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CENTRES RESPONSIBLE FOR THE CATALYTIC ACTIVITY
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Résumé. — Des catalyseurs à base de molybdate de fer avec ou sans excès d'oxydes de Mo ou de Bi ont été caractérisés. La réduction de *bulk* de tous les échantillons par le méthanol ou le 1-butène porte à la formation de β-FeMoO$_4$. Dans tous les cas la réoxydation de bulk a redonné des échantillons identiques aux catalyseurs frais calcinés. Des corrélations entre activité catalytique et réduction et réoxydation de *bulk* ont été proposées. L'excès de MoO$_3$ n'a pas d'influence sur l'activité catalytique spécifique ni sur les marches de réduction et de réoxydation. Son importance semble être liée seulement à des propriétés texturelles. Le β-FeMoO$_4$ ne semble pas être le composant actif pour l'oxydation du butène. Les résultats indiquent que la phase active et sélective est due à la migration du Bi dans le molybdate de fer.

Abstract. — Fe(III)-molybdate based catalysts with and without Mo and Bi oxides excess have been characterized. Bulk reduction of all the samples implies the formation of β-FeMoO$_4$ both with methanol and 1-butene as reagents. In all cases bulk reoxidation gave back samples equal to the fresh calcined catalysts. Correlations between catalytic activity data and bulk reduction and re-oxidation have been proposed. MoO$_3$ excess proved to have no influence on the specific activity nor on the steps of bulk reduction and re-oxidation. Its importance seems to be related only to textural properties. β-FeMoO$_4$ seemed not to be the active component for 1-butene oxidation. Evidence was drawn that the active and selective phase arises from the migration of Bi within the Fe(III)-molybdate structure.

1. Introduction. — The ternary systems containing Fe-Mo and Fe-Mo-Bi oxides are of great industrial interest, the former being widely used in the selective oxidation of methanol while the latter represents the most recent generation of catalysts for the selective oxidation and ammoxidation of olefines.

The reasons for which the Fe-Mo oxides are selective in the oxidation of methanol only while in the oxidation of olefines the presence of Bi at least in small quantities, is necessary, are not yet clear. In particular the nature of the active component of these selective systems is not established : some authors [1] proposed that it is a surface layer of Bi-molybdate 2/1, while others [2] suggest that it is a ternary compound, namely Bi$_3$(FeO$_4$) (MoO$_4$)$_2$.

Different amounts of Bi and Mo added to pure Fe(III)-molybdate matrix [3] could throw light on this problem.

The single step of reduction and of re-oxidation of these systems both with methanol and with an olefine do not concern only the surface : vacancies or oxygen diffusion into the bulk can break down the catalyst structure. The understanding of the bulk reactivity and its correlation with the catalytic activity can throw light on the nature of the active centers.

2. Experimental. — Pure Fe(III)-molybdate was impregnated with Bismuth nitrate (0-14 % Bi$_2$O$_3$ b. w.), while samples with MoO$_3$ excess (35 % b. w.) were prepared with a typical commercial technique.

Mössbauer absorption spectra of the Fe^{57} 14.4 keV γ-radiation have been measured by keeping the source (10 mCi Co^{57} diffused in a Chromium matrix) at 25 °C and the samples at temperatures ranging from room temperature to 500 °C. The transducer was of the electromechanical type working at constant acceleration. During the measuring time the thin lamina of the analyzed samples were kept in a vacuum of 10^{-3} torr.

X-ray patterns were obtained with a Philips Geiger counter spectrogoniometer with CuKα radiation. Pulse microreactor runs were performed with 0.3 g

of samples under He flow. Pulses consisted of 1 ml of a 1-butene-He mixture (3 % 1-butene). The analysis was made by gas chromatography. Methanol oxidation was performed in a CSTR reactor while for 1-butene oxidation a quartz microreactor was used.

