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Structural Study of a Methanol Oxidation Catalyst

G. FAGHERAZZI AND N. PERNICONE

G. Donegani Research Institute, Montecatini Edison S.p.A., Novara, Italy

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An X-ray structural study was made on a MoO_3-$Fe_2(MoO_4)_3$ catalyst. By comparison with pure $Fe_2(MoO_4)_3$ (I), it was found that the unit cell of the iron molybdate (II) present in the catalyst is larger and that such enlargement mainly occurs along some crystallographic directions. These results support the hypothesis that II is Fe-defective, i.e., contains an excess of Mo with respect to the stoichiometry. Mo^{+6} ions should replace some Fe^{+3} ions in octahedral coordination and O^{-2} ions should insert in the lattice to establish the electroneutrality. Such insertion is allowed by the typical structure of iron molybdate. Furthermore, some evidence for the presence of lattice disorder in II, possibly due to the insertion of O^{-2} ions, was obtained. The compound II seems to be the active component of the Fe-Mo catalyst for methanol oxidation to formaldehyde.

INTRODUCTION

The most widely used methanol oxidation catalyst is a mixture of MoO_3 and $Fe_2(MoO_4)_3$ (*1*). Studies on the phase composition of the catalyst and on the relationship between Mo/Fe ratio and catalytic activity were carried out by Boreskov *et al.* (*2*). These authors stated that $Fe_2(MoO_4)_3$ is the active component of the catalyst; however, their experimental data show that the maximum of catalytic activity is obtained for a molar ratio $R =$ Mo/Fe $= 1.7$ and that the activity rapidly decreases for $R < 1.7$. On the basis of these and other results, Pernicone, Liberti, and Ersini (*3*) hypothesized that iron molybdate, to be an active catalyst in methanol oxidation, should be Fe-defective, i.e., contain a Mo excess with respect to the stoichiometry. To verify the validity of this hypothesis, we have carried out an X-ray structural study on the iron molybdate present in a methanol oxidation catalyst.

EXPERIMENTAL

The mixed catalyst MoO_3-$Fe_2(MoO_4)_3$ was prepared by precipitating an amorphous hydrous iron molybdate with $R = 2$ according to Kerr *et al.* (*4*) and by heating it at 400°C in flowing oxygen. For comparison, pure iron molybdate (I) was prepared by heating the mixed catalyst at 700°C in flowing oxygen until the complete disappearance of MoO_3.

The powder diffraction patterns were obtained with Mn-filtered FeKα radiation using a Nonius cylindrical camera with a radius of 57.3 mm. The angular positions of the X-ray lines were carefully measured with a linear comparator which could be read to ±0.02 mm.

The mean values of particle size were obtained using three methods: (1) from the breadth of X-ray powder lines microphotometered with a Joyce-Loebl III CS microdensitometer; (2) by electron microscopy with a Philips 300 EM; (3) from the value of the specific surface, measured with a Perkin-Elmer-Shell sorptometer, assuming a spherical shape of the particles.

RESULTS AND DISCUSSION

The observed and calculated lattice spacings d_{hkl} of the sample I and of the iron molybdate present in the mixed catalyst (II) are reported in Table 1. For brevity, the lattice spacings higher than 2.5 Å were not reported. The spacings corresponding

TABLE 1
COMPARISON OF X-RAY DATA OF STOICHIOMETRIC (I) AND Fe-DEFECTIVE (II) IRON MOLYBDATE

I				II		
Found	*d* spaces (calcd.)[a]	Intensity[b]	Index (*hkl*)	Found	*d* spaces (calcd.)[c]	Intensity[b]
6.36	6.385	vw	200	6.42	6.451	vw
5.77	5.775	w	012	5.79	5.798	w
4.54	4.548	vw	112	4.55	4.566	vw
4.33	4.334 4.333	w	211 120	4.35	4.366 4.350	w
4.08	4.104 4.061	m	$\bar{1}22$ $\bar{2}14$	4.10	4.128 4.115	m
3.900	3.912 3.900	w	022 $\bar{2}22$	—	—	—
3.862	3.857 3.855	vs	$\bar{3}14$ 202	3.885	3.932 3.878	vs
3.561	3.556	vw	212	3.576	3.576	vw
3.458	3.456	m	122	3.469	3.469	m
3.344	3.352 3.350 3.344 3.335	vw	$\bar{3}23$ $\bar{3}21$ $\bar{2}15$ $\bar{3}15$	—	—	—
3.233	3.227	m	$\bar{2}24$	3.252*	3.259	m
3.190	3.179	vw	400	3.225	3.225	vvw
3.133	3.142 3.134 3.128	vw	$\bar{1}15$ $\bar{1}24$ 203	3.148	3.163 3.153 3.143	vw
2.955	2.962 2.956 2.947	m	213 222 114	2.965	2.976 2.970 2.958	w
2.891	2.887	vw	024	2.899	2.899	vw
2.838	2.836 2.832	w	032 $\bar{2}32$	2.851	2.846 2.851	vw
2.648	2.648	vw	132	—	—	—
2.625	2.624 2.616	w	$\bar{1}16$ 420	2.640*	2.640 2.644	w
2.549	2.547	vw	$\bar{6}03$	—	—	—

Note: Values marked by an asterisk are the spacings corresponding to the diffraction lines superimposed to those pertaining to MoO_3.

