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Redox Processes at the Surfaces of Fe_2O_3–MoO_3/SiO_2 Catalysts

M. CARBUCICCHIO

Istituto di Fisica dell'Università, Gruppo Nazionale di Struttura della Materia del C.N.R., Parma, Italy

AND

F. TRIFIRÒ

Istituto di Tecnologie Chimiche Speciali dell'Università, Bologna, Italy

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Mössbauer and catalytic measurements have been carried out on Fe_2O_3–MoO_3 supported on silica with different surface areas. The Mössbauer study of the catalyst reducibility (using methanol) and reoxidizability at high temperature has indicated that, as a consequence of the interaction between the support and the active species, both Fe and Mo enter the silica. This process, however, is limited to the surface of the support where the iron valence and coordinations are stabilized. Supported iron–molybdate can form only on this film. The comparative analysis of the Mössbauer and the catalytic data indicates that the high activity and selectivity, observed for catalysts with low surface areas, is connected with the presence of an iron–molybdate thin film. For high areas the iron–molybdate destruction determines the lower activity and selectivity.

INTRODUCTION

Iron–molybdate-based catalysts are widely used for the commercial oxidation of methanol to formaldehyde. However, due to the very low mechanical strength of these catalysts, the methanol oxidation is normally carried out in fixed bed reactors (*1–3*).

In order to increase the catalyst strength (*4*) and therefore to obtain the oxidation of methanol in fluidized bed reactors these catalysts can be supported. In this way, moreover, it is possible to increase the catalyst surface area (*5, 6*).

However, previous investigations carried out on Fe_2O_3–MoO_3 sustained by supports with different surface areas (*7, 8*) have pointed out that reactions occur between the supports and the active species. In this way the nature of the reaction product is determined by the kind of support. For a given quantity of active species and depending on the support area, this reaction product can coexist with supported Fe(III)–molybdate.

In this work Mössbauer and catalytic measurements were carried out in order to investigate the reducibility by methanol, the reoxidizability, and the catalytic behavior of Fe_2O_3–MoO_3 supported on silica. The amount of active species was very small and the percentage was constant in all the samples, while the support area spanned a wide range of values. This was done in order to analyze the nature and the catalytic behavior both of the supported Fe(III)–molybdate and of the product of the reaction which occurs between the support and the active species.

EXPERIMENTAL PROCEDURE

Silica (Grace), calcined at 1100°C for different periods of time in order to obtain supports with different surface areas, had been sprayed with an aqueous solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, citric acid, and $Fe(NO_3)_3 \cdot 9H_2O$ in vacuum under rotation; after drying, the samples were calcined in a fluidized bed reactor in a flow of air and thus the temperature slowly increased (10 hr) until 360°C. They were then kept in an

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oven for 16 hr at 430°C. In all of the samples the amounts of Fe and Mo, in the form of Fe_2O_3 and MoO_3, were 2.3% by weight with a molar ratio $Mo/Fe \simeq 2$.

In the following sections the samples will be labeled by indicating the support and, in brackets, the surface area.

For measuring the catalytic activity a fluidized bed reactor made of Pyrex has been used. The reagent was distributed from a porous disc with ~ 15 μm holes. the length of the bed was $H_0 = 45$ cm and the linear velocity was $U = 5.6$ cm/sec. The concentration of methanol was 5.5% in air.

The Mössbauer absorption spectra of ^{57}Fe 14.4 keV γ-radiation were measured by means of a standard constant acceleration spectrometer. The source was 25 mCi ^{57}Co diffused in a Rh matrix. The spectra have been fitted by least squares to a series of Lorenzian peaks. The variable quantities were the linewidths, the amplitudes, and the positions of the lines. All the fits were within statistical error.

The reducibility by methanol of the supported catalysts was investigated by carrying out room temperature Mössbauer measurements on samples that had been kept in a nitrogen–methanol stream (6.21 ml/min) for 2 hr at $T = 320°C$. To study the catalyst reoxidizability, Mössbauer measurements at room temperature were made on reduced catalysts which had then been kept in air for different periods of time at $T = 365°C$.

It must be pointed out that due to the very small amount of iron contained in the samples—in particular when broadenings or splittings of the lines occur—the Mössbauer spectra need very long counting times in order to reduce sufficiently the statistical error.

RESULTS AND DISCUSSION

The Mössbauer spectra for low area samples (up to 1 m^2/g) display a single peak with the same linewidth and isomer shift as that measured for the unsupported $Fe_2(MoO_4)_3$ (*9*) (see Table 1). For higher areas (Figs. 1a and 2a), the spectra become broader; the linewidth increases with increasing sample surface while the isomer shift remains in the Fe^{3+} ion range.