3. Results and discussion. — 3.1 CHARACTERIZATION OF THE NEWLY OXIDIZED CATALYSTS. — The Mössbauer absorption spectra of the Fe(III)-molybdate pure and with 35 % MoO_3 excess display a single line (Fig. 1a) in the whole range of the investi-
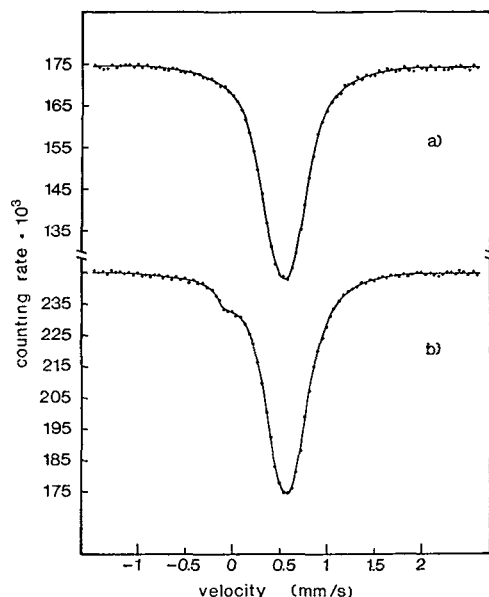

FIG. 1. — Mössbauer spectra of : a) pure and b) Bi-doped Fe(III)-molybdate (14 % Bi_2O_3 b. w.) carried out at room temperature.

FIG. 2. — Shift (δ) of the Mössbauer lines of oxidized catalysts (dashed line) and of ε and η doublets of the reduced catalysts (solid line) vs. temperature ; quadrupole splitting (Δ) of ε and η doublets (dashed and solid line) of reduced catalysts vs. temperature ; squares, circles and triangles refer to pure Fe(III)-molybdate, Fe(III)-molybdate with 35 % MoO_3 and with 5 % Bi_2O_3 respectively.

gated temperatures. This fact indicates that Mo ions in excess do not occupy the empty lattice sites of the Fe(III)-molybdate structure and therefore the known segregation of MoO_3 [4] crystals at high temperature is an almost complete process. The shift of the Mössbauer line vs temperature of both samples is reported in figure 2.

The spectra of Bi-doped Fe(III)-molybdate display in addition to the predominant single line due to Fe(III)-molybdate, a shoulder that can be attributed to Fe^{+3} ions located in distorted sublattices. The X-ray pattern of Bi-doped samples (Table I) shows the formation in addition to the $Fe_2(MoO_4)_3$ of a new phase : Bi-molybdate 2/1. However the Bi-doped samples are not a simple mixture of the two pure phases Fe(III)-molybdate and Bi-molybdate 2/1 because of the presence of the above shoulder in the Mössbauer spectra. It must be advanced that some Fe^{3+} migrate in the Bi-molybdate structure or that some Bi ions set themselves in empty lattice sites of Fe(III)-molybdate.
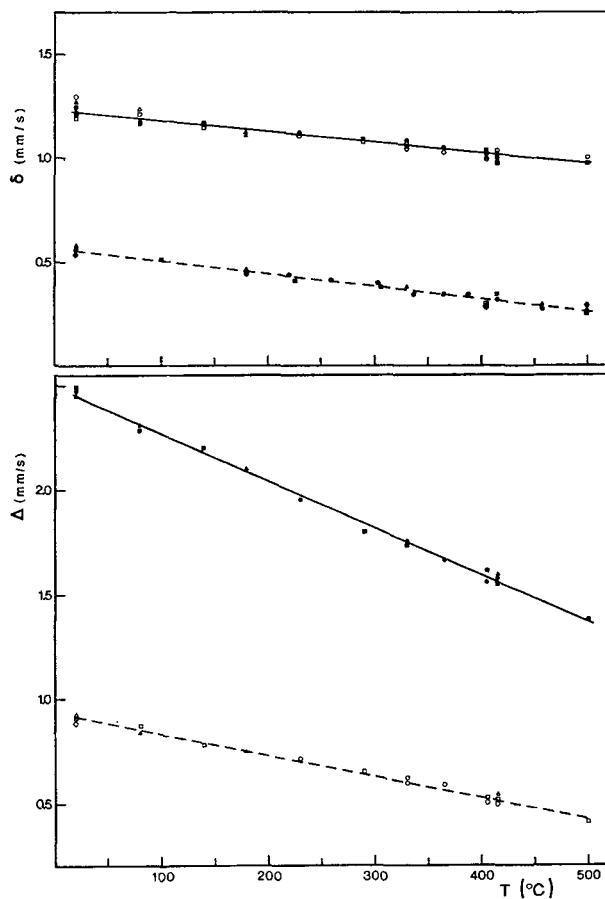
In agreement with this result an additional absorption band at about 20 000 cm^{-1} in the diffuse reflectance spectra has been found [3] and can be attributed to charge transfer between Fe and Bi inside the same lattice.

