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New Unsupported [100]-Oriented MoO_3 Catalysts

II. Catalytic Properties in Propylene Oxidation

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Part I (B. Mingot *et al.*, *J. Catal.* **118,** 424, 1989) described the preparation and characterization of new unsupported [100]-oriented MoO_3 catalysts. In this second part, the catalytic properties of a series of these catalysts have been compared with more conventional vapor-grown MoO_3 samples in the propylene oxidation reaction. This study confirms the structure sensitivity of this reaction: the exposed (120) faces, more developed on the [100]-oriented MoO_3 crystallites, lead nearly exclusively to acrolein, whereas the basal (010) planes are active in total oxidation. The selectivity for acrolein formation on the (120) faces has been related to the atomic structure of such faces characterized by the presence of dual sites. © 1992 Academic Press, Inc.

1. INTRODUCTION

As previously described in Part I (*1*), a new method of preparation of MoO_3 catalysts, based on the complete oxidation of metallic molybdenum foils, has been devised. As evidenced by X-ray and electron diffraction, the individual MoO_3 crystallites are characterized by a preferential [100] orientation normal to the surface of the oxidized foil. A detailed shape analysis by SEM has shown that the side faces, (100) and (001), are more developed than on conventional vapor-grown crystallites. Furthermore, the (100) faces are actually truncated to probably more stable (1k0) surface faces (mainly (120) faces). Such (120) faces can be viewed on an atomic scale composed of the addition of (100) and (010) facets and look like stepped planes.

In the present work, the structure sensitivity of the propylene oxidation reaction has been reexamined on these new MoO_3 catalysts. Indeed, there is still no general agreement on the nature of the MoO_3 active faces in the selective partial oxidation of propylene to acrolein: they are the (100) faces according to Volta *et al.* (*2–6*), the (010) faces according to Haber and coworkers (*7, 8*), the (001) faces according to Ziółkowski (*9*), and Andersson and Hansen (*10*). The occurrence of a structure-sensitivity effect in this reaction on MoO_3 has been questioned recently by Oyama (*11*).

2. EXPERIMENTAL

A series of MoO_3 catalysts has been prepared by oxidation of Mo foils (0.25 mm in thickness) under a pure oxygen flow (1.125 liter/h) at atmospheric pressure for temperatures varying from 536 to 680°C; the time of oxidation, longer for the lower temperatures, was always adjusted to ensure the complete oxidation to the α-MoO_3 state as checked by X-ray diffraction, Raman spectroscopy, and XPS analysis. As shown in

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TABLE 1

Geometrical Characteristics and Relative Area of Exposed Surface Faces of MoO_3 Crystallites Depending on the Preparation Mode (Dimensions A, B, and C Refer to the Scheme Depicted in Fig. 1)

Prep. mode[a]	$A_{(\mu m)}$	$B_{(\mu m)}$	$C_{(\mu m)}$	$\frac{B}{C}$	$\frac{B}{A}$	$m\%(120)$	$n\%(010)$ ($\pm 10\%$)	$p\%(001)$
536–190	1.6	0.2	0.9	0.22	0.13	10.5	72.8	16.7
570–65	2.9	0.4	1.6	0.25	0.14	11.2	70.5	18.3
590–48	4.0	0.6	2.0	0.30	0.15	11.7	67.3	21.0
620–24	4.6	0.9	3.2	0.28	0.20	14.8	65.7	19.5
650–12	5.0	1.1	4.0	0.28	0.22	16.4	64.7	18.9
660–8	6.0	1.6	5.8	0.28	0.27	19.2	62.3	18.5
670–6	5.8	1.7	5.7	0.30	0.29	20.4	60.2	19.4
680–6	8.0	2.6	7.8	0.33	0.33	21.6	57.5	20.9
Vapor-grown MoO_3	350	25	1000	0.025	0.071	7.4	90.3	2.3

[a] Numbers refer to temperature and time, e.g., 536–190 means 536° for 190 h.

