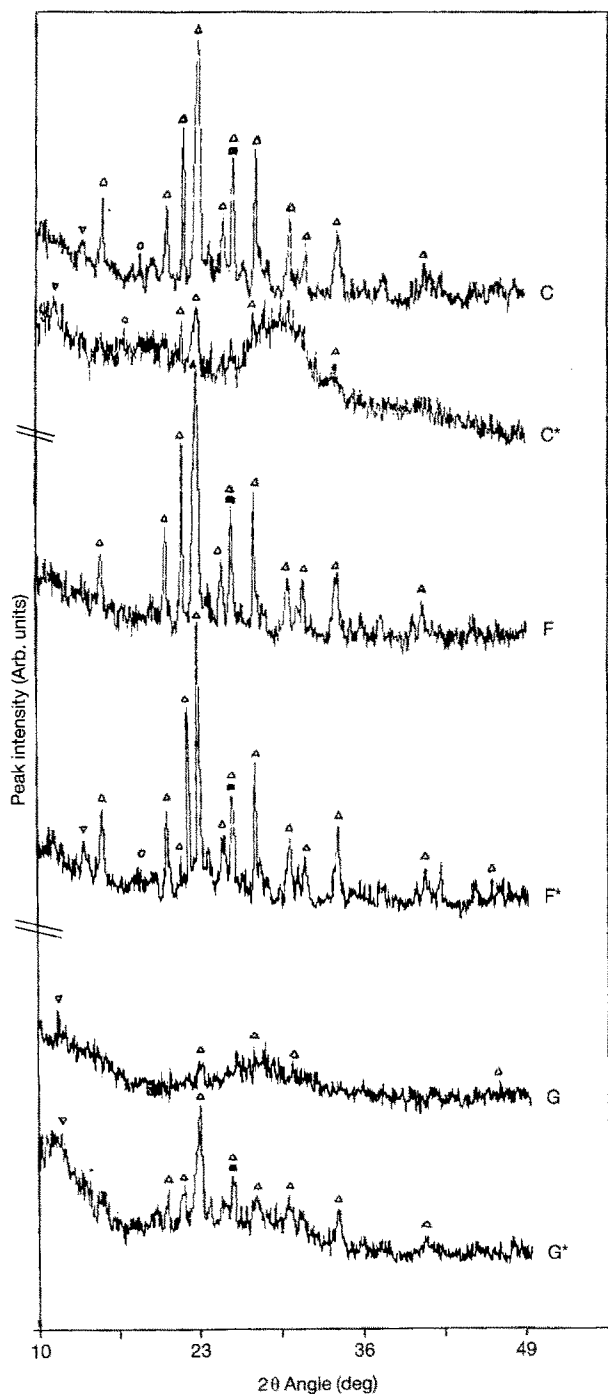


Figure 3 X-ray diffraction patterns of fresh (C, F, G) and used (C\*, F\*, G\*) catalysts ( $\Delta$ )  $\text{Fe}_2(\text{MoO}_4)_3$ ; ( $\blacksquare$ )  $\text{MoO}_3$ ; ( $\circ$ )  $\text{Fe}_2\text{Mo}_x\text{O}_x$ ; ( $\nabla$ )  $\text{Fe}_2\text{O}_3$  3-4  $\text{MoO}_3$ .

not well defined species of molybdenum generally designated as oxo-Mo, "pseudo-molybdates" and polymolybdates (samples A, D, E, G, H).

In short, in all the studied samples, two phases could co-exist, one of iron(III) molybdate, generally crystalline if the Mo:Fe ratio is not high, and perfectly detectable by SEM-EDX and XRD, and another generally amorphous (not detectable except in the industrial catalyst), in a highly dispersed state whose abundance and composition are dependent on the Mo:Fe ratio, rich in iron if it was inferior to 1.5, and in molybdenum if it was superior to 1.5.