[a] Calculated for monoclinic unit cell (*5*), $a = 15.52$ Å; $b = 9.21$ Å; $c = 18.10$ Å; $\beta = 125°$.

[b] w = weak, m = medium, s = strong, v = very. The intensities were estimated visually.

[c] Calculated for monoclinic unit cell, $a = 15.93$ Å; $b = 9.24$ Å; $c = 18.38$ Å; $\beta = 125°55'$.

to the diffraction lines superimposed to those pertaining to MoO_3 are marked with an asterisk (in the mixed catalyst there was about 20% MoO_3). The calculation of the lattice spacings of I and their indexing were made on the basis of the monoclinic unit cell found by Plyasova *et al.* (*5*) with a single crystal study. As may be seen in Table 1, the observed d_{hkl} values of I satisfactorily agree with the calculated ones. On the contrary, all the observed d_{hkl} values of II are higher. The unit cell parameters of II were calculated from the observed *d* spaces of four isolated and independent reflections of its diffraction pattern.

The enlargements, Δd_{hkl}, of the lattice of II with respect to the lattice of I were

TABLE 2

DATA FOR THE ENLARGEMENTS OF THE LATTICE OF Fe-DEFECTIVE IRON MOLYBDATE (II)

hkl	d_{hkl}^{sc} (I) (from single crystal)	d_{hkl}^{p} (I) (from powder pattern)	d_{hkl}^{p} (II) (from powder pattern)	Δd_{hkl}[a]	$\Delta' d_{hkl}$[b]
100	12.713	12.731	12.903	0.190	0.018
010	9.210	9.210	9.241	0.031	0.000
001	14.828	14.863	14.892	0.064	0.035
110	7.459	7.462	7.513	0.054	0.003
011	7.824	7.829	7.852	0.028	0.005
101	7.711	7.722	7.757	0.046	0.011
$\bar{1}01$	14.665	14.709	15.053	0.388	0.044
111	5.912	5.917	5.941	0.029	0.005
$\bar{1}11$	7.799	7.806	7.875	0.076	0.007

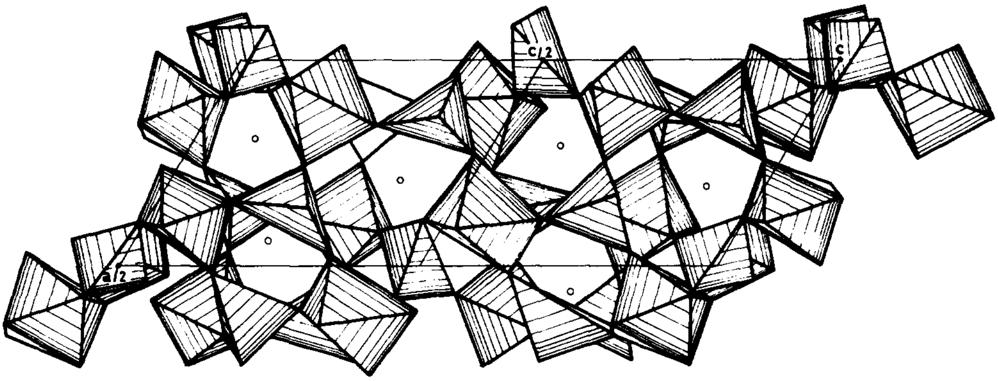
[a] $\Delta d_{hkl} = d_{hkl}^{p}$ (II) $- d_{hkl}^{sc}$ (I).

[b] $\Delta' d_{hkl} = d_{hkl}^{p}$ (I) $- d_{hkl}^{sc}$ (I).

calculated along several crystallographic directions $[hkl]$. The results are reported in Table 2. In order to evaluate the significance of such enlargements, we have used, to calculate the unit cell of I, the same method employed in the calculation of the unit cell of II. Now the differences, $\Delta' d_{hkl}$, between the d_{hkl} values of I obtained from this unit cell and those obtained from the single crystal data of Plyasova *et al.* may be considered as a measure of the error affecting the values of the abovementioned enlargements.