Table 1, these catalysts are characterized by different ratios between the surface faces: with increasing temperature of preparation from 536 to 680°C, the relative area of the (120) faces goes from ≈ 10 to $\approx 20\%$ with a complementary decrease of the area of the (010) faces. These figures have been obtained on the basis of a statistical analysis of the SEM pictures, using a schematic model of the MoO_3 crystallites exposing

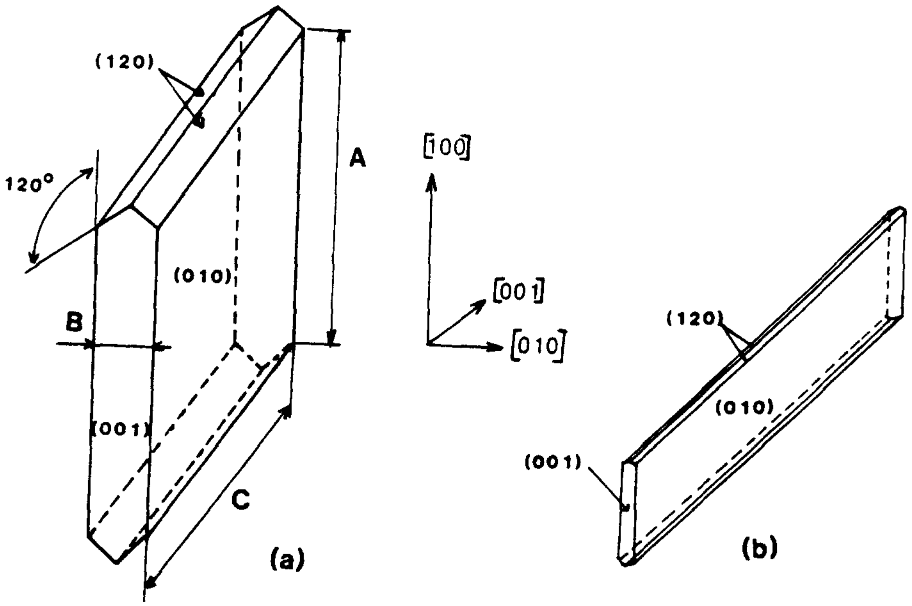

FIG. 1. Schematic representation of α-MoO_3 crystallites prepared (a) by oxidation of molybdenum sheets (magnification $\times 10^4$) at 650°C, 12 h, (b) by a vapor-grown process (magnification $\times 50$).

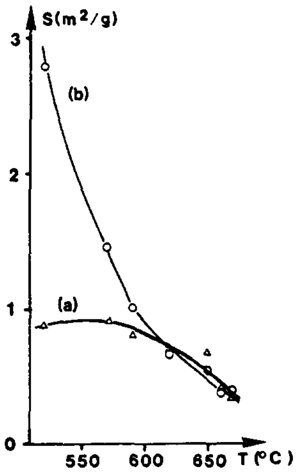

FIG. 2. Specific surface area of MoO_3 catalysts prepared by oxidation of molybdenum sheets at different temperatures (from 536 to 680°C). (a) Experimental. (b) Theoretical.

only the (010), (001), and (120) surface faces as depicted in Fig. 1. Table 1 also shows for comparison the geometric characterization of a vapor-grown MoO_3 sample prepared by sublimation of a pure MoO_3 powder at 800°C in an oxygen flow (*12*). This sample is characterized by much larger individual crystallites exposing mostly the basal cleavage (010) plane, whereas the side faces (001) and (120) are very poorly developed.

The BET specific surface area decreases when the temperature of the preparation increases, from 0.9 to 0.27 $m^2\ g^{-1}$, in agreement with the increase in the average size of the crystallites (Table 1). For vapor-grown crystallites, the surface area is only 0.04 $m^2\ g^{-1}$. Figure 2 shows the measured BET area (Fig. 2a) compared with the calculated area (Fig. 2b) assuming that the entire external surface of each crystallite depicted in Fig. 1 is accessible to gases: the agreement is fairly good with the exception of the preparations at 536 and 570°C, where the crystallites are quite small and so closely packed, as shown by SEM, that the assumption of complete gas accessibility appears to be unrealistic.

