JOURNAL OF CATALYSIS 93, 467–470 (1985)

NOTES

Structure Sensitivity of MoO_3 in Mild Oxidation of Propylene

Structure sensitivity in the sense that different crystal faces possess different catalytic properties has become a new concept for oxidation catalysts. We have observed that MoO_3 is a structure-sensitive oxide for the oxidation of propylene (*1–3*) and of alcohols (*4, 5*), and the work has recently been extended to the oxidation of 1-butene and isobutene (*6*). The results have been observed simultaneously on graphite-supported MoO_3 catalysts and on unsupported MoO_3 microcrystals. It has been concluded that the (100) MoO_3 face is specific for allylic oxidation, while the (010) face is specific for complete oxidation. The importance of specificity of these planes depends on the geometry of the olefin, and this has been interpreted by steric considerations (*6*).

Ziółkowski (*7*) has commented on our results in the case of propylene oxidation on graphite-supported MoO_3 catalysts. In this Note we make an improvement in the interpretation of our previous experimental results (*2, 3*) and we reply to the article by Ziółkowski (*7*).

The preparation of the MoO_3/graphite catalysts has already been described (*1–3, 6, 8*). The precursor is a Sri Lanka graphite–$MoCl_5$ intercalation compound. Orthorhombic MoO_3 crystals have been obtained by an oxyhydrolysis calcination of the precursor. The size of the MoO_3 crystals differs depending on the temperature (420–496°C) and the time of heating (6–61 h). Identification of the different crystal faces (Fig. 1) has been made by electron diffraction and scanning electron microscopy (*3*). In this way it has been possible to measure the mean crystal size in different planes (denoted by parentheses) and crystallographic directions (denoted by brackets) by a statistical counting for each sample (Table 1), and to determine the mean area of the external faces of the MoO_3 crystals.

Insofar as the angles between the [101], $[\bar{1}01]$, and [100] directions are known from the MoO_3 structure (Fig. 1), Ziółkowski has calculated the MoO_3 crystal dimensions along [101] + $[\bar{1}01]$, taking into account our experimental values along the [100] direction and vice versa (*7*). These values are given in Tables 2 and 3, respectively.

The difference observed between the calculated values of Ziółkowski (Tables 2 and 3) and our experimental results (Table 1) is not very large. The catalytic oxidation of propylene was studied on our catalysts in initial kinetic conditions at $T = 380°C$ and $C_3H_6/O_2/N_2 = 100/100/560$ Torr. Acrolein and CO_2 were the major products. Since ethanal and propanal were minor products, they are not considered in the further calculations.

Intrinsic activities (A_x) are generally expressed as the activity for formation of

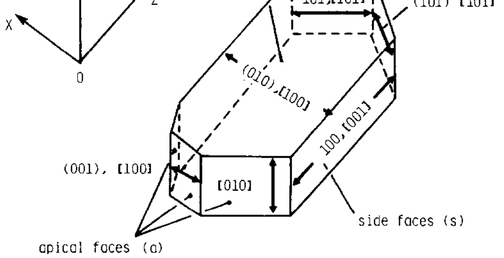

FIG. 1. Identification of the different crystal faces by electron diffraction and scanning electron microscopy.

0021-9517/85 $3.00

TABLE 1

Mean Lengths of MoO_3 Crystals (μm) Measured on the Oriented MoO_3/Graphite Catalysts in Different Planes ( ) and Directions [ ][a]

Sample[b]	[010]	(100) [001]	(001) [100]	(010) [100]	(101) and $(\bar{1}01)$ $[\bar{1}01]$ [101]
420-6	1	18	0	6	8
420-61	4	40	0	13	20
471-6	6	20	0	12	14
496-6	2.5	9	0	6	6
496-61	1.5	5	3	3	0

[a] From Refs. (*1–3*).

[b] The first number refers to the temperature of calcination in °C and the second to the time (in hours) of heating at this temperature.

product X by a specific surface unit. If we assume that the intrinsic activity depends on the crystallographic faces, but is constant on each face, it is possible to determine an intrinsic activity relative to a specific face. For example, A_x^a is relative to the intrinsic activity for the formation of product X on face a (units of mol h^{-1} m^{-2}). For acrolein and carbon dioxide formation, it can be expressed as follows:

$$A_{\mathrm{acro}} = \alpha A_{\mathrm{acro}}^{\mathrm{b}} + \beta A_{\mathrm{acro}}^{\mathrm{s}} + \gamma A_{\mathrm{acro}}^{\mathrm{a}}$$
$$A_{\mathrm{CO_2}} = \alpha A_{\mathrm{CO_2}}^{\mathrm{b}} + \beta A_{\mathrm{CO_2}}^{\mathrm{s}} + \gamma A_{\mathrm{CO_2}}^{\mathrm{a}}$$

