

Surface and Bulk Redox Processes in Iron-Molybdate-Based Catalysts

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The bulk reduction process of iron-molybdate-based catalysts as a function of temperature has been investigated by Mössbauer measurements on pure $\text{Fe}_2(\text{MoO}_4)_3$ and $\text{Fe}_2(\text{MoO}_4)_3 \cdot \text{MoO}_3$ which had been held in a nitrogen-methanol stream for different times and temperatures. The reduction takes place at temperatures $T \geq 230^\circ\text{C}$; the whole catalyst participates in the reaction and its reduced form has been proved to be $\beta\text{-FeMoO}_4$. The reversibility of the process has also been studied by Mössbauer measurements carried out on the catalysts which were prereduced and then held in an oxygen atmosphere for different times and temperatures. The reduced catalyst can be completely reoxidized and this process occurs at $T \geq 270^\circ\text{C}$ with a rate which increases with temperature. These data are discussed together with catalytic results obtained for the oxidation of methanol in the presence of the same catalysts in a stirred-tank flow reactor.

INTRODUCTION

Iron-molybdate mixed oxides are well-known catalysts for the selective oxidation of methanol to formaldehyde (1). As regards the mechanism of catalytic oxidation, many authors (2-4) suggest that the lattice oxygen of catalysts is the oxidizing agent.

Jirù *et al.* (2) proposed a two-stage oxidation reduction mechanism to describe the rate of oxidation of methanol on iron-molybdate catalyst:

$$r = \frac{k_1 p_{\text{Me}}^m}{1 + (\alpha k_1 p_{\text{Me}}^m / k_2 P_{\text{O}_2}^n)}, \quad (1)$$

and the degree of reduction of the catalyst:

$$\theta = \frac{1}{1 + (\alpha k_1 p_{\text{Me}}^m / k_2 P_{\text{O}_2}^n)} \quad (2)$$

where steady state conditions and activities equal to partial pressures have been assumed: k_1 indicates the rate constant of oxidation of methanol by oxygen from the oxidized catalyst, k_2 indicates the rate constant of oxidation of the reduced catalyst by gaseous oxygen, m and n indicate the reaction order referred to methanol and oxygen, respectively, p_{Me} and P_{O_2} indicate the partial pressure of methanol and oxygen, respectively, and α indicates the number of oxygen molecules required for converting one methanol molecule to formaldehyde.

These equations were obtained for a reduction-oxidation process that occurs at the surface of the catalyst. It was assumed that the available oxygen ions or vacancies located in the surface of the catalyst are

equivalent, in the reaction, to the molecules in the gaseous phase.

This hypothesis implies that under catalyst reduction conditions the surface oxygen taking part in the reaction exhausts itself after a certain time and that diffusion of oxygen atoms from the bulk to the surface then occurs, changing the physical and chemical properties of the catalyst.

The transformations which take place within the bulk of the catalysts which have interacted with methanol can be studied by means of the Mössbauer effect. The resonant absorption spectra of ^{57}Fe 14.4 keV γ -radiation are sensitive to the electronic structure of iron ions and to the symmetry of the coordination of iron ions.

Popescu *et al.* (5, 6) have carried out Mössbauer measurements on iron-molybdate-based catalysts, $\text{Fe}_2(\text{MoO}_4)_3 \cdot \text{MoO}_3$, having different percentages of MoO_3 excess; the catalysts were kept in a nitrogen-methanol flux at the temperatures $T = 20^\circ\text{C}$ and $T = 300^\circ\text{C}$. The spectra obtained at $T = 20^\circ\text{C}$ show a single peak due to Fe^{3+} ions of unreduced catalysts. At $T = 300^\circ\text{C}$, the two-line spectra first reported (5) were interpreted as due to Fe^{3+} and Fe^{2+} ions, while in the later paper (6) much more complex spectra were interpreted as due to Fe^{2+} ions in two different phases. One phase seems to originate only with low contents of MoO_3 and cannot reoxidize; the other can completely reoxidize in compounds with a high amount of MoO_3 and it seems to be responsible for the activity of the catalysts.

