



## $^{57}\text{Fe}$ Mössbauer Studies in Mo–Fe Supported Catalysts

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(Received: 10 October 2000; accepted 3 May 2001)

**Abstract.** Industrially, the Mo–Fe catalysts used in the selective oxidation of methanol to formaldehyde can rapidly deactivate. The use of support materials may reduce the high temperatures in the catalytic bed and/or increase thermal and mechanical resistance. However, during the preparation of these catalysts, or even during reaction conditions, the active species may react with the support material losing their catalytic activity. In this work silica, silicium carbide and titania were studied as supported catalysts by Mössbauer spectroscopy which proved to be a useful technique in the choice of supported materials.

### 1. Introduction

In industrial practice, the partial oxidation of methanol to formaldehyde using iron-molybdate-based catalysts based on Mo–Fe mixed oxides leads to quick deactivation of the catalyst (after 6–12 months) mainly in hot spot regions. The use of an appropriate support based on materials with high thermal and mechanical resistances can significantly attenuate this problem. However, during the preparation of these catalysts, or even during reaction conditions, the active species can react with the support material losing their catalytic activity. Therefore, some studies using different techniques, namely Mössbauer spectroscopy, have been carried out in order to find an adequate material for support of active species [1, 2].

In the present study we verified that Mössbauer spectroscopy is a very useful technique in the choice of supported materials. Different supported materials were analysed, namely, silica, already studied by other authors [2–6], silicium carbide and titania.

### 2. Experimental

The analysed samples, with an atomic ratio  $\text{Mo/Fe} = 2.5$ , were prepared by the following methods. A iron-molybdate-based catalyst (M) was prepared by coprecipitation using aqueous solution of ferric nitrate and aqueous solution of paramolybdate of ammonium. The resulting gel was aged at 45 °C for 30 min, then dried at 65 °C for 48 h and thermally decomposed at 450 °C for 4 h [7].

The ceramic supports we studied were used in the preparation of compositum catalysts and of supported catalysts. The compositum catalysts, named as cSiO and cSiC were prepared by a mechanical mixture of the supports ( $\text{SiO}_2$  and SiC) and the iron-molybdate-based catalyst (prepared by co-precipitation) in a ratio 1/4, Senegal gum was also added. Grains with 3 mm diameter were obtained and further submitted to thermal decomposition at  $120^\circ\text{C}$  for 1 h, then 3 h at  $250^\circ\text{C}$  and 1 h at  $420^\circ\text{C}$  [7].

The supported catalysts, sSiO, sSiC<sub>1</sub>, sSiC<sub>2</sub> and sTiO, were prepared as follows. The support grains (53–74  $\mu\text{m}$ ) were thermally treated at different temperatures in order to eliminate impurities and obtain different porosities. Then impregnation was carried out at room temperature by using an aqueous solution of decomposable Mo–Fe salts, ammonium molybdate and ferric nitrate ( $\text{Mo/Fe} = 2.5$ ), being citric acid also added to ensure an adequate pH. This “pre-solution” was sprayed in the form of very minute droplets on the support maintained under motion in a rotating flask kept at a residual pressure of 50–100 mmHg. The impregnated particles were then dried up to  $120^\circ\text{C}$  and the thermal decomposition was carried out at  $360^\circ\text{C}$  for 50 min and at  $420^\circ\text{C}$  for 12 h [8].

The specific surface area was determined by the BET method with nitrogen; for areas inferior to  $5\text{ m}^2/\text{g}$  krypton was used.

$^{57}\text{Fe}$  Mössbauer spectra were registered at room temperature with a 25 mCi Co/Rh source in a transmission geometry. The fitting of the spectra was carried out by a set of Lorentzian lines using a least-squares minimum procedure. The isomer shifts are relative to  $\alpha\text{-Fe}$ .