The catalytic oxidation of propylene has been studied in a differential flow microreactor under atmospheric pressure in the temperature range 350–420°C. The composition of the reaction mixture was $C_3H_6/O_2/N_2$ = 100/100/560. As this reaction is very exothermic ($\Delta H = -322$ kJ mol^{-1}), the mass m of the catalyst (0.2 to 1 g) and the gas flow D (0.28 to 3 $cm^3\ s^{-1}$) have been chosen to limit the conversion to below 2%. It has also been frequently checked that there is no significant catalytic contribution of the glass walls of the reactor, and that the homogeneous reaction can be neglected.

The reaction products have been analyzed by gas chromatography: organic compounds with a flame ionization detector and mineral compounds with a thermal conductivity detector. The reaction products are mainly acrolein and carbon dioxide with, to a lesser extent, ethanal, propanal, and traces of acetone and propylene oxide.

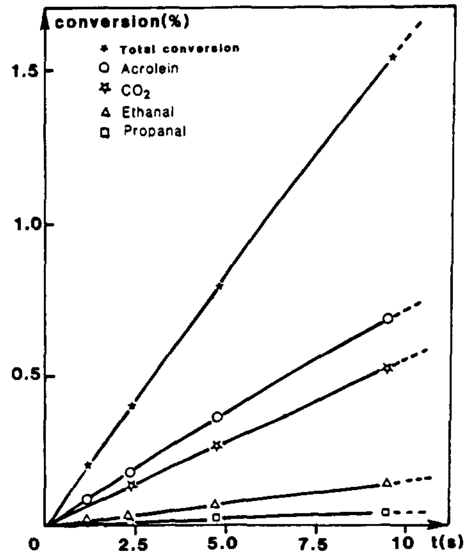

FIG. 3. Linear variation of total conversion and yield in the different products as a function of the time of contact in the oxidation of propylene at 400°C ($O_2/C_3H_6/N_2$: 100/100/560) on MoO_3 (670-6). (Time of contact = $1/D \times V$, where D is the gas flow and V is the volume of the catalyst).

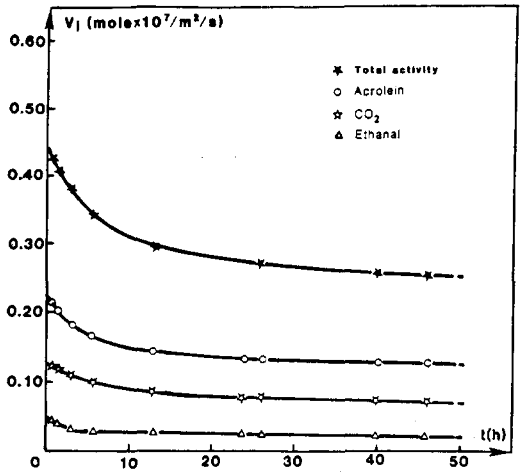

FIG. 4. Progressive stabilization with the reaction time of the intrinsic activity of MoO_3 (670-6) at 400°C in the propylene oxidation reaction.

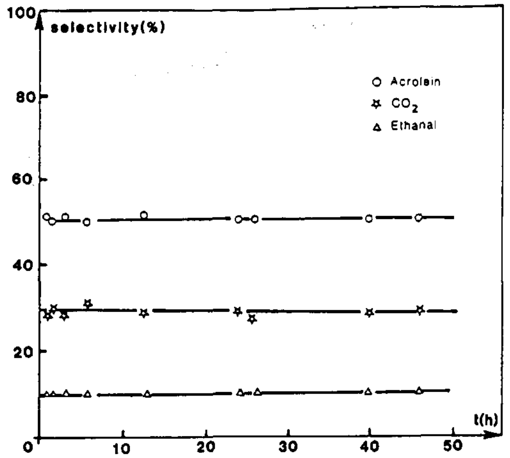

FIG. 5. Selectivities in acrolein, CO_2, and ethanal in the course of the run given in Fig. 4.