Previous analysis of the shape of the spectra and of the line-broadening behavior observed as a function of the sample area (*7, 8*) allowed one to interpret these spectra as the superposition of a double-line spectrum (caused by two kinds of Fe^{3+} ions within the silica) on a single-line spectrum due to supported Fe(III)–molybdate. By increasing the support area the Fe(III)–molybdate contribution decreases while the other contribution to the spectra increases. For very high surface areas this latter contribution is the only one present (Fig. 1b).

The Mössbauer analysis carried out in order to investigate the reducibility of these supported catalysts is in agreement with the above interpretation.

Figures 1a and c show the room tempera-

TABLE 1

Mössbauer parameters for β-Fe MoO_4 and for Fe_2O_3-MoO_3/SiO_2 catalysts. Isomer shifts (IS) referred to Rh, quadrupole splittings (QS) and linewidths (Γ) are in mm/sec. The error for all the reported parameters is ±0.02 mm/sec.

Sample	Single peak		Quadrupolar doublets											
			γ			θ			ϵ			η		
	IS	Γ	IS	QS	Γ	IS	QS	Γ	IS	QS	Γ	IS	QS	Γ
$SiO_2[0.5]_{calc.}$	0.30	0.47												
$SiO_2[2]_{calc.}$	0.26	0.55												
$SiO_2[2]_{red.}$			0.25	0.67	0.57	0.24	0.85	0.55	0.98	0.91	0.75	0.95	2.45	0.77
β-$FeMoO_4$									0.99	0.90	0.40	0.94	2.44	0.42
$SiO_2[300]_{calc.}$			0.24	0.66	0.56	0.24	0.87	0.55						

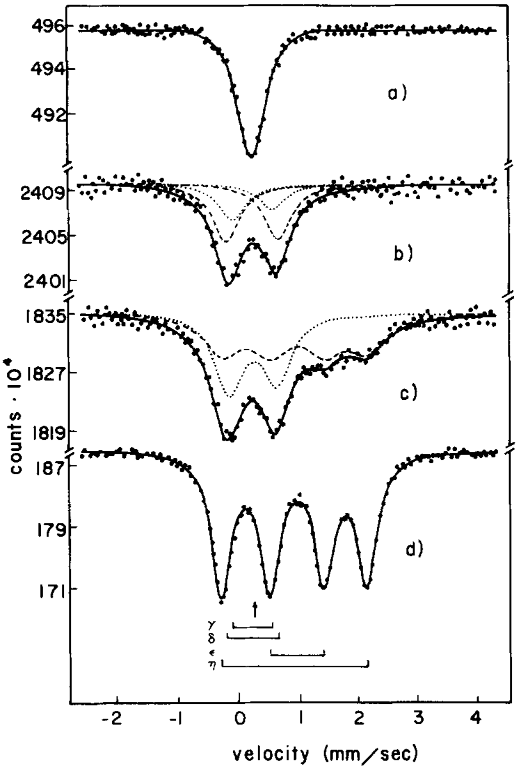

FIG. 1. Room temperature Mössbauer spectra for (a) SiO_2[2], (b) SiO_2[300], and (c) for SiO_2[2] which had been kept in a nitrogen–methanol stream at 320°C for 2 hr. For comparison, (d) the room temperature spectrum for $Fe_2(MoO_4)_3$ reduced by methanol under the same conditions as SiO_2[2].

ture spectra carried out on the SiO_2[2] sample before and after it had been kept in a nitrogen–methanol flow at high temperature. It can be seen that, as a consequence of the methanol interaction, the shape of the spectrum drastically changes and that, corresponding to the $Fe_2(MoO_4)_3$ line position (indicated with an arrow in Fig. 1), no absorption peak is detectable.

Figure 1d shows the room temperature Mössbauer spectrum obtained for unsupported $Fe_2(MoO_4)_3$ kept under the same conditions in the same nitrogen–methanol flow: the spectrum is due to the β-$FeMoO_4$ compound (*9–11*) (Table 1).

A reasonable fit to the spectrum for the reduced SiO_2[2] sample (Fig. 1c) has been obtained by superimposing four quadrupole doublets (γ, δ, ϵ, η).