α, β, and γ are the relative contributions of the three faces to the total surface ($\alpha + \beta + \gamma = 1$), respectively, for basal (b), side (s), and apical (a) faces. $A_{\mathrm{acro}}^{\mathrm{b,s,a}}$ and $A_{\mathrm{CO_2}}^{\mathrm{b,s,a}}$ are the intrinsic activities for the formation of acrolein (acro) and carbon dioxide (CO_2) on b, s, and a faces.

In practice, it is not possible to measure the intrinsic activities directly because the active MoO_3 area of the MoO_3/graphite samples is not known, but we can express selectivities as

$$S_{\mathrm{acro}} = A_{\mathrm{acro}}/A_{\mathrm{total}} \quad \text{and} \quad S_{\mathrm{CO_2}} = A_{\mathrm{CO_2}}/A_{\mathrm{total}}.$$

The ratio of selectivities is then

$$\frac{S_{\mathrm{acro}}}{S_{\mathrm{CO_2}}} = \frac{A_{\mathrm{acro}}}{A_{\mathrm{CO_2}}}$$

(independent of total activity A_{total})

and

$$\frac{S_{\mathrm{acro}}}{S_{\mathrm{CO_2}}} = \frac{\alpha A_{\mathrm{acro}}^{\mathrm{b}} + \beta A_{\mathrm{acro}}^{\mathrm{s}} + \gamma A_{\mathrm{acro}}^{\mathrm{a}}}{\alpha A_{\mathrm{CO_2}}^{\mathrm{b}} + \beta A_{\mathrm{CO_2}}^{\mathrm{s}} + \gamma A_{\mathrm{CO_2}}^{\mathrm{a}}} = Y \quad (1)$$

If $A_{\mathrm{acro}}^{\mathrm{b}}/A_{\mathrm{CO_2}}^{\mathrm{b}} = X_1$, $A_{\mathrm{acro}}^{\mathrm{s}}/A_{\mathrm{CO_2}}^{\mathrm{b}} = X_2$, $A_{\mathrm{acro}}^{\mathrm{a}}/A_{\mathrm{CO_2}}^{\mathrm{b}} = X_3$, $A_{\mathrm{CO_2}}^{\mathrm{s}}/A_{\mathrm{CO_2}}^{\mathrm{b}} = X_4$, $A_{\mathrm{CO_2}}^{\mathrm{a}}/A_{\mathrm{CO_2}}^{\mathrm{b}} = X_5$, and $\beta/\alpha = r_1$, $\gamma/\alpha = r_2$, Eq. (1) becomes

$$Y = \frac{X_1 + r_1X_2 + r_2X_3}{1 + r_1X_4 + r_2X_5}.$$

The optimization will be obtained by the least-squares method ($\Sigma(Y_{\mathrm{exp}} - Y_{\mathrm{calc}})^2 = \Delta^2$ minimum), simultaneously for X_1, X_2, and X_3 which gives a system of three equations which permits us to calculate X_1, X_2, X_3, and Δ^2 as a function of the experimental parameters and X_4, X_5. A numerical calculation by iteration, made with a HP 9820 A

TABLE 2

Variation of the Mean Length of the MoO_3 Crystals Calculated by Ziółkowski (*7*) from the Measured Values by Volta *et al.*[a]

Sample	[010]	(100) [001]	(001) [100]	(010) [100]	(101)[b] and $(\bar{1}01)$[b] $[\bar{1}01]$[b] [101][b]
420-6	1	18	0	6	8.20
420-61	4	40	0	13	17.77
471-6	6	20	0	12	16.40
496-6	2.5	9	0	6	8.20
496-61	1.5	5	3	3	0

[a] From Refs. (*1–3*).

[b] Calculated from the experimental value of [100] in (010) of Table 1 (Refs. *1–3*).

TABLE 3

Variation of the Mean Length of the MoO_3 Crystals Calculated by Ziółkowski (*7*) from the Measured Values by Volta *et al.*[a]

Sample	[010]	(100) [001]	(001) [100]	(010) [100][b]	(101) and $(\bar{1}01)$ $[\bar{1}01]$ [101]
420-6	1	18	0	5.85	8
420-61	4	40	0	14.63	20
471-6	6	20	0	10.24	14
496-6	2.5	9	0	4.38	0
496-61	1.5	5	3	3	0

[a] From Refs. (*1–3*).