The contradictory data in Refs. (5) and (6) indicate that it is very difficult to carry out Mössbauer study on reduced catalysts. Particular care must be taken to avoid further modifications of the catalyst after the reaction, i.e., during the measurements.

Moreover, there are some unresolved questions. In particular, it is important to study the conditions under which the bulk reduction and reoxidation processes take

place and to determine the changes that can occur within the iron-molybdate structure. It is also not clear how many iron ions can participate in the reactions, and what role is played by the MoO_3 excess contained in iron-molybdate-based catalysts. The extent to which the bulk reduction-oxidation processes and the surface ones are linked together is also an important problem.

In order to investigate these questions, we have carried out Mössbauer measurements both on pure $\text{Fe}_2(\text{MoO}_4)_3$ ¹ and on $\text{Fe}_2(\text{MoO}_4)_3$ with 35% MoO_3 . In this way both the bulk reduction and the bulk reoxidation processes have been studied as a function of temperature. The resulting Mössbauer data have been compared with catalytic results for the oxidation of methanol on pure $\text{Fe}_2(\text{MoO}_4)_3$ and $\text{Fe}_2(\text{MoO}_4)_3 \cdot \text{MoO}_3$ obtained in a stirred-tank flow reactor.

EXPERIMENTAL PROCEDURE

The Mössbauer absorption spectra of the ^{57}Fe 14.4 keV γ -radiation have been measured by means of a Mössbauer velocity transducer of the electromechanical type working at constant acceleration and have been coupled to a multichannel analyzer operating in a multiscaler time-mode. Measurements were made with standard transmission geometry. The source was 5 mCi ^{57}Co diffused in a chromium matrix. Natural iron foils have been used for calibration.

The absorbers were polycrystalline thin pellets of pure $\text{Fe}_2(\text{MoO}_4)_3$ and $\text{Fe}_2(\text{MoO}_4)_3$ with 35% MoO_3 excess. The detailed description of their preparation, X-ray, infrared, and Raman analyses are reported in Refs. (7) and (8), respectively.

The Mössbauer absorption spectra of the catalysts were measured with the source at room temperature (RT) and the absorb-

¹ Pure $\text{Fe}_2(\text{MoO}_4)_3$ recently has been prepared in a reproducible way by Trifirò *et al.* (7).

ers at different temperatures ranging from RT to 415°C .

To study the reduction process, Mössbauer measurements were carried out on the oxides after keeping them at different temperatures (T_f) in a nitrogen-methanol stream (2.90 ml/min) for different times (t_f). To study the reoxidation process, Mössbauer measurements were made on the completely reduced catalysts which had then been kept in an oxygen atmosphere for different times (t_a) and at different temperatures (T_a). In the oven assembly, the temperature was monitored using a thermocouple in contact with the heater element, and it was possible to reduce the pressure around the samples to 10^{-3} Torr by dynamical pumping in order to avoid reactions with methanol or oxygen during the measuring times.

X-ray diffraction patterns were recorded at room temperature with a Geiger-counter Philips spectrogoniometer with $\text{CuK}\alpha$ radiation.

The kinetic investigations were carried out at 220 – 340°C using a stirred-tank flow reactor (9) and 1 g of catalyst in cylindrical pellets of 2-mm diameter and 4-mm length. Contact time was 0.75 sec, and the methanol concentration was 5% in different oxygen-nitrogen mixtures.

RESULTS AND DISCUSSION

Bulk Reactivity Measurements

Starting compounds. The Mössbauer absorption spectra of pure $\text{Fe}_2(\text{MoO}_4)_3$ (Fig. 1) and $\text{Fe}_2(\text{MoO}_4)_3 \cdot \text{MoO}_3$ catalysts display a well-defined absorption line in the full range of investigated temperatures from room temperature (RT) to 415°C . The isomer shift (0.57 ± 0.03 mm/sec at room temperature) is in the range typical for high spin ferric ions.