3.2 BULK REDUCTION MEASUREMENTS. — In figure 3a, b and c the Mössbauer spectra of pure Fe(III)-molybdate after interaction with 1-butene (1.5 kg/cm² pressure) at 370 ºC for 6 h, at 410 ºC for 4 h and for 6 h are reported respectively. The measurements were carried out at the same temperatures. No difference was detected for samples added with Bi or containing a Mo excess.

At temperatures $T < 400$ ºC (Fig. 3a) all the examined catalysts did not react with 1-butene ; at $T > 400$ ºC (Fig. 3b and c) the single line due to Fe^{3+} ions of the unreduced catalyst gradually disappears being replaced by a more complex spectrum. By comparing the Mössbauer spectra carried out at the temperature of reduction with the ones obtained at

TABLE I

X-ray patterns

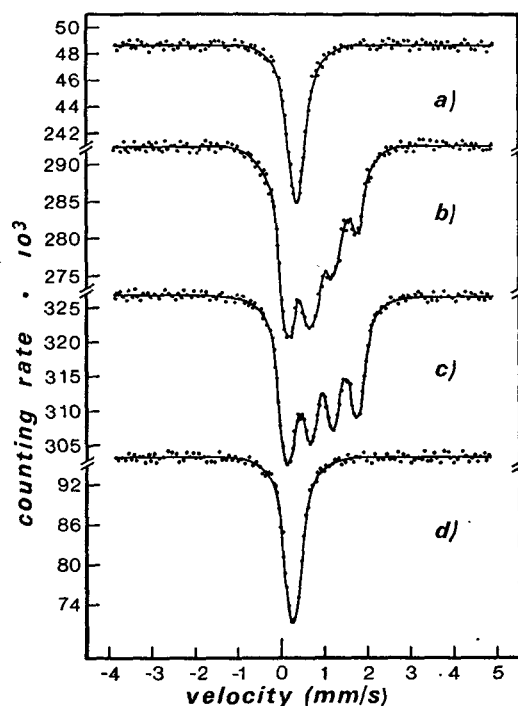| Fe(III)-molybdate after interaction with 1 % butene in N₂ flow at 470 °C		Fe(III)-molybdate after re duction with 4 % CH₃OH in N₂ flow at 330 °C		Fresh Fe(III)-molybdate or re-oxidized 2 hrs in air at 450 °C		Fe(III)-molybdate with 14 % Bi₂ O₂ (oxidized sample)	
$\overline{6.81}$	4	$\overline{6.82}$	6	$\overline{d}$	%	$\overline{d}$	%
				6.40	6	6.36	5
				5.79	13	5.78	10
				4.57	8	4.55	8
				4.35	18	4.35	17
				4.07	24	4.078	26
3.86	6	3.86	11	3.86	100	3.87	100
				3.75	11	3.76	14
3.55	5	3.55	7	3.57	17	3.56	18
3.40	100	3.40	100	3.46	29	3.46	26
3.30	10	3.30	20	3.35	9	3.35	9
3.26	2	3.26	7	3.24	21	3.24	23
				3.20	10	3.20	11
3.15	9	3.16	6	3.14	6	3.15	71
				2.96	20	2.96	22
				2.89	8	2.89	10
2.82	10	2.82	11	2.84	10	2.84	12
2.76	3	2.76	4			2.75	15
2.68	10	2.68	14			2.692	3
2.43	55	2.47	24	2.63	21	2.63	28
		2.43				2.48	4
				2.39	10	2.39	7
				2.20	19	2.20	5
				2.01	6	2.01	8
				1.94	7	1.94	8
1.722	10					1.92	17
1.706	80	1.715	31	1.72	17	1.72	14
						1.63	14

FIG. 3. — Mössbauer spectra of pure Fe(III)-molybdate kept in 1-butene a) at 370 °C for 6 h, b) at 410 °C for 4 h, c) at 410 °C for 6 h and d) re-oxidized at 410 °C for 5 h.

lower temperatures it can be deduced that the quenching does not modify the structure of the sample.