Detailed studies of the naturally amorphous products were made using FT-IR. As can be seen in Fig. 4 all of the prepared catalysts presented characteristic bands for iron(III) molybdate, which consisted in an intense broad band at  $835\text{ cm}^{-1}$ , associated with stretching of Mo=O bonds, another much weaker and narrower band which appeared as a shoulder at  $958\text{ cm}^{-1}$ , related to an elevated degree of condensation of the Mo-O species, and a third band located at  $566\text{ cm}^{-1}$ , associated with bridging of Mo-O-Mo bonds [19]. The observed differences between the fresh samples appeared to be principally related to the

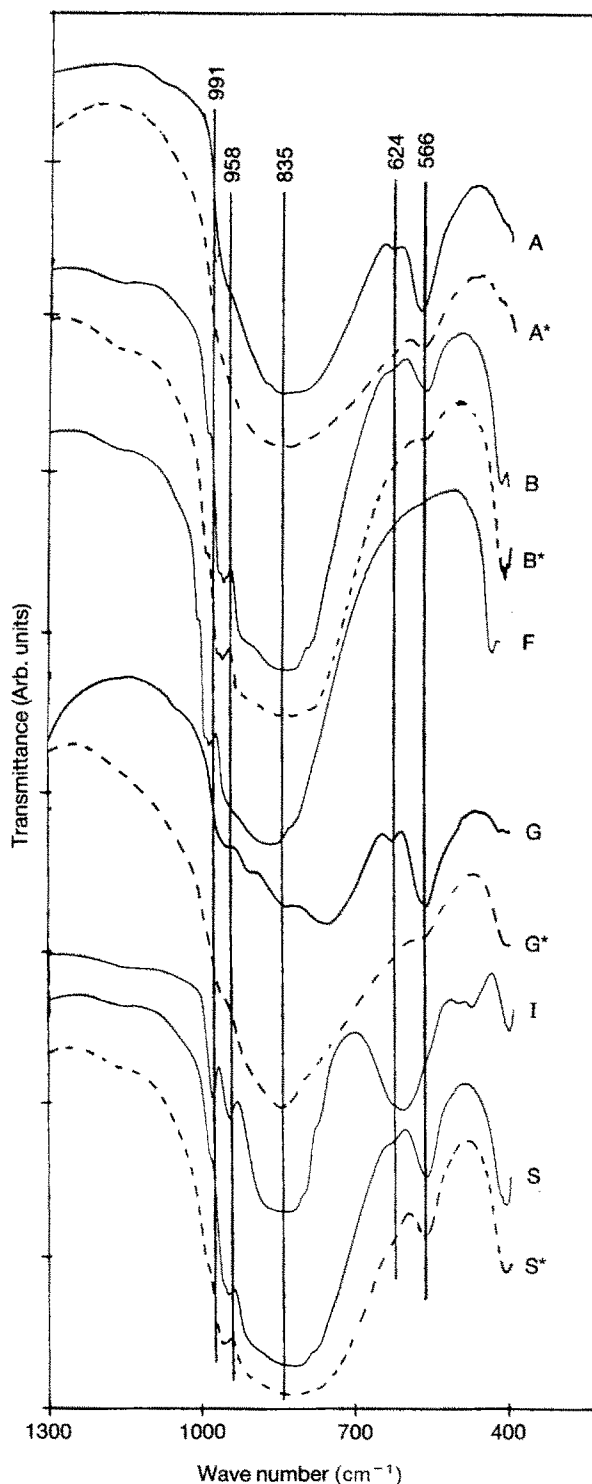


Figure 4 Infrared spectra of (—), fresh and (---) used catalysts.

Mo:Fe atomic ratio, the pH and the ageing period. The samples from series 1, in which the Mo:Fe ratio was less than the stoichiometric one, also exhibited the band at  $566\text{ cm}^{-1}$  which progressively weakened as the atomic ratio decreased and vanished in catalyst F. In addition, the existence of  $\text{MoO}_3$  in the industrial catalyst was confirmed by the appearance of a narrow band at  $991\text{ cm}^{-1}$  and a broad one at  $624\text{ cm}^{-1}$  which overlap in part with the band of molybdate at  $566\text{ cm}^{-1}$ , causing its widening. In the corresponding spectra of the other series (catalysts A, D, E, G and H) in which the Mo:Fe atomic ratio was higher than the stoichiometric requirement, the widening and shifting towards shorter frequencies of the band at  $835\text{ cm}^{-1}$ , together with an increase in the intensity of the bands between  $900$  and  $1000\text{ cm}^{-1}$  appeared with pH and the Mo:Fe ratio, all of which could be associated with the progressive formation of amorphous polymeric molybdenum compounds with varying stoichiometry [12, 18]. The presence of a weak band at  $624\text{ cm}^{-1}$  and another at  $991\text{ cm}^{-1}$  typical of  $\text{MoO}_3$ , stood out. Apparently, an excess of molybdenum provoked the rupture of the order in the existing crystalline network of molybdate and the segregation of polymeric amorphous material in a state of high dispersion.