These spectra are due to iron ions located in different slightly distorted octahedral sites (10). The electric quadrupole interactions and the possibly different isomer shifts

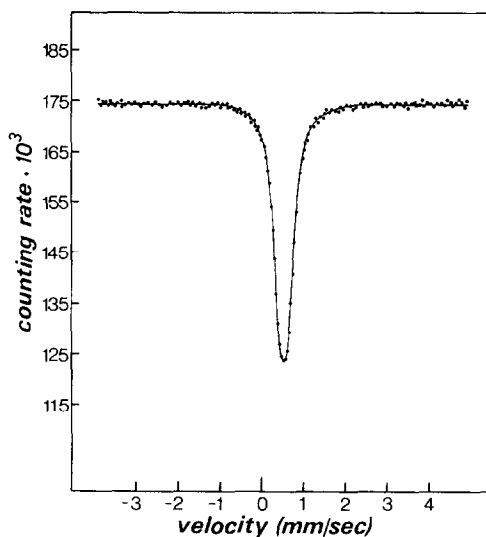


FIG. 1. Room temperature Mössbauer spectrum for a pure $\text{Fe}_2(\text{MoO}_4)_3$ catalyst.

of the ferric ions at the different octahedral sites give rise to separations in energy which are small compared to the linewidth (11).

In Fig. 2, we show (dashed line) the shift of the Mössbauer absorption line of the ferric ions as a function of temperature.

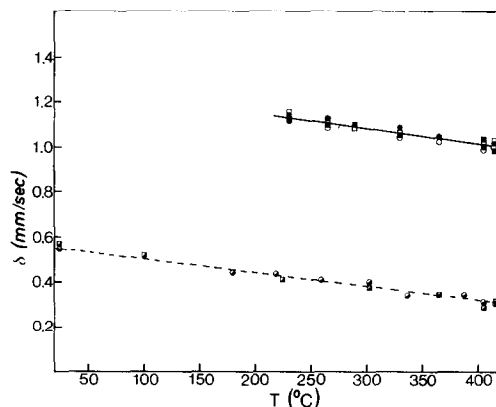


FIG. 2. Line shift of ferric ions at the octahedral sites of $\text{Fe}_2(\text{MoO}_4)_3 \cdot \text{MoO}_3$ (●) and pure $\text{Fe}_2(\text{MoO}_4)_3$ (■) and line shift for ϵ and η doublets of reduced catalysts as a function of temperature. Open and full circles refer, respectively, to ϵ and η doublets for MoO_3 -doped catalyst, and open and full squares refer, respectively, to ϵ and η doublets for pure catalyst.

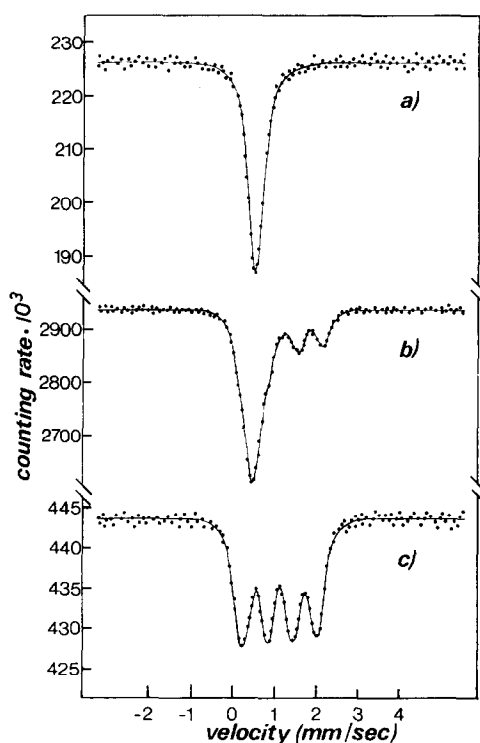


FIG. 3. Mössbauer spectra for a pure $\text{Fe}_2(\text{MoO}_4)_3$ catalyst that had been kept in a nitrogen-methanol flow for 5 hr at $T = 220^\circ\text{C}$ (a), at $T = 230^\circ\text{C}$ (b), and for 2 hr at $T = 330^\circ\text{C}$ (c).