### 3. Results and discussion

Table I shows the BET surface areas and the corresponding calcinations temperatures of the studied samples. The departure values of the BET areas of the support materials were those commercially available, being further reduced by thermal treatment in order to attain lower values. Regarding  $\text{SiO}_2$  supports, the literature

Table I. Surface areas of the samples obtained by the BET method

Sample	Calcinations temperatures	$S$ ( $\text{m}^2/\text{g}$ )
M	$450^\circ\text{C}/4\text{ h}$	6.7
cSiO	$420^\circ\text{C}/1\text{ h}$	338.4
sSiO	$1150^\circ\text{C}/5\text{ h}$	0.2
cSiC	$420^\circ\text{C}/1\text{ h}$	2.3
sSiC <sub>1</sub>	$1150^\circ\text{C}/1\text{ h}$	6.6
sSiC <sub>2</sub>	$900^\circ\text{C}/5\text{ h}$	8.3
sTiO	$450^\circ\text{C}/4\text{ h}$	7.9

points out surface areas  $<1 \text{ m}^2/\text{g}$  in order to prevent reaction between support and active species [12] and following this preparation procedure a value of  $0.2 \text{ m}^2/\text{g}$  was obtained in our case. For SiC supports such studies were not found. We tried different values ( $6.6$  and  $2.3 \text{ m}^2/\text{g}$ ) lower than the one corresponding to the commercial samples we had ( $8.3 \text{ m}^2/\text{g}$ ), having in mind the BET surface areas of the industrial iron-molybdate-based catalysts ( $5.1 \text{ m}^2/\text{g}$ ). When  $\text{TiO}_2$  supports were used a strong reaction between support and active species was detected, indicating that it would not be worthwhile to pursue with further studies, as referred below. The analysis of Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TG) also showed that during the final heating of cSiO and cSiC samples, water removal was followed by further segregation and crystallization of some  $\text{MoO}_3$ . In the supported samples also the decomposition of salts of iron and molybdenum into active species took place during calcinations.

Figure 1 shows  $^{57}\text{Fe}$  Mössbauer spectra obtained for M, sSiO and cSiO samples. The spectrum of the iron-molybdate-based catalyst (M) has just one doublet. The hyperfine parameters  $IS = 0.42 \text{ mm/s}$  and  $QS = 0.19 \text{ mm/s}$  (see Table II) are

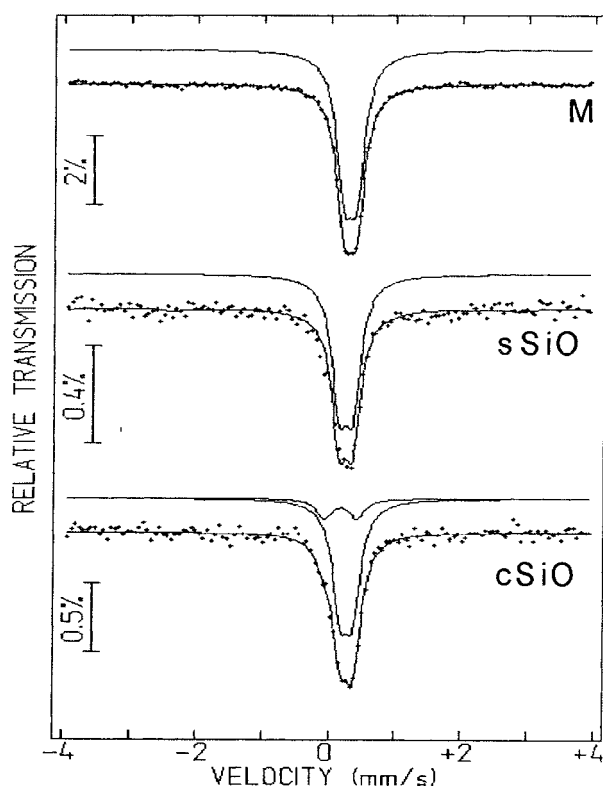


Figure 1. Mössbauer spectra of the iron-molybdate-based catalyst (M), the silica supported catalyst (sSiO) and the silica compositum catalyst (cSiO).