3. RESULTS

3.1. *Preliminary Observations*

(*a*) *Influence of the mass of the catalyst and of the gas flow.* Insofar as the catalyst was not a powder but several thin pieces of oxidized foil, it was important to make sure that the experimental conditions gave rise to a reaction rate proportional to the quantity of the catalyst and to $1/D$: this is shown in Fig. 3.

(*b*) *Stabilization of the catalyst.* The activity of the catalyst in the propylene oxidation reaction at 400°C was observed to decrease with time, as shown in Fig. 4. However, the activity becomes nearly stable after a period of 24 h and measurements have thus been taken after this stabilization time. We have not studied the causes for this slow deactivation especially, but XPS analysis suggests that this phenomenon could be due to a carbonaceous deposit. We were mainly interested in selectivity measurements, which remain quite stable with time (±2%), as shown in Fig. 5.

(*c*) *Apparent activation energies.* Plotting $\log V_i$ (the intrinsic rate) as a function of $1/T$ in the temperature range 350–420°C gives straight lines as shown in Fig. 6, suggesting no change in the reaction mechanism in this domain. The activation energies calculated in this way (see Fig. 6) compare well with the values obtained previously in our laboratory on more conventional MoO_3 catalysts. It may be noted that the activation energy for acrolein formation (120 kJ mol^{-1}) is only slightly higher than the corresponding energy for CO_2 formation (104 kJ mol^{-1}) in agreement with the fact that the ratio of the selectivities to acrolein and CO_2 is nearly

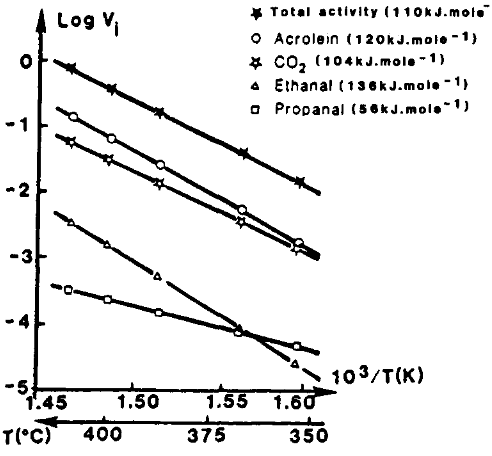

FIG. 6. Arrhenius plots for the different reaction products.

TABLE 2

Specific Surface Area, Intrinsic Activity, and Selectivities in the Propylene Oxidation Reaction at 400°C for the Different Catalysts

Catalyst	Conv. (%)	S ($m^2 g^{-1}$)	V^a ±3%	Selectivity (%) ±3%			
				Acrolein	CO_2	Ethanal	Propanal
536–190	0.80	0.90	0.65	36	42	8	6
570–65	0.84	0.92	0.70	38	44	8	4
590–48	0.80	0.83	0.70	41	41	9	3
620–24	0.72	0.72	0.60	42	38	10	2
650–12	0.80	0.67	0.65	45	33	9	4
660–12	0.76	0.73	0.65	50	31	9	3
670–6	0.72	0.39	0.70	50	29	10	3
680–6	0.30	0.27	0.40	52	24	12	6
Vapor-grown MoO_3	0.06	0.04	0.60	16	57	12	9

[a] $10^7 \times$ mol $m^{-2} s^{-1}$.

independent of the temperature (*13*). The measured activation energies further confirm that the catalysts are working in the kinetic-controlled temperature range. Furthermore, the values given in Fig. 6 for a particular catalyst are well representative of the activation energies measured on all studied samples.

3.2. *Results of the Catalytic Study*

The results relative to the oxidation of propylene at 400°C, after a stabilization during 24 h at the same temperature, are summarized in Table 2. For each MoO_3 catalyst several runs were taken, starting always with a fresh catalyst. The reproducibility of the measurements was quite good.