Since the pure $\text{Fe}_2(\text{MoO}_4)_3$ and $\text{Fe}_2(\text{MoO}_4)_3 \cdot \text{MoO}_3$ compounds display the same Mössbauer spectra, it can be deduced, within the experimental errors, that molybdenum ions in excess do not localize in empty lattice sites of the structure (10).

Reduction process. In Fig. 3a, b, and c, we report the Mössbauer spectra of pure $\text{Fe}_2(\text{MoO}_4)_3$ catalyst for $T_f = 220^\circ\text{C}$ and $t_f = 5$ hr, $T_f = 230^\circ\text{C}$ and $t_f = 5$ hr, $T_f = 330^\circ\text{C}$ and $t_f = 2$ hr, respectively. No difference in the spectra of the $\text{Fe}_2(\text{MoO}_4)_3 \cdot \text{MoO}_3$ catalyst carried out under the same conditions was detected.

Below 230°C (Fig. 3a), there is no interaction of the catalyst with methanol, the spectra always displaying a single absorption peak even after a long contact time. The line shift ranged from (0.57 ± 0.03) mm/sec at room temperature to

(0.42 ± 0.03) mm/sec at $T = 220^\circ\text{C}$. By comparing these values with those of Fig. 2 (dashed line), we can conclude that the single peak is due to Fe^{3+} ions and that methanol has not interacted with the catalysts.

The spectra obtained after a long contact time with methanol at $T = 230^\circ\text{C}$ (Fig. 3b) can be interpreted as a superposition of some quadrupole doublets on a predominant single line. The line shift of the single peak has the same value as the one measured at the same temperature before the interaction with methanol ($\delta = 0.40 \pm 0.03$ mm/sec). The single line is therefore due to Fe^{3+} ions of the unreduced catalyst, while the observed doublets are due to iron ions of that part of the catalyst which has participated in the reaction.

By further increasing the temperature, the interaction of the catalyst with methanol occurs more rapidly: the intensity of the single line decreases and consequently the quadrupolar doublets become more evident (Fig. 3c).

In Fig. 4a and b, we report the Mössbauer spectra of pure $\text{Fe}_2(\text{MoO}_4)_3$ catalyst cooled to room temperature after having been kept in the nitrogen-methanol flow (2.90 ml/min) for a time $t_f = 2$ hr at temperature $T_f = 265^\circ\text{C}$, and for $t_f = 1$ hr at $T_f = 330^\circ\text{C}$, respectively. The spectra measured under the same conditions for $\text{Fe}_2(\text{MoO}_4)_3 \cdot \text{MoO}_3$ show no difference with respect to the pure catalyst spectra. By comparing the Mössbauer spectra carried out at 265 and 330°C with those at room temperature (Fig. 4a and b), it appears that the changes which occur within the catalyst that interacted at high temperature with methanol are not influenced by decreasing the temperature to RT . Figure 4a indicates that only a part of the catalyst has participated in the reaction, while Fig. 4b indicates that nearly all the catalyst has taken part.

The four lines of the spectra we have measured can be interpreted in two different ways: (i) as a superposition of two quadru-

pole doublets due to Fe^{3+} ions and Fe^{2+} ions or (ii) as due only to Fe^{2+} ions located in two different lattice sites. In either case, the presence of Fe^{2+} ions indicates the formation of a FeMoO_4 compound in the reduced catalyst.