Table II. Mössbauer parameters of the studied samples: isomer shift (IS), quadrupole splitting (QS), half-height linewidth ( $\Gamma$ ) and relative area percentage (%)

Sample	IS (mm/s)	QS (mm/s)	$\Gamma$ (mm/s)	%
M	0.42	0.19	0.29	100
cSiO	0.39	0.19	0.29	84
	0.29	0.50	0.29	16
sSiO	0.45	0.16	0.29	100
cSiC	0.37	0.14	0.29	63
	0.30	0.48	0.29	37
sSiC <sub>1</sub>	0.32	0.15	0.29	62
	0.28	0.48	0.29	38
sSiC <sub>2</sub>	0.31	0.15	0.29	61
	0.26	0.55	0.29	39
sTiO	0.12	0.91	0.29	50
	0.05	0.50	0.29	50

characteristic of ferric ions of high spin with octahedral coordination. This is in accordance with a ferric molybdate structure described in literature [9–11].

The spectrum of cSiO sample was fitted with two different contributions: a doublet with a small quadrupole splitting similar to the one found for the M sample and another doublet with a larger quadrupole splitting  $QS = 0.50$  mm/s and  $IS = 0.29$  mm/s. These parameters are characteristic of Fe(III) of high spin with tetrahedral coordination, and can be ascribed to the presence of resulting substances from the reaction between active species and the support. These substances can be formed due to the interstitial substitution of silicon ions from silica by ferric molybdate Fe(III) ions leading to the Fe–MoSiO<sub>2</sub> formation [12]. It can be assumed that it is not only Fe that substitutes Si ions but also Mo. These results also show that 84% of the sample did not react with silica support, corresponding to ferric molybdate, in spite of its elevated surface area. Although a reaction has occurred, this sample can be revealed as a good catalyst because the increase of surface area compensates the lower percentage of catalytic active species.

It was observed that the sSiO sample did not react with the support. The spectrum is characteristic of ferric ions of high spin with octahedral coordination, indicating that the Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> is present. The spectrum is very similar to the one of the M sample. Different results for cSiO and sSiO may not be only attributed to the preparation method but also to the different surface areas. Other authors concluded that there is no reaction for internal areas lower than 1 m<sup>2</sup>/g [12]. So one can conclude that the occurrence of reaction depends essentially on the surface area and is more extended for higher areas. The reaction takes place interstitially and is essentially due to the Fe and Mo entering the silica structure and substituting for Si,