To summarize, it can be said that the variables used in the preparation process notably influenced the physical chemical and structural properties of the materials, but not the oxidation states of iron and molybdenum. With a strict control of these variables it should be possible to obtain catalysts with different chemical compositions, morphologies and, as a consequence, surface areas. If the Mo:Fe atomic ratio was less than or slightly higher than that required stoichiometrically, the final products appeared as ordered lamellae aggregated in globular form with relatively high surface areas. The most important phase present was crystalline and corresponded to orthorhombic iron(III) molybdate. The slight excess of iron, in some

cases, or of molybdenum, in others, contributed to variations in the final crystallinity of the samples and gave rise to the formation of a second amorphous phase in which the elements retained their same oxidation states and high degree of dispersion.

### 3.2. Activity measurements

The specific activities of all the catalysts studied, expressed as  $\mu\text{mol m}^{-2}\text{ s}^{-1}$ , are presented in Table III. The reaction products under the reaction conditions were formaldehyde (in the form of methylal), dimethylether, methylformate, water, methane and carbon dioxide. The presence of carbon monoxide was not detected. The specific activity of the industrial catalyst (I), with an excess of molybdenum in the form of crystalline  $\text{MoO}_3$  at a low degree of dispersion, was low and had a similar behaviour to the standard sample of iron molybdate (S). The reaction products were also similar in both samples and thus, the activity could not be attributed to the excess of molybdenum in the form of crystalline  $\text{MoO}_3$ . The rest of the samples of series 1, all of them with very crystalline structures, presented different activities which appeared to be related to the presence in the surface of terminal Mo–O–Mo bonds, detected by FT–IR at  $570\text{ cm}^{-1}$  (Fig. 4), and to the surface Mo:Fe ratio ( $(\text{Mo}/\text{Fe})_{\text{XPS}}$ ). Thus, we could observe that catalyst F, with Mo:Fe atomic ratio less than stoichiometric and no band at  $570\text{ cm}^{-1}$ , was practically inactive, whereas catalyst C, with a less than stoichiometric ratio but with a band at  $570\text{ cm}^{-1}$  was as active as the standard sample (S) and the industrial one (I). Finally, the catalyst B, with a ratio  $(\text{Mo}/\text{Fe})_{\text{XPS}} > 1.5$  and with the band at  $570\text{ cm}^{-1}$  was much more active. The same may be applied to the catalysts of series 2 and 3 in which catalysts B and G, both synthesized with an initial Mo:Fe ratio of 1.1, demonstrated better activity. The necessity of the terminal Mo–O bond was

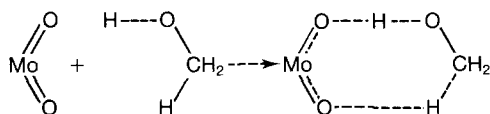
TABLE III Activity and selectivity of the catalysts at different reaction temperatures<sup>a</sup>

Catalyst	Reaction temp. (K)	A ( $\mu\text{mol m}^{-2}\text{ s}^{-1}$ )	S <sub>DME</sub> (%)	S <sub>FM</sub> (%)	S <sup>b</sup> <sub>Formaldehyde</sub> (%)
A	453	0.23	5.59	0.99	45.42
	463	0.54	7.63	2.28	44.58
	473	0.63	11.13	5.13	38.19
B	453	0.35	3.19	2.29	49.65
C	453	0.14	3.55	3.05	46.10
E	453	0.34	7.47	5.58	33.81
F	453	0.04	15.7	0.0	16.12
	473	0.09	26.94	0.07	18.63
	493	0.18	37.72	0.03	15.01
G	453	0.51	12.03	4.44	45.66
	473	1.17	11.49	7.11	20.67
H	453	0.18	8.91	8.51	42.35
S	453	0.14	7.79	0.46	47.51
	473	0.30	8.01	3.35	29.05
I	453	0.15	7.04	1.23	61.48
	473	0.32	7.75	3.59	23.62

<sup>a</sup> Prior to reaction the samples were treated in air at 573 K for 12 h.