Magnetic, Mössbauer, and structural studies on the three modifications of FeMoO_4 have been carried out by Sleight *et al.* (12). The Mössbauer absorption spectra of $\alpha\text{-FeMoO}_4$ and $\text{FeMoO}_4\text{-II}$, measured at room temperature, display only one quadrupole doublet, while the room temperature spectrum of $\beta\text{-FeMoO}_4$ shows four absorption lines.

The Mössbauer parameter relative to all the possible quadrupole doublets of our room temperature spectra are not in agreement with those measured at room temperature for phases $\alpha\text{-FeMoO}_4$ and $\text{FeMoO}_4\text{-II}$. As concerns $\text{FeMoO}_4\text{-II}$, this

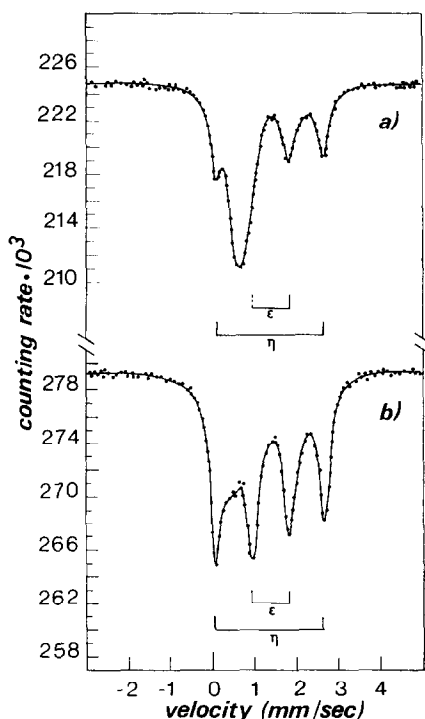


FIG. 4. Room-temperature Mössbauer spectra for a pure $\text{Fe}_2(\text{MoO}_4)_3$ catalyst that had been kept in a nitrogen-methanol flow for 2 hr at $T = 265^\circ\text{C}$ (a), and for 1 hr at $T = 330^\circ\text{C}$ (b).

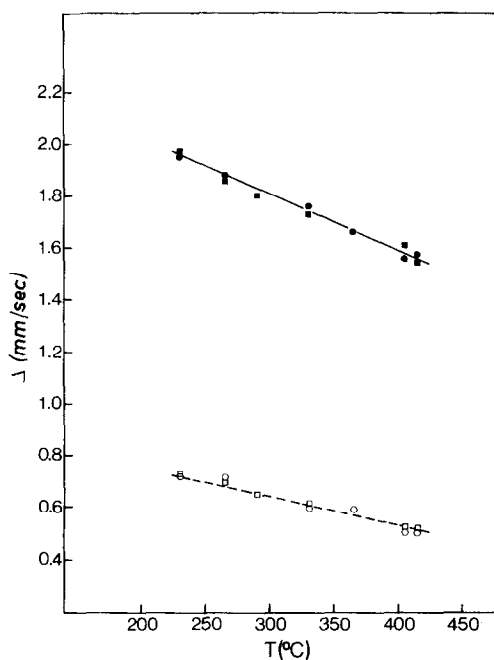


FIG. 5. Temperature dependence of the quadrupole splitting for ^{57}Fe nuclei in the two different lattice sites of reduced catalysts. Symbols as for Fig. 2.

fact is not surprising because this phase appears only at high pressure.

The quadrupole splitting and the isomer shift for the doublet η (Fig. 4) are (2.50 ± 0.05) mm/sec and (1.25 ± 0.05) mm/sec, respectively; the quadrupole splitting and the isomer shift for the doublet ϵ (Fig. 4) are (0.90 ± 0.05) mm/sec and (1.25 ± 0.05) mm/sec, respectively. These data, within experimental error, are in good agreement with the corresponding values for the $\beta\text{-FeMoO}_4$ phase (12).