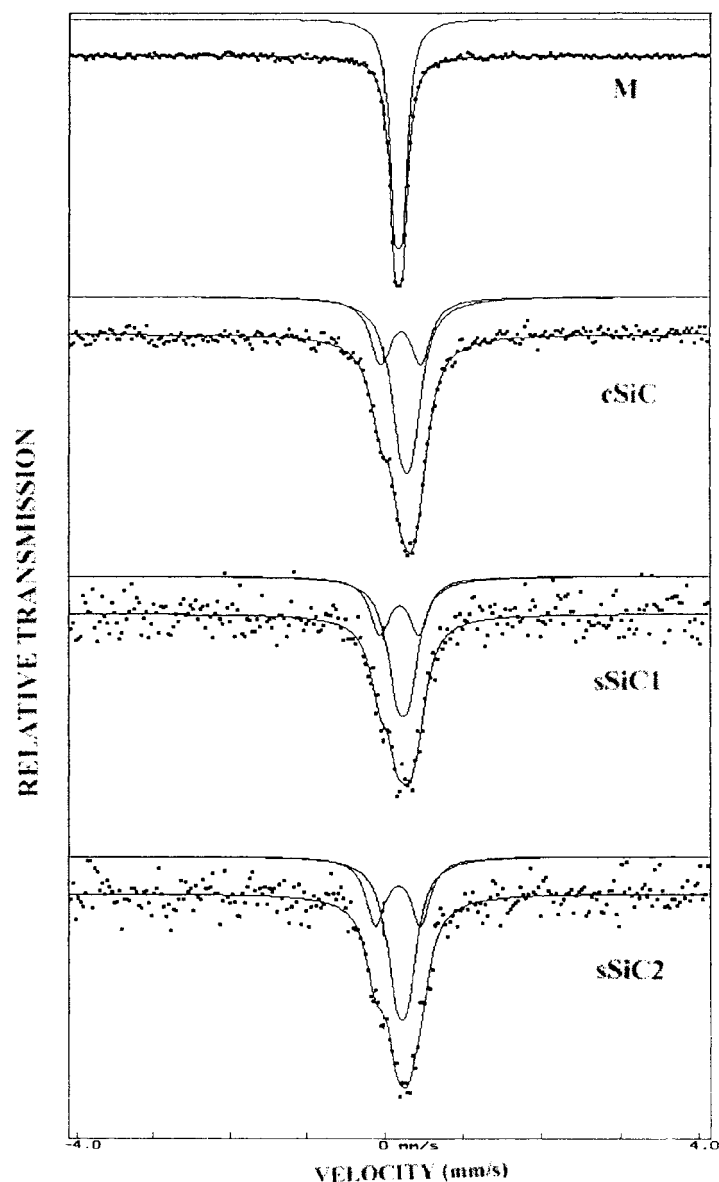


Figure 2. Mössbauer spectra of the iron-molybdate-based catalyst (M), the silicium carbide compositum catalyst (cSiC) and the silicium carbide supported catalysts (sSiC<sub>1</sub> and sSiC<sub>2</sub>).

which leads to the formation of Mo-SiO<sub>2</sub> compound. But we may not exclude the formation of another Mo species, which will depend on the Mo amount reacting with the silica.

Figure 2 shows the spectra for M, cSiC, sSiC<sub>1</sub> and sSiC<sub>2</sub> samples. Table II presents the hyperfine parameters resulting from the fitting to the spectra. The spectra of the silicium carbide supported catalysts (cSiC, sSiC<sub>1</sub> and sSiC<sub>2</sub> – sam-

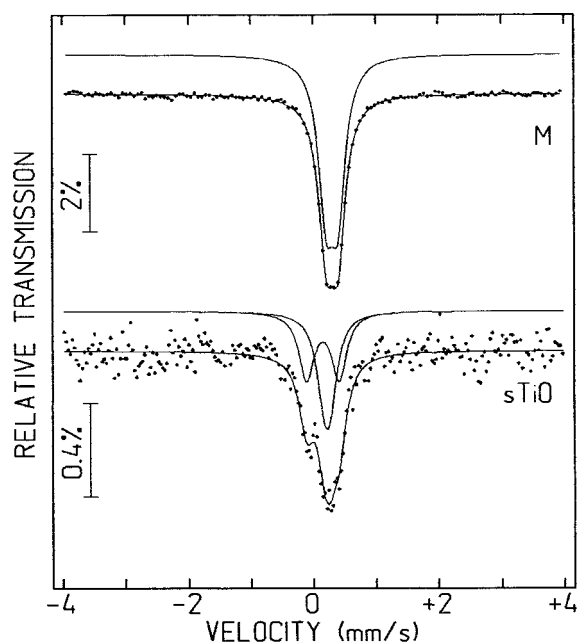


Figure 3. Mössbauer spectra of the iron-molybdate-based catalyst (M) and the titania supported catalyst (sTiO).

ples) reveal the existence of new species. In the spectra of cSiC there is a doublet characteristic of ferric molybdate, corresponding to 63% of the sample. The second doublet is due to the presence of Fe(III)-O with tetrahedral coordination.