Similar spectra were also obtained by interaction of the catalysts with methanol. However the reduction begins at 230 °C. Also in this case no modification of the structure of the catalyst was observed by quenching down to room temperature. Figure 4b and c) shows the spectra of Fe(III)-molybdate containing 5 % Bi₂O₃ cooled to room temperature after reduction in a nitrogen-methanol stream (10 % CH₃OH, total flow 2.90 ml/min.) at 265 °C for 2 h and 330 °C 1 h, respectively.

Also for the interaction with methanol no difference was observed between the spectra of Fe(III)-molybdate, pure or containing Bi or MoO₃ excess, reduced under the same conditions.

The temperature dependence of the quadrupolar splittings and of the isomer shifts of η and ε doublets (1st-4th and 2nd-3rd lines) of the spectra obtained for 1-butene reduction is the same as the one obtained for methanol (Fig. 2). The reduction product of Fe(III)-molybdate with methanol was shown to be β-FeMoO₄ [5] ; besides the values of the parameters given in figure 2 are in good agreement with the data given by Sleight et al. [6] for the same compound ;
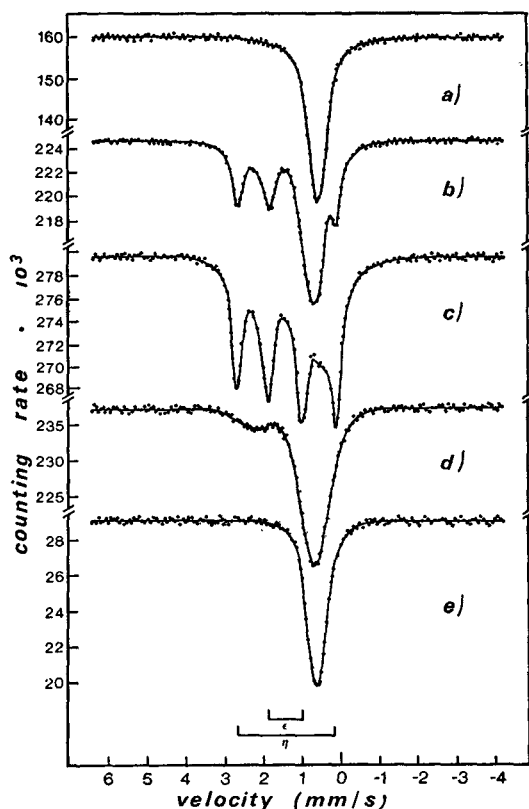
Fig. 4. — Room temperature Mössbauer spectra of Fe(III)-molybdate containing 5 % Bi$_2$O$_3$: a) unreduced, b) and c) reduced in CH$_3$OH—N$_2$ stream at 265 °C for 2 h and 330 °C 1 h respectively ; d) and e) partial and total re-oxidation in oxygen at 330 °C for 20 min. and 7 h respectively.

it can therefore be concluded that all catalysts both with methanol and 1-butene give β-FeMoO$_4$ as product of reduction.

These results were confirmed by X-ray measurements shown in table I. It appears that in addition to β-FeMoO$_4$ also a MoO$_2$ phase forms by reduction with 1-butene, while no other phase in addition to β-FeMoO$_4$ was detected after reduction with methanol at 350 °C.

IR spectra carried out on the same samples confirmed the nature of the products of reduction.

3.3 BULK RE-OXIDATION MEASUREMENTS. — Mössbauer measurements were performed on catalysts completely reduced both with methanol and 1-butene and kept in an atmosphere containing oxygen for different times and temperatures ; the spectra were measured at the temperature of interaction (Fig. 3d) and at lower values (Fig. 4d and e). At T < 270 °C the re-oxidation was not detected while for higher temperatures the rate of the process increases with temperature. At T > 400 °C a great enhancement of the rate of re-oxidation was detected. The line width and isomer shift of the single line measured for the completely re-oxidized samples are identical to the ones of the fresh oxidized catalysts. X-ray patterns confirm the reversibility of the process (Table I).