[b] Calculated from the experimental value of $[\bar{1}01]$ in (101) and [101] in $(\bar{1}01)$ of Table 1 (Refs. *1–3*).

TABLE 4

Initial Selectivities and Contribution of the Different Exposed MoO_3 Faces in Catalysis of Propylene Oxidation at $T = 380°C$, $C_3H_6/O_2/N_2 = 100/100/560$ Torr and Conversion <1%

Sample:	420-6	420-61	471-6	496-6	496-61
S_{acro}:	24.4	32.8	42.0	41.6	52.0
S_{CO_2}:	62.9	55.7	44.0	44.2	36.0
% (100)					
Volta *et al.* (Table 1)	10	16	18	18	28
Ziółkowski I (Table 2)	12	19	23	20	28
Ziółkowski II (Table 3)	12	17	26	26	28
% (010)					
Volta *et al.* (Table 1)	85	76	61	64	55
Ziółkowski I (Table 2)	83	72	58	62	55
Ziółkowski II (Table 3)	82	74	55	56	55
% (101) and ($\bar{1}01$)					
Volta *et al.* (Table 1)	5	8	21	18	0
Ziółkowski I (Table 2)	5	9	19	18	0
Ziółkowski II (Table 3)	5	9	18	18	0
% (001)					
Volta *et al.*	0	0	0	0	17

calculator, allows us to determine by X_4 incrementation (X_5 being fixed), the values of X_1, X_2, X_3, and X_4 corresponding to a minimum of Δ^2. This calculation can be iterated after incrementation of X_5, which gives a new minimum for Δ^2, and so on. The final values will be those corresponding to a minimum of the minimum of $\Delta^2 = f(X_4)$ with positive values for the X_i's. A negative value for the parameter X_i indicates a reverse reaction which cannot occur in our kinetic conditions.

This method allows us to optimize simultaneously all X_i parameters. It is then not necessary to postulate a restrictive hypothesis such as Ziółkowski does in order to determine correlations between the nature of faces and intrinsic activities.

The results of our calculation with our experimental values and calculated values of Ziółkowski (*7*) (Table 4) are summarized below:

Our results (*Table 4*). $X_1 = 0.063$, $X_2 = 2.264$, $X_3 = 0.7$, $X_4 = 0$, $X_5 = 0$, which, taking $A^{b}_{CO_2} = 1$ as a reference, gives $A^{b}_{acro} = 0.1$; $A^{s}_{acro} = 2.3$; $A^{a}_{acro} = 0$; $A^{b}_{CO_2} = 1$; $A^{s}_{CO_2} = A^{a}_{CO_2} = 0$. It appears that acrolein is principally formed on the (100) side face. CO_2 is formed exclusively on the (010) basal face. The agreement between experiment and simulation is very good as can be seen in Fig. 2.

Results of Ziółkowski I (*Table 4*). $X_1 = -0.07$; $X_2 = 2.81$; $X_3 = 0.08$; $X_4 = 0$; $X_5 = 0$; which with $A^{b}_{CO_2} = 1$ gives $A^{b}_{acro} = 0$; $A^{s}_{acro} = 2.8$; $A^{a}_{acro} = 0.1$; $A^{b}_{CO_2} = 1$; $A^{s}_{CO_2} = A^{a}_{CO_2} = 0$. These results are very close to ours (see previously), acrolein being formed on the (100) face and CO_2 on the (010) face.

Results of Ziółkowski II (*Table 4*). No significance can be found with these results, because the values of X_i are not simultaneously positive. For example, a correlation is found for $X_1 = -0.3$; $X_2 = 7.9$; $X_3 = -7.9$; $X_4 = -0.2$; $X_5 = 0$.

Ziółkowski's calculation may then be rejected. Restrictive hypothesis:

—(001) and (101) + ($\bar{1}01$) inactive or (100), (001), and (101) + ($\bar{1}01$) faces equivalent are not necessary.

—(100) face inactive or (010) face inactive are in opposition with the experimental results.