<sup>b</sup> Account was made as methylal ( $2\text{ CH}_2\text{O} + \text{CH}_3\text{OH}$ ).

related to the existence of two terminal oxygens in the octahedral coordination sphere of molybdenum [20, 21] which could coordinate the methanol molecule following



and facilitate the labilization of the methylene group by activation of the hydrogen in the hydroxy group and formation of  $-\text{CH}_3^-$  species. The importance of the Mo:Fe atomic ratio in the activity, earlier found in the bibliography [16], was obvious from Fig. 5 in which the appearance of a maximum around 1.7 can be appreciated. On the basis of the previous points and the behaviour of catalyst H which, although it possessed the polymeric molybdenum species (FT-IR), had a much lower activity than the similar catalyst E and G, the major activity was associated with the presence of a coprecipitated Mo-Fe-O deficient in iron and with molybdenum in a polymeric state and/or dispersion degree which favoured the electron transfer processes [1].

It is of note that the major selectivity towards formaldehyde in the industrial catalyst (I), appeared to be due to the presence of orthorhombic  $\text{MoO}_3$  in the system, detected by XRD, in accordance with earlier work [10], which emphasized the low activity and high selectivity of the compound for oxidation products, formaldehyde and methylal.

### 3.3. State of the catalyst after reaction

During the course of the reaction the catalysts suffered evident changes in their morphology (Fig. 1), especially noticeable in some samples ( $\text{A}^*$ ,  $\text{C}^*$  and  $\text{G}^*$  for example), which could be related in a certain manner to the degree of activity. These changes in some cases consisted in the rupture of the predominant morphological groups in each sample (globular, laminar or

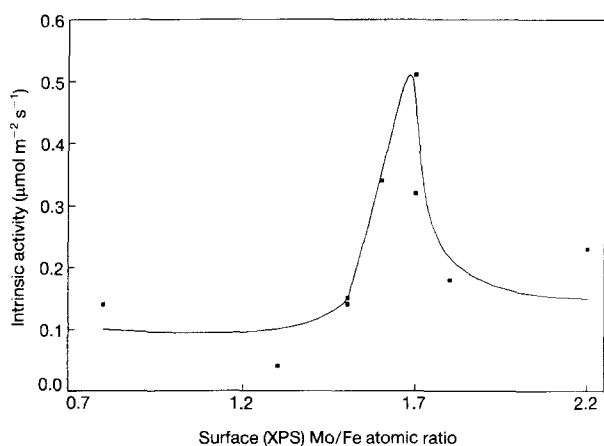


Figure 5 Intrinsic activity (at 453 K) versus surface (XPS) Mo/Fe atomic ratio.

particular) giving rise to new structures in some of them (catalyst  $\text{G}^*$ ).

In many cases, these morphological changes were accompanied by important structural changes. In Fig. 3 the diffractograms of some samples after reaction are presented which can be compared with the corresponding fresh samples. Without being a general phenomenon, there was a tendency for the amorphization of the crystalline catalysts (catalyst  $\text{C}^*$ ), or the crystallization of the amorphous ones (catalyst  $\text{G}^*$ ) which, however, was hardly detectable in some cases.

There were also notable variations in the infrared spectra of the catalysts after reaction (Fig. 4). In general terms, a reduction in the band at  $566 \text{ cm}^{-1}$ , associated with bridging of Mo-O-Mo bonds, which in catalyst  $\text{G}^*$  was accompanied by narrowing of the most intense band at  $833 \text{ cm}^{-1}$ , attributed to vibration of the Mo=O bond. Both effects were associated with the presence of polymolybdates in the fresh samples. This confirmed the progressive loss of the disperse amorphous phase during the reaction, in quantities related, although not quantitatively, to the activity of the corresponding catalyst.

In spite of the above, SEM-EDX studies demonstrated that the Mo:Fe ratio was identical before and after the reaction, in all samples. Then, no active phase was lost and the changes were exclusively structural. These results appeared to indicate that during the chemical reaction important structural readjustments in the catalysts took place as a consequence of the diffusion process operating across the molybdate network which can be understood with Mo:Fe ratios different from the stoichiometric one, and which, presumably, reaches a maximum at 1.7, thus justifying the obtained activity results. The catalysts underwent changes during the reaction which affected the crystallinity of the molybdate phase in one sense or another depending on the original state.