γ and δ Quadrupolar Doublets

The positions, the widths, and the relative intensities of the lines of the γ and δ doublets for the reduced SiO_2[2] sample are the same as those of the Lorenzian lines, the superimposition of which fit the spectrum obtained for high area, i.e., for SiO_2[300] (see Table 1). On the other hand, the Mössbauer spectrum for SiO_2[300] (Fig. 1b), which had been kept under the same conditions as SiO_2[2] in the same nitrogen–methanol flow, does not display any appreciable change compared with the one observed before the methanol interaction.

These facts allow one to conclude that the methanol changes neither the coordination nor the valence of the iron ions of the compound that gives rise to the γ and δ quadrupolar doublets. It follows that:

(1) This iron compound, whose spectrum has been measured for very high area (Fig. 1b), also grows in supported catalysts with low area thus causing the observed spectra broadening. The reduction by methanol of low area supported catalysts makes it possible to separate its spectra contribution.

(2) The γ and δ quadrupolar doublets are not due to iron ions located at the $Fe_2(MoO_4)_3$ surface: the Fe(III)–molybdate can be reduced by methanol at high temperature, the reduction process actually starting at the catalyst surface. Therefore these doublets must be due to a reaction product between the support and the active species.

(3) The γ and δ doublets cannot be attributed to iron(III)-oxide even in the form of very small particles. Indeed, Fe_2O_3 can be reduced by methanol at high temperature and this should be even more valid for iron oxide in the form of very small particles. It should be noted that the same conclusion can be arrived at by carrying out low-temperature Mössbauer measurements for high area supported catalysts (*8*): the double-line spectrum (Fig. 1b) does not transform into a six-line spectrum as one might expect for iron oxide particles having a superparamagnetic behavior (*12–14*).

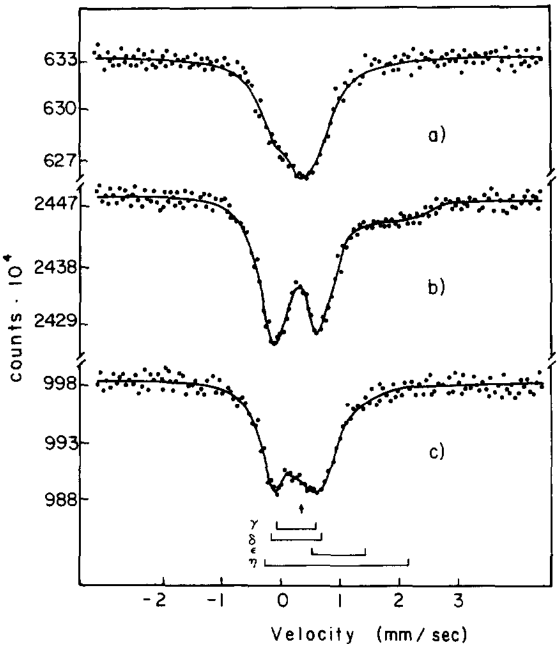

FIG. 2. Room temperature Mössbauer spectra for SiO_2[100]: (a) calcined sample, (b) after it had been kept in a nitrogen–methanol stream at 320°C for 2 hr, and (c) then kept in air at 365°C for 3 hr.

(4) The Mössbauer parameters for the iron-substituted silica compound (*13*), which could result from the reaction between only the iron and the support, are not coincident with the ones for the γ and δ quadrupolar doublets.

Since neither only the Mo nor only the Fe reacts with the support (no formation of Fe_2O_3 or of $(Fe_{1-x}Si_x)O_2$, respectively) it can be assumed that both Fe and Mo, substituting for Si and/or occurring interstitially, enter the silica structure: this Fe–Mo–SiO_2 compound is the one responsible for the γ and δ quadrupolar doublets. It is worth noting that the presence of this compound does not exclude the formation of another Mo species: this will depend on the Mo amount that reacts with the silica.

ϵ and η Quadrupolar Doublets

The position and the relative intensities for the ϵ and η doublets for the reduced SiO_2[2] sample (Fig. 1c) are the same as those detected for the reduced form of unsupported $Fe_2(MoO_4)_3$, i.e., for β-$FeMoO_4$ compound (Fig. 1d). However, the linewidths are larger (Table 1). This indicates a distribution of iron sites with slightly different quadrupole interactions, and the mean values of the quadrupole splitting coincide with those of the unsupported β-$FeMoO_4$. It follows that:

(1) As in the case when Fe(III)–molybdate is not supported, its reduced form is the β-$FeMoO_4$ compound that contains iron only in the Fe^{2+} ionic state located in two different sublattices (*9–11*).

(2) The supported β-$FeMoO_4$ has the iron sublattices distorted as compared with those of the unsupported one, thus indicating that, in SiO_2[2], it grows as a very thin surface film.