From the comparison between Δd_{hkl} and $\Delta' d_{hkl}$, it is clear that the enlargement of the unit cell in the case of II is distinctly established and that the highest increases occur along $[\bar{1}01]$ and [100]. The enlargement along $[\bar{1}01]$ is mainly due to the increase of the β angle from 125° to 125° 55′, and therefore it is not very meaningful. On the contrary the enlargement along [100] is quite significant. It may be explained by supposing the presence of an excess of O^{-2} ions with respect to the stoichiometry of pure iron molybdate. This hypothesis is quite feasible from a crystallographic point of view, because the oxygen packing found by Plyasova *et al.* in the structure of I is very loose (*5*, *6*).

On the basis of the atomic coordinates reported by these authors, it was possible to find some interstitial positions for the excess oxygen ions, from which the smallest



o Possible positions for the interstitial oxygen ions.

FIG. 1. A diagrammatic representation of the structure of iron molybdate, $Fe_2(MoO_4)_3$, projected on a plane normal to the b axis. The octahedrons around iron ions and the tetrahedrons around molybdenum ions are indicated. Each vertex of octahedrons and tetrahedrons is occupied by an oxygen ion.

distances to the neighboring ones are about 2.3 Å (Fig. 1). As the unit cell of II is wider than that of I and as the presence of excess O^{-2} ions should cause local lattice distortions, the insertion of O^{-2} ions (diameter 2.8 Å) in such interstitial positions as indicated in Fig. 1 should be allowed. Moreover, the preferential enlargement observed in the direction perpendicular to the *bc* plane should be considered a consequence of the presence of interstitial oxygen ions among the layers parallel to this plane, in which the oxygen ions tetrahedrally coordinated to Mo^{+6} and octahedrally coordinated to Fe^{+3} are more closely packed.

The hypothesis that in the mixed catalyst the iron molybdate is Fe-defective (*3*) is strongly supported by the above results. Indeed, the replacement of two Fe^{+3} ions by two Mo^{+6} ions is possible, for the electroneutrality of the crystal, through the insertion of three O^{-2} ions. It is noteworthy that very often Mo is octahedrally coordinated in its oxides; therefore the replacement of Fe^{+3} by Mo^{+6} in iron molybdate seems quite feasible.

It is also suitable to take into account the method of preparation of the mixed catalyst. During the heating of the amorphous hydrous iron molybdate, a dehydration occurs with formation of an amorphous anhydrous iron molybdate (III) with $R = 2$. At about 380°C, a complex process occurs during which segregation of MoO_3 from III and crystallization of both MoO_3 and Fe-defective iron molybdate (II) take place (exothermic DTA peak). In such conditions, the presence of an iron molybdate containing an excess of Mo with respect to the stoichiometric $Fe_2(MoO_4)_3$ seems quite likely. The complete segregation of MoO_3, to give pure iron molybdate, should occur by heating at higher temperatures.

Some evidence for the presence of lattice disorder in II, possibly due to the insertion of excess O^{-2} ions, was achieved by comparing the effective particle size obtained by X-ray methods with the values obtained by electron microscopy and surface area measurements. The width of the diffraction lines of II is much higher than that of the corresponding lines of I, which may be considered as broadened only for instrumental reasons. Owing to the low crystallographic symmetry of iron molybdate, it was not possible to separate the broadening due to particle size from that due to lattice strain. Neglecting the influence of the latter, the effective particle size could be calculated using the Scherrer formula (*7*) applied to the X-ray lines included in the 2θ range 40°–60°:

$$\bar{D} = \frac{0.9\lambda}{\beta_{1/2}\cos\theta}$$

where $\bar{D}$ is the value of particle size averaged in the different directions (hkl) under examination, λ is the wavelength of X-ray radiation ($\lambda = 1.9373$ Å), $\beta_{1/2}$ is the half-maximum width, and 2θ is the Bragg angle of the considered line. The $\beta_{1/2}$ value was obtained after correction for the instrumental broadening and for the broadening due to the separation of the $K\alpha_1\alpha_2$ doublet, assuming a shape of the profiles intermediate between Gaussian and Cauchyan (*7*). The found value of $\bar{D}$ is 180 Å. The particle size of II was also directly measured by a Philips EM 300 electron microscope. The mean value, calculated over a large number of particles of a sample ultrasonically dispersed in methanol suspension, is 760 Å. The mean value of particle size, calculated from the surface area, is 930 Å. Both the latter values are in good accordance with each other, but are much higher than the value calculated from the broadening of X-ray lines. Although it is well known (*8*) that the latter technique gives lower particle size values than electron microscopy and surface area measurements, in our case the effect is so large that it can be explained only by assuming that a part of the broadening of X-ray lines is due to lattice strain, which probably arises from the presence of excess O^{-2} ions in the structure of II.

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