The existence of a second molybdenum-rich phase, although being a necessary condition, is not sufficient in itself, but, additionally, needs to be found in a high degree of dispersion. This explains why the excess of molybdenum in the form of crystalline  $\text{MoO}_3$  in the industrial catalyst I is not operative and, also, the observed differences in the activity between catalysts I and A ( $0.15$  and  $0.23 \mu\text{mol m}^{-2} \text{s}^{-1}$ , respectively), both with a similar, 2.2, Mo:Fe atomic ratio.

## 4. Conclusions

From this study, it could be seen that through control of the preparation variables the production of Fe-Mo catalysts with very different physical, chemical and structural properties was possible. The activity of the catalysts in the oxidation of methanol to formaldehyde was dependent on the presence of non-stoichiometric iron(III) molybdate. The most active catalysts initially had an Mo:Fe atomic ratio in excess of the stoichiometric one, thus presenting an amorphous or scarcely crystalline structure. During the reaction, the catalysts, especially the most active ones, underwent important structural changes which resulted in variations in crystallinity with respect to their original

state, In the changes of the molybdate phase, an amorphous polymolybdate with a high degree of dispersion seems to be involved. This could explain the maximum catalytic activity which corresponded to catalysts with an excess of molybdenum.

## References

1. J. EDWARDS, J. NICOLAIDIS, M. B. CUTLIP and C. BENNETT, *J. Catal.* **50** (1977) 24.
2. N. PERNICONE, F. LAZZERIN, G. LIBERTI and G. LANZAVECCHIA, *ibid.* **14** (1969) 293.
3. D. G. KLISSURSKI, in "Proceedings of the Fourth International Congress on Catalysis" (Moscow, 1968), Paper 36.
4. P. L. VILLA, A. SZABO and F. TRIFIRO, *J. Catal.* **47** (1977) 122.
5. P. FORZATTI and P. L. VILLA, *ibid.* **76** (1982) 188.
6. G. FAGHERAZZI and N. PERNICONE, *ibid.* **16** (1970) 321.
7. M. CARBUCICCHIO, *ibid.* **45** (1976) 77.
8. U. OZKAN and G. L. SCHRADER, *ibid.* **95** (1985) 120.
9. K. BRÜCKMAN, R. GRABOWSKI, J. HABER, A. MAZURKIEWICZ, J. SŁOCZYNSKI and T. WILTOWSKI, *ibid.* **104** (1987) 71.
10. J. M. TATIBOUET and J. E. GERMAIN, *ibid.* **72** (1981) 375.
11. P. L. GAI and P. A. LABUN, *ibid.* **94** (1985) 79.
12. F. TRIFIRO and V. de VECCHI, *ibid.* **15** (1969) 8.
13. P. FORZATTI and G. BUZZI-FERRARIS, *Ind. Eng. Chem. Process Des. Dev.* **21** (1982) 67.
14. Y. H. MA and S. J. KMIOTEK, *J. Catal.* **109** (1988) 132.
15. R. L. PLACKETT and J. P. BURMAN, *Biometrika* **33** (1946) 305.
16. G. K. BORESKOV, B. I. POPOV, E. S. ROZINSCHNIKOVA and V. N. BIBIN, *Kinet. Kat.* **9** (1968) 796.
17. H. CHEN, *Mater. Res. Bull.* **14** (1979) 1583.
18. C. E. DELTCHEFF, M. AMIROUCHE, M. CHE, J. M. TATIBOUET and M. FOURNIER, *J. Catal.* **125** (1990) 292.
19. O. I. GONCHAROVA, A. A. DAVYDOV and T. M. YURIEVA, *Kinetics and Catalysis* **25** (1984) 124.
20. F. TRIFIRO, S. NOTARBARTOLO and I. PASQUON, *J. Catal.* **22** (1971) 324.
21. F. TRIFIRO and I. PASQUON, *ibid.* **12** (1968) 412.

*Received 16 April 1993  
and accepted 27 May 1994*