In conclusion, if we refer the intrinsic activities of the MoO_3 crystal faces to that of CO_2 being exclusively formed on the basal

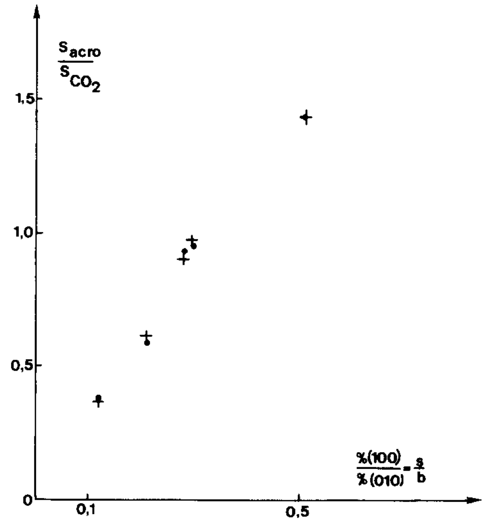

FIG. 2. Formation of acrolein on the (100) side face and CO_2 on the (010) basal face. (●) Experimental, (+) simulation.

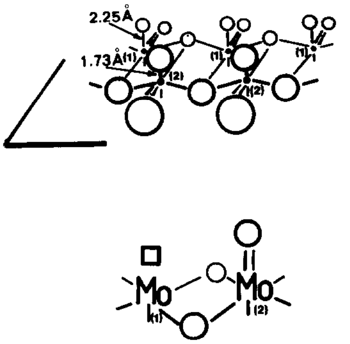

FIG. 3. Structure of the (100) MoO_3 face. Acidic Lewis Mo_1 and dehydrogenating Mo_2 centers shown.

(010) face, it appears from the previous considerations that, in all cases, acrolein is mainly formed on the side (100) face. This result supports our previous conclusions (*1–3*).

The specific activity of the (100) MoO_3 face for allylic oxidation has now been extended to the case of isobutene and 1-butene oxidation (*6*). This can be explained by the peculiar structure of this face (Fig. 3). Indeed under catalytic conditions, two types of molybdenum centers have to be considered on this face:

(i) Acidic Lewis Mo_1 centers: these sites correspond to uncoordinated Mo cations associated with the breaking of the long Mo–O bonds (2.25 Å), a situation which can be postulated under reaction conditions.

(ii) Dehydrogenating Mo_2 centers: these sites are associated with the short Mo–O bond (1.73 Å) with a double-bond character equivalent to that observed in the (010) face (the Mo═O bond length is 1.67 Å in this face).

Allylic oxidation should first proceed by the chemisorption of olefin (basic reagent) on the acidic Mo_1 centers and the further capture of an allylic H atom on the dehydrogenating Mo_2 centers. Models have been constructed which support this view (*6*). Moreover, the bifunctional character of the (100) face has been evidenced in the case of alcohol oxidation (*9*, *10*).

REFERENCES

1. Volta, J. C., and Moraweck, B., *J. Chem. Soc. Chem. Commun.*, 338 (1980).
2. Volta, J. C., Desquesnes, W., Moraweck, B., and Tatibouet, J. M., "Proceedings, 7th International Congress on Catalysis, Tokyo 1980." p. 1398. Kodansha/Elsevier, Tokyo/Amsterdam, 1981.
3. Volta, J. C., Forissier, M., Theobald, F., and Pham, T. P., *Faraday Discuss. Chem. Soc.* **72,** 225 (1981).
4. Tatibouet, J. M., and Germain, J. E., *J. Chem. Res.* (S) **268,** (M) 3070 (1981).
5. Tatibouet, J. M., and Germain, J. E., *J. Catal.* **72,** 375 (1981).
6. Volta, J. C., Tatibouet, J. M., Phichitkul, C., and Germain, J. E., "Proceedings, 8th International Congress on Catalysis, Berlin 1984." Vol. IV, p. 451. Verlag Chemie, Weinheim, 1984.
7. Ziółkowski, J., *J. Catal.* **80,** 263 (1983).
8. Volta, J. C., Desquesnes, W., Moraweck, B., and Coudurier, G., *React. Kinet. Catal. Lett.* **12,** 241 (1979).
9. Tatibouet, J. M., and Germain, J. E., *J. Catal.* **72,** 365 (1981).
10. Tatibouet, J. M., Germain, J. E., and Volta, J. C., *J. Catal.* **82,** 240 (1983).

J. C. VOLTA

Institut de Recherches
sur la Catalyse, CNRS
2 Avenue Albert Einstein
69626 Villeurbanne, France

J. M. TATIBOUET

Laboratoire de Catalyse Organique
LA 231, CNRS
Université Claude Bernard Lyon I
43 Boulevard du 11 Novembre 1918
69622 Villeurbanne, France

Received May 31, 1983