If we look first at the selectivity values relative to [100]-oriented catalysts, a correlation clearly emerges between first the selectivity in acrolein and the relative area of the (120) faces, and second between the selectivity in CO_2 and the relative area of the (010) faces. For example, the formation of acrolein is maximum on the catalyst prepared at 680°C with an area of 21.6% of the (120) faces, whereas the selectivity in CO_2 is minimum (24%) in line with only 57.5% of the (010) area.

The measurements relative to the vapor-grown MoO_3 catalyst further confirms this correlation insofar as this catalyst displays a high selectivity for complete oxidation in agreement with the large development of the area of the (010) faces (≈90%).

It should also be noted that the selectivity in acrolein or in CO_2 cannot be related to the relative area of the (001) faces (this area remains nearly the same on the series of [100]-oriented catalysts). It can be seen also that there is no clear structure-sensitivity effect for the formation of the minor products (ethanal and propanal) whose selectivity remains nearly the same whatever the catalyst.

The ratio of the selectivities to acrolein and CO_2 is given by the ratio of the sum of the intrinsic activities $\mathbf{A}_{acro}$ and $\mathbf{A}_{CO_2}$, for these two products (*2*, *4*, *12*) relative to the different faces,

$$R = \frac{S_{(acro)}}{S_{(CO_2)}} = \frac{m\mathbf{A}^{(120)}_{acro} + n\mathbf{A}^{(010)}_{acro} + p\mathbf{A}^{(001)}_{acro}}{m\mathbf{A}^{(120)}_{CO_2} + n\mathbf{A}^{(010)}_{CO_2} + p\mathbf{A}^{(001)}_{CO_2}}, \quad (1)$$

where m, n, and p are the relative area (in

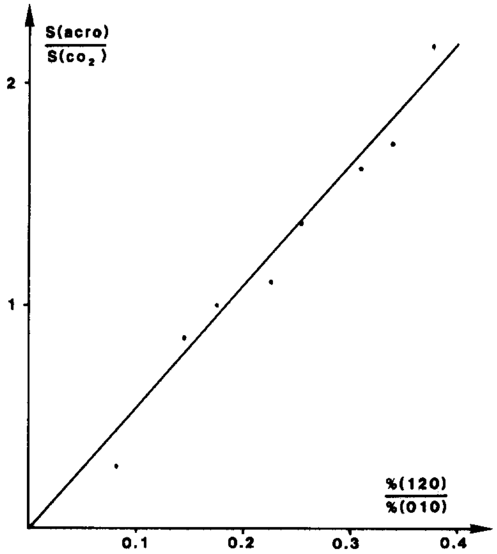

FIG. 7. Ratio of the selectivities for acrolein/CO_2 vs the ratio of the relative surface area of (120) faces/(010) faces.

percent) of the (120), (010), and (001) faces, respectively, as given in Table 1.

If acrolein is formed exclusively on the (120) faces and CO_2 exclusively on the (010) faces, one obtains

$$\frac{S_{(\text{acro})}}{S_{(\text{CO}_2)}} = \frac{m}{n} \times \frac{\mathbf{A}_{\text{acro}}^{(120)}}{\mathbf{A}_{\text{CO}_2}^{(010)}}. \qquad (2)$$

If one plots such a ratio, one should obtain a straight line through the origin. As shown in Fig. 7 the experimental data (Tables 1 and 2) are in agreement with Eq. (2) giving a straight line that nearly intercepts the origin with a slope

$$\text{Slope} = \frac{\mathbf{A}_{\text{acro}}^{(120)}}{\mathbf{A}_{\text{CO}_2}^{(010)}} \approx 5.6.$$

This result means that the MoO_3 (120) faces are 5.6 times more active in the formation of acrolein than the MoO_3 (010) faces in the formation of CO_2. Figure 7 therefore shows that acrolein is produced almost solely on the (120) faces. The straight line depicted in Fig. 7 also implies the same activation energy of formation for acrolein (or CO_2) on the whole series of catalysts, in agreement with the results previously described.