The Mössbauer results show that the support is not inert but reacts with Fe and Mo oxides. In the case of SiC also Fe and probably Mo enter in the SiC structure, where Fe acquires tetrahedral coordination maintaining its oxidation state. FTIR analysis revealed the same results. However, XRD measurements were unable to detect any reaction; in fact, for the support samples a very thin layer of active species was present.

When the surface area increases a total reaction occurs, since it was not possible to observe the characteristic doublet of octahedral coordination of iron with oxygen, as shown in Figure 2 and Table II. In this case new doublets appear, indicating the presence of new species, which may result from the reaction between the support and the active species. Therefore, we can conclude that SiC particles are not adequate to support the Mo and Fe oxides, since this material is not inert to the active species, destroying them. As a consequence, the sample loses its catalytic properties to the oxidation of methanol to formaldehyd.

Figure 3 presents the spectra of M and sTiO samples, which are clearly different. The results of the fittings to the spectra are shown in Table II. The isomer shift and quadrupole splitting values may not be attributed to molybdate ferric, because the characteristic values are very different. They must be due to a reaction product

between the support and the active species. This shows that titania is very reactive destroying the active species since the characteristic spectrum of  $\text{Fe}_2(\text{MoO}_4)_3$  is not observed.

#### 4. Conclusions

Considering the compositum catalysts, cSiO and cSiC samples, one can observe that the silicium carbide is much more reactive than silica because the reaction between the support and the active species was higher in spite of its lower area.

In the case of the catalysts supported in silicium carbide, cSiC, sSiC<sub>1</sub> and sSiC<sub>2</sub>, when the surface area changes it is observed that for small areas ( $S = 2.3 \text{ m}^2/\text{g}$ ) there is a new doublet due to the fact that  $\text{Fe}^{3+}$  is no more octahedrally coordinated with oxygen but tetrahedrally. Meanwhile the doublet characteristic of the ferric molybdate maintains in the sample, so that only a given percentage of the sample reacts. In the case of higher surface areas, the doublet characteristic of ferric ions of high spin with octahedral coordination disappears, the doublet characteristic of ferric ions of high spin with tetrahedral coordination maintains and a new doublet appears. This new doublet must be due to a reaction product between the support and the active species, and the other doublet is due to Fe entering in the SiC structure, where Fe acquires tetrahedral coordination. The same must occur with Mo, which must diffuse interstitially in the support resulting new products between the support and Mo.

Comparing the studied supports it is observed that titania is more reactive with active species and silica is less reactive. It is also observed that there is a higher percentage of reaction in the supported catalysts than in the composite. A reasonable interpretation could be that as a consequence of the reaction between support and active species a film forms covering the whole supported area and that only on this film does the ferric molybdate grow, as observed by other authors [12]. This is due to the fact that in the case of supported catalysts a thin film has been deposited on the support, and in some cases it has reacted totally with the support. As the quantity of deposited active species is always the same, when the surface area increases the reaction also increases because the thickness of the film is smaller. In the case of compositum catalysts the particles of the iron-molybdate-based catalyst contact with the particles of the support and the reaction occurs only in the interparticle region so that there is always a portion of active species that is not destroyed by a reaction with the support, even for elevated areas of  $338.4 \text{ m}^2/\text{g}$ , cSiO sample.

The results showed that silica with a small superficial area is a promising support material for the Fe-Mo oxides. The carbide silicium, titania and silica with high superficial area are inadequate to support these oxides. The study of new supports is a promising area of research because so far there were not yet been found adequate supports for these species. Silica is not a true solution for this problem

because the permitted area is very small. Unfortunately, the carbide silicium that has a good thermal conductivity and high mechanical resistance is not inert.

We also concluded that Mössbauer spectroscopy permits not only to detect if the reaction occurs but also what kind of reaction is involved, its extension and identification of the reaction products.

### Acknowledgement

The authors would like to thank the LABGRAN laboratory for the availability of BET equipment.

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