Different samples of pure $\text{Fe}_2(\text{MoO}_4)_3$ and $\text{Fe}_2(\text{MoO}_4)_3 \cdot \text{MoO}_3$ for different reaction temperatures with methanol were analyzed in order to detect the temperature dependence of the quadrupole splitting for ^{57}Fe nuclei in the two different lattice sites (Fig. 5).

In Fig. 2, we report (solid line) the line shifts for ϵ and η doublets of reduced mixed oxides as a function of temperature.

In order to confirm the Mössbauer

TABLE 1
 X-Ray Patterns

β -FeMoO ₄ (12)		Observed pattern after reduction with 2% CH ₃ OH in N ₂ flow at 330°C		Fresh Fe(III)- molybdate and reoxidized sample 2 hr in air at 450°C	
$d(\text{Å})$	I/I_0	$d(\text{Å})$	I/I_0	$d(\text{Å})$	I/I_0
6.807	65	6.82	6.2	6.40	6
	5			5.79	13
4.664	5			4.57	8
				4.35	18
				4.07	24
3.862	15	3.86	11	3.86	100
				3.75	11
				3.57	17
3.547	10	3.55	7	3.46	29
3.403	113	3.40	100	3.35	9
3.303	20	3.30	20	3.24	21
3.256	10	3.26	7	3.20	10
		3.16	6	3.14	6
2.827	20	2.82	11	2.96	20
2.751	10	2.76	4	2.89	8
				2.84	10
2.675	15			2.63	21
2.672	15	2.68	14		
2.469	10	2.47	24.2	2.39	10
		2.43			
2.349	10			2.20	9
2.342	5				
2.332	5				
2.269	35			2.01	6
		1.715	30.75	1.94	7
				1.72	17

results, X-ray measurements were also carried out at room temperature on a pure Fe₂(MoO₄)₃ sample reduced with 2% CH₃OH in N₂ at 330°C. The X-ray pattern (Table 1) can be easily interpreted as β -FeMoO₄ by considering the values given by Sleight *et al.* (12).

Therefore, we may conclude that the reduction process of the catalysts occurs by the formation of β -FeMoO₄. At a suitable temperature, the whole catalyst can participate in the reaction which implies the reduction of Fe³⁺ ions to Fe²⁺ ions, located in two different sublattices. This process depends only on the temperature and on the interaction time with methanol.

Reoxidation process. The spectra obtained at temperatures $T < 270^\circ\text{C}$ showed that interaction of the reduced catalysts with oxygen does not occur: after a long contact-time with oxygen ($t_a = 10$ hr) the shape of the spectra and the relative intensities of the four lines remained the same.

The reoxidation process was observed only at $T \geq 270^\circ\text{C}$ with a rate which increased with temperature: the quadrupolar doublets gradually decreased and, consequently, the single line due to Fe³⁺ appeared. At $300^\circ\text{C} < T < 400^\circ\text{C}$, the reoxidation rate was at first very high; subsequently the process became very slow. As an example, Fig. 6a and b show that, while after 20 min of interaction with oxygen at 350°C an almost complete reoxidation already occurs, the complete reoxidation takes place only after 7 hr. At $T > 400^\circ\text{C}$, a great enhancement of the reoxidation rate was observed.

In the reoxidation process, too, no difference was detected between pure Fe(MoO₄)₃ and Fe(MoO₄)₃·MoO₃. The completely reoxidized catalyst has the same line shift and line width as the original one.

These results were confirmed by X-ray measurements. In Table 1, the X-ray pattern of the completely reoxidized catalyst is reported; it appears to be identical to the pattern of the fresh catalyst.

Catalytic Measurements

In Fig. 7, we show the conversion of methanol and the selectivity to CO for a pure Fe₂(MoO₄)₃ catalyst, as a function of

temperature. All the measurements were made in 20% oxygen concentration.