In Fig. 2a the room temperature Mössbauer spectrum for the SiO_2[100] sample is reported. In agreement with the above analysis, this spectrum can be fitted by superimposing a single peak with isomer shift characteristic for $Fe_2(MoO_4)_3$ to the γ and δ quadrupolar doublets.

Figure 2b shows the room temperature spectrum for SiO_2[100] that has interacted with methanol under the same conditions as

SiO_2[2]. From Fig. 2b, compared with Fig. 1c, it appears that on a percentage basis the contribution to the spectrum of the ϵ and η quadrupolar doublets is less. This indicates that the amount of supported β-$FeMoO_4$ decreases by increasing the sample area. A reasonable interpretation could be that as a consequence of the reaction between support and active species, Fe–Mo–SiO_2 (γ and δ doublets) form as a thin film covering the whole support area and that only on this film does the iron–molybdate grow.

Mössbauer analysis of the reoxidation process of the supported catalysts has also been performed by keeping the reduced samples in air for different times at a temperature known to produce reoxidation of the iron–molybdate-based catalysts (*9*, *11*).

Figure 2c shows the room temperature spectrum for the reduced SiO_2[100] catalyst (Fig. 2b) which had been subsequently kept in air for 3 hr at 365°C. This spectrum indicates an almost complete reoxidation of the catalyst; the contribution to the spectrum of ϵ and η quadrupolar doublets is strongly reduced and consequently the single line due to the Fe(III)-molybdate appears to superimpose itself on the γ and δ doublets. Only after 7 hr does reoxidation completely occur: the Mössbauer spectrum becomes identical to the one obtained for the original SiO_2[100] sample (Fig. 2a). Analogous results have been obtained for low area supported catalysts.

Therefore, for supported iron–molybdate, not only the reduction but also the reoxidation process occurs under the same conditions as for the unsupported one.

Figure 3 reports the conversion of methanol (X) and the selectivity to formaldehyde (S) as a function of the temperature for supported catalysts with different surface areas. By increasing the area both activity and selectivity remain practically constant up to 40 m^2/g and afterward rapidly decrease.

From the comparison of the catalytic and Mössbauer data it follows that:

(1) Up to surface area values of 40 m^2/g, the catalytic behavior remains practically constant. This could be due to the increase of the iron–molybdate area that compensates for its overall percentage decrease.

(2) The lower values of activity and selectivity for catalysts with area $\geq$100 m^2/g occurs with the destruction of the iron–molybdate. This is in agreement with the fact that $Fe_2(MoO_4)_3$ is known to be an active and selective species in methanol oxidation (*9*).

As regards SiO_2[300], in which $Fe_2(MoO_4)_3$ is not present, it is possible to hypothesize as the active component a Mo species formed as a consequence of the iron–molybdate decomposition. Indeed the species containing Fe^{3+} which cannot be reduced by methanol very probably does not participate in the mechanism of catalytic oxidation. This hypothesis is in agreement with the activity data obtained for MoO_3 on SiO_2 (*7*): these data are comparable with the ones measured for SiO_2[300].

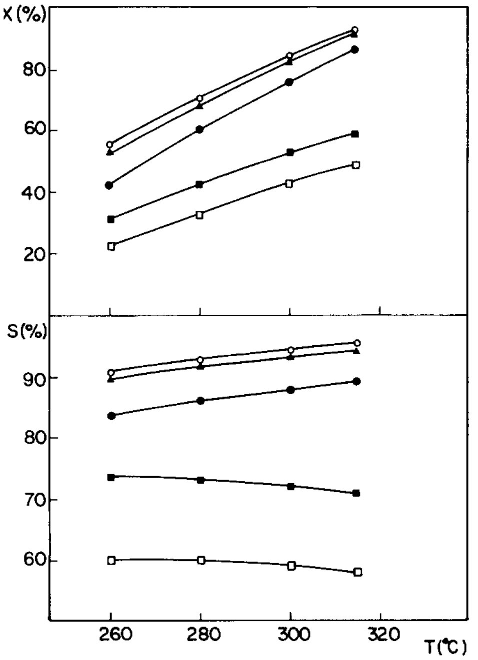

FIG. 3. Conversion of methanol (X) and selectivity to formaldehyde (S) as a function of the temperature for Fe_2O_3–MoO_3/SiO_2 catalysts with different surface areas: SiO_2[2] (○), SiO_2[15] (▲), SiO_2[39] (●), SiO_2[100] (■), and SiO_2[300] (□).

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