It can be seen in Table 2 that the intrinsic activity remains nearly constant whereas it could be expected that the most selective catalysts for acrolein would be the most active ones by roughly a factor 2, since the percentage of the most active (120) faces increases by about 10 to 20%. However, there is also a large variation in the size of the crystallites (see Table 1) and one could expect some additional contribution of the edge sites, which are more numerous on the samples composed of the smaller crystallites. Nevertheless, the activity of such edge sites is not prevalent inasmuch as their number increases by nearly an order of magnitude from catalyst (680-6) to catalyst (536-190) with only a slight increase in the intrinsic activity.

4. DISCUSSION

The present catalytic study carried out on new [100]-oriented MoO_3 catalysts clearly shows that the propylene oxidation reaction

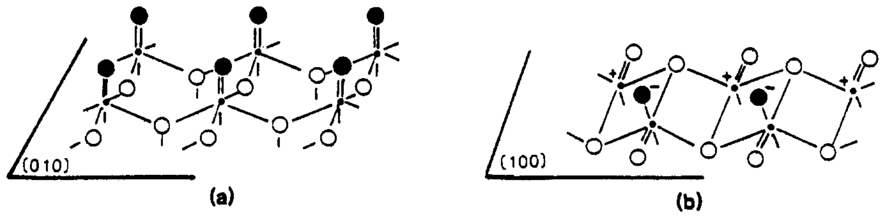

FIG. 8. Structural model of MoO_3 (100) and (010) surface sites (oxygen atoms pointing outward are depicted by solid circles).

is structure-sensitive, the partial oxidation into acrolein occurring almost solely on the (120) faces whereas the basal (010) faces lead to total oxidation as deduced from the linear representation depicted in Fig. 7.

Moreover, the (120) faces appear to be about five times more active than the (010) faces. These conclusions are not at variance with the first proposals of Volta *et al.* (*2–5*) relating the activity for partial oxidation to the MoO_3 (100) faces. As discussed in Part I (*1*), the MoO_3 (100) planes are actually truncated to mainly (120) surface faces, such faces probably being more stable than (100) faces.

The activity of these (120) faces must be related to their peculiar stepped structure (*1*) with the juxtaposition of (100) and (010) sites as shown in Fig. 8. As evidenced in a previous study (*6*), the (120) faces exhibit mild acidic properties as deduced by TPD of basic molecules and isopropanol dehydration to propylene. Such acidic properties have been related to the oxygen vacancies located on the (100) sites. Such sites (coordinatively unsaturated Mo cations) would be active in the initial activation of propylene to allylic surface species.

XPS observations (*6*) have also shown that the partial surface reduction of Mo^{VI} to Mo^{V} occurs more easily on the (010) faces and it may then be assumed that the oxygen involved in acrolein formation comes from the (010) sites. Such a proposal is in agreement with the conclusions of Haber and co-workers (*7, 8*) and with the studies on bismuth molybdate (*14*).

On the basis of this discussion the structural scheme represented in Fig. 9 may be proposed. C_3H_6 would be first adsorbed on the unsaturated Mo cations present on the (100) sites, leading to a π-allyl species. The π-allyl once formed would interact with a terminal oxygen atom belonging to the (010) sites as illustrated in the proposed scheme. However, the nature of the active oxygen in partial oxidation is still debated: it may be terminal or bridging oxygen. Further experiments must be performed to elucidate this alternative and to reinforce the present tentative model.

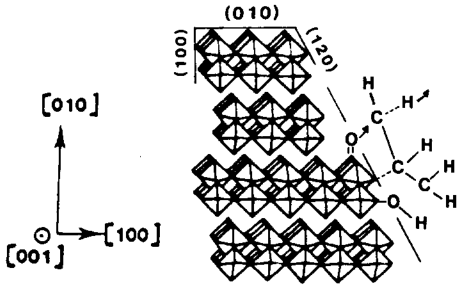

FIG. 9. Schematic structural representation of a propylene molecule reacting on a MoO_3 (120) face (with the cross section line of (010), (100), and (120) faces).

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