In Table 2, the conversion of methanol and the selectivity to CH_2O for a pure $\text{Fe}_2(\text{MoO}_4)_3$ catalyst at $T = 270^\circ\text{C}$ and $T = 320^\circ\text{C}$ for a different percentage of oxygen are reported. For a comparison, analogous data for a $\text{Fe}_2(\text{MoO}_4)_3 \cdot \text{MoO}_3$ catalyst, with 20% oxygen concentration, are also shown.

For a given oxygen concentration (see Fig. 7) the conversion of methanol is practically a linear function of temperature, while the percentage of CO strongly increases at $T > 300^\circ\text{C}$.

At $T < 300^\circ\text{C}$ (see Table 2) the conversion of methanol depends on the oxygen concentration, while at $T > 300^\circ\text{C}$ it is independent of the oxygen concentration.

All these facts indicate that at $T \approx 300^\circ\text{C}$ a strong modification in the catalytic behavior of pure $\text{Fe}_2(\text{MoO}_4)_3$ must occur.

It is worth noticing that the selectivity to CH_2O of the $\text{Fe}_2(\text{MoO}_4)_3 \cdot \text{MoO}_3$ catalyst

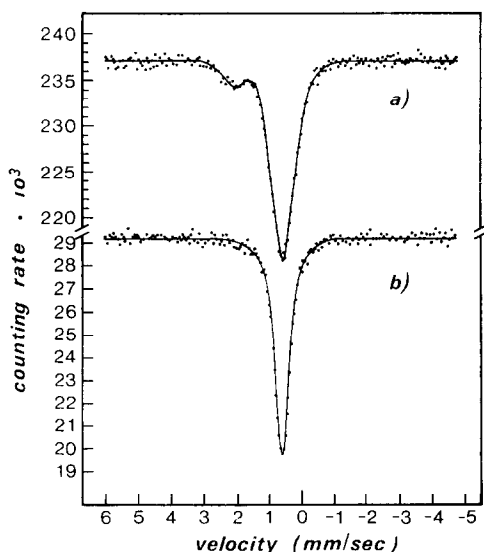


FIG. 6. Room temperature Mössbauer absorption spectra of $\text{Fe}(\text{MoO}_4)_3 \cdot \text{MoO}_3$ catalyst after complete reduction and then (a) partial reoxidation in an oxygen atmosphere at 350°C for 20 min or (b) total reoxidation in an oxygen atmosphere at 350°C for 7 hr.

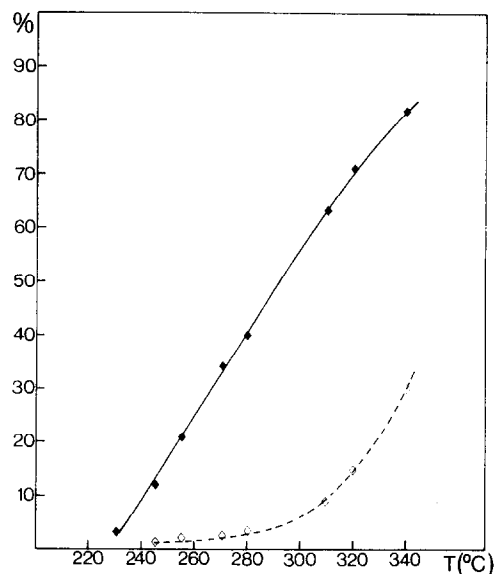


FIG. 7. Conversion of methanol (solid line) and selectivity to CO (dashed line) for a pure $\text{Fe}_2(\text{MoO}_4)_3$ catalyst in 20% oxygen concentration as a function of temperature.

is practically the same as that of pure $\text{Fe}_2(\text{MoO}_4)_3$. The conversion of methanol on a compound containing MoO_3 is higher than that on a pure iron-molybdate catalyst. However, by taking into account the surface areas of the two compounds, we

TABLE 2
Catalytic Data for Iron-Molybdate-Mixed Oxides

Catalyst	$T(^{\circ}\text{C})^a$	$\text{O}_2\%$ ^b	$X\%$ ^c	$S\%$ ^d
$\text{Fe}_2(\text{MoO}_4)_3$	280	5	30	98
	280	10	34	97
	280	20	40	96
	320	5	72	91
	320	10	71	88
	320	20	71	85
$\text{Fe}_2(\text{MoO}_4)_3 \cdot \text{MoO}_3$	280	20	70	94
	320	20	95	86

^a Temperature of reaction.