3.4 CATALYTIC MEASUREMENTS. — Activity runs carried out with 1-butene showed that all catalysts start being active at about 250 °C. By adding Bi to pure Fe(III)-molybdate a drastic enhancement of the selectivity to butadiene was observed even within a very narrow range (0-1 % Bi$_2$O$_3$ b. w.). A typical behaviour is shown in figure 5a where the data obtained at T = 310 °C are plotted against the Bi$_2$O$_3$ content. By performing pulse runs in the absence of oxygen, it appeared that pure Fe(III)-molybdate may oxidize 1-butene to butadiene (Fig. 5b) showing that the total
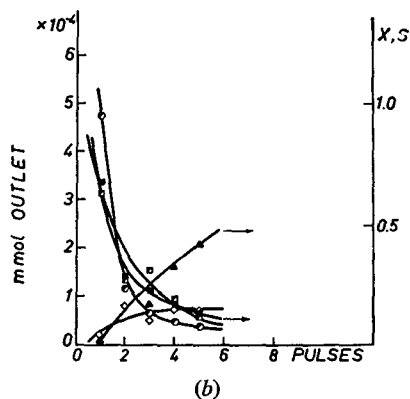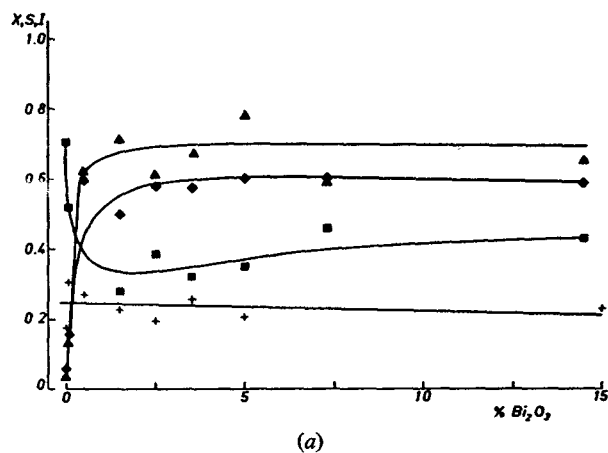

(a)

(b)

Fig. 5. — a) Flow reactor values against Bi$_2$O$_3$ content in the catalysts at 310 °C ; b) Pulse reactor data against pulse number at 350 °C. ■ Conversion, ▲ Selectivity to butadiene, + Isomerizing power, ◆ butadiene yield (normalized data to take into account the differences of the catalysts surface area), ◖ CO$_2$ + CO, ◨ Δx = 1-butene inlet — (Σ butenes + butadiene + (CO + CO$_2$)/4) outlet.

oxidation is probably related to some adsorbed species of oxygen. At T > 400 °C pure Fe(III)-molybdate in the absence of oxygen and also Bi-doped samples showed a strong decrease in the selectivity.

Methanol oxidation runs showed a similar activity and selectivity for all the investigated systems (pure or with Mo and/or Bi excess) in terms of specific area. The activity started at about 220 °C while around 300 °C all the catalysts showed a strong decrease in the selectivity.

4. Conclusions. — The excess of MoO_3 seemed to have no appreciable influence on the specific catalytic activity. However, its presence is important for properties such as surface area and catalyst hardness.

An easy correlation between bulk redox processes and catalytic reactivity was found in the case of methanol, the lowest temperature for the catalyst to be active being equal to that of onset bulk reduction, while the temperature where selectivity decreases corresponds to that of onset bulk re-oxidation.

A more difficult correlation was found for 1-butene. Indeed the catalytic activity starts already at 250 °C while the temperature of onset bulk reduction is only at 400 °C which corresponds to a decrease in the selectivity of the catalytic runs.

Reduction runs with methanol show that β-$FeMoO_4$ can form at low temperature also as a bulk compound. The fact that with 1-butene no β-$FeMoO_4$ forms at temperatures where the catalysts proved to be active and selective seems to indicate that this compound at least for this reaction is not the active component.

The Mössbauer and diffuse reflectance spectra indicate that by doping with Bi a structure modification occurs in the oxidized samples. This distortion might be due to a Bi migration into Fe(III)-molybdate structure or to a migration of Fe inside the Bi-molybdate 2/1.

However considering that the selectivity in the oxidation of 1-butene reaches a top level in a range where no Bi-molybdate 2/1 was found with all the techniques used, the probable active and selective compound is a Fe(III)-molybdate doped by Bi.

Pulse runs with pure Fe(III)-molybdate in absence of oxygen indicate that this catalyst can oxidize to butadiene and that probably reactive oxygen species are responsible for the very poor selectivity of this catalyst. By entering inside Fe(III)-molybdate Bi probably prevents the formation of these reactive species of oxygen.

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