^b Oxygen concentration.

^c Ratio between methanol converted and methanol introduced.

^d Ratio between CH_2O formed and methanol converted.

can affirm that their specific activity is practically the same.

CONCLUSIONS

The comparative Mössbauer analysis together with the catalytic measurements on pure $\text{Fe}_2(\text{MoO}_4)_3$ and $\text{Fe}_2(\text{MoO}_4)_3 \cdot \text{MoO}_3$ mixed oxide demonstrates that: (a) in $\text{Fe}_2(\text{MoO}_4)_3 \cdot \text{MoO}_3$, the molybdenum ions in excess do not occupy the empty lattice sites of the iron-molybdate structure, since they do not change the oxidation state of iron ions and do not distort their coordination polyhedra; the known segregation of MoO_3 crystals at high temperature (13) therefore seems to be an almost complete process; (b) the starting temperatures and the rate of the reduction and reoxidation processes are not influenced by MoO_3 excess; (c) the reaction products in all stages of the processes show no differences either for pure or for MoO_3 -doped catalysts. These facts indicate, therefore, that the molybdenum in excess does not participate in the reactions.

The Mössbauer study has also revealed that the bulk reduction process of mixed oxides takes place only at temperatures $T \geq 230^\circ\text{C}$ and depends on the contact time with methanol. By increasing the temperature, the rate of the process also increases. The whole catalyst participates in the reaction and its reduced form has been proved to be $\beta\text{-FeMoO}_4$, which contains iron only in the Fe^{2+} ionic state located in two different lattice sites. The oxidation of methanol, therefore, implies reduction of Fe^{3+} ions, a change of the iron-molybdate structure, and involves the whole volume of the catalyst.

As regards the bulk reduction-oxidation mechanism of the catalyst, it is possible to hypothesize that the lattice oxygens, or vacancies, diffuse into surface positions where they can react with gaseous molecules.

The starting temperature for the bulk reduction of the catalyst coincides with the starting temperature of catalytic activity.

However, the fact that the bulk reduction of the catalyst occurs after a long contact time with methanol seems to indicate that the rate of the process is influenced by the rate of the diffusion of oxygen atoms into surface positions. The increasing bulk reduction rate with the temperature can be due to the increase of the diffusion rate with the temperature.

The Mössbauer study on the bulk re-oxidation process of catalysts has proved that the reduced catalyst can be completely converted into its unreduced state: gaseous oxygen can reoxidize all the Fe^{2+} ions and restore the original iron-molybdate structure. This process starts at $T > 270^\circ\text{C}$ and its rate increases with temperature.

The behavior deduced from the Mössbauer measurements at $T > 300^\circ\text{C}$ is in good agreement with the catalytic data. Indeed, they show that at $T < 300^\circ\text{C}$ the rate of methanol oxidation depends on the partial pressure of oxygen, while at $T \geq 300^\circ\text{C}$ it does not. This fact implies that at $T \geq 300^\circ\text{C}$ expressions (1) and (2) in the Introduction Section are no longer valid. If we assume that $k_2 p_{\text{O}_2} \gg k_1 p_{\text{Me}}$, the expression for the rate of methanol oxidation becomes: $r \simeq k_1 p_{\text{Me}}$.

At $T = 300^\circ\text{C}$, formation of CO begins. The corresponding decrease of selectivity in CH_2O production can be due to the high diffusion rate of oxygen to the surface and to the high oxidation rate of the catalyst surface itself.

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