

## Structure-Sensitive Catalytic Oxidation: Alcohols on Graphite-Supported Molybdenum Trioxide

We have shown previously that methanol (1) and ethanol (2) oxidation on crystalline orthorhombic molybdenum trioxide are structure-sensitive catalytic reactions. The results were obtained on "large" MoO<sub>3</sub> crystallites (about 1 mm) prepared by sublimation. In the present work, we extend our conclusions to "small" graphite-supported MoO<sub>3</sub> crystallites (about 10 μm) which have a similar shape (hexagonal plates) (Fig. 1).

The preparation of these catalysts by oxy-hydrolysis of MoCl<sub>5</sub>-graphite intercalation compounds has been fully described elsewhere (3, 5). The α-MoO<sub>3</sub> crystallite size is a function of the temperature (420–496°C in this work) and the time of heating (6 or 61 h in the present case). Scanning electron microscope photographs (4, 5) (Fig. 2) permit a statistical evaluation of the 3 dimensions defined in Fig. 1 (length *L*, width *l*, and thickness *e*) and the percentage extent of the exposed faces:

*b*% for (010) basal

*s*% for (100) side

*a*% for (001) + (101) apical [mostly (101)].

Five samples have been used in the present study and their characteristics are shown in Table 1. The sample designation indicates the preparation conditions: temperature (in °C, first number) and heating time (h, second number).

The main difference between the "small" graphite-supported crystallites and the "large" crystallites previously used (1) is the extent (*a*%) of apical faces (up to 20%, against less than 4% of the total surface).

All catalytic tests were performed in an isothermal continuous flow reactor under steady-state conditions; gas chromatogra-

phy was used for analysis of inlet and outlet streams.

*Methanol reactions.* A standard test mixture: MeOH/O<sub>2</sub>/He 6.8/18.6/74.6 (molar), was fed to the reactor at 291°C and 1.1 atm; initial (low conversion) activities and selectivities were measured. Formaldehyde (F), methylal (M) dimethylether (E), and water were the only products. As shown in Table 2, selectivities change with crystallite shapes.

These results are treated as indicated before (1). If  $A_X^Y$  is the intrinsic activity of face *y* (*y* is *b*, *s*, or *a*) for the product *X* (*X* is F, M, or E), all selectivities may be expressed in terms of the  $A_X^Y$  values. For example,

$$\frac{S_F}{S_M} = \frac{bA_F^b + sA_F^s + aA_F^a}{bA_M^b + sA_M^s + aA_M^a}$$

The experimental results in Table 2 are best fit with the following set of relative values of *A*'s (taking  $A_F^b = 1$ ):

Product	Face activity			(I)
	<i>A</i> <sup>b</sup>	<i>A</i> <sup>s</sup>	<i>A</i> <sup>a</sup>	
F	1	0	1.7	
M	0	0.9	0	
E	0	0	1.1	

These agree fairly well with the values found for large unsupported crystallites of MoO<sub>3</sub>, with two discrepancies:

- The larger value of  $A_F^a$  (1.7): this is readily explained by the fact that in large crystallites the percentage of apical face was small (less than 4%) and their formaldehyde activity was masked by the activity of basal faces (*b*% ≈ 70%).

TABLE 1  
Characteristics of  $\alpha$ -MoO<sub>3</sub> Samples

Sample	$\bar{L}$ ( $\mu\text{m}$ )	$\bar{l}$ ( $\mu\text{m}$ )	$\bar{e}$ ( $\mu\text{m}$ )	b [% (010)]	s [% (100)]	a [% (001) + (101)]
420-6	18	6	1	85	10	5
420-61	40	13	4	76	16	8
471-6	20	12	6	61	18	21
496-6	9	6	2.5	64	18	18
496-61	5	3	1.5	55	28	17

• The smaller value of  $A_E^a$  (1.1 instead of 2.5), which has the same origin (underestimation of a% in large crystallites).

The reaction of methanol in the absence of oxygen was tested with the standard mixture: MeOH/He 7.6/92.4 (molar) at 238°C and 1 atm. The only products then were water, methylal (M), and ether (E); measurements were taken after 1 h on stream. During that period the ratio E/M decreased down to the steady state values reported in Table 3.

A similar treatment of these data leads to the following set of relative values for intrinsic activities  $A$  ( $A_E^a = 1$ ):

Product	Face activity		
	$A^b$	$A^s$	$A^a$
F	0	0	0
M	0	0	1.2
E	0	0.45	1

(II)

From the matrices (I) and (II) the following conclusions can be drawn.

• Formaldehyde is formed on (010) basal faces and on apical faces [(001) + (101)] in the presence of oxygen gas; no formaldehyde is produced in the absence of O<sub>2</sub>.

• Methylal forms on side faces (100) in the presence of oxygen gas, and on apical faces [(001) + (101)] in the absence of oxygen gas.

• Dimethylether forms on apical faces in the presence of oxygen gas, and on apical and side faces in the absence of O<sub>2</sub>.

The formal reaction scheme:

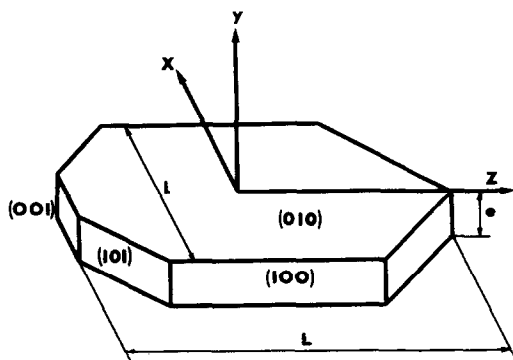
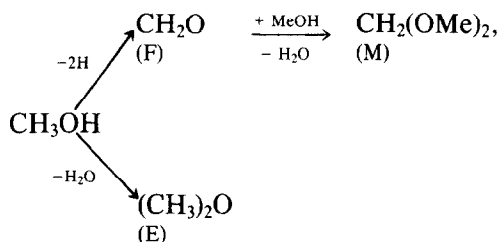


FIG. 1.  $\alpha$ -MoO<sub>3</sub> Crystallite faces and dimensions.

TABLE 2

Methanol Oxidation. Selectivities for Formation of Formaldehyde ( $S_F$ ), Methylal ( $S_M$ ), and Dimethylether ( $S_E$ )

Sample	$S_F$ (%)	$S_M$ (%)	$S_E$ (%)
420-6	77.7	7.5	14.8
420-61	76.7	14.4	8.9
471-6	71.4	12.0	16.6
496-6	77.4	12.4	10.2
496-61	78.1	12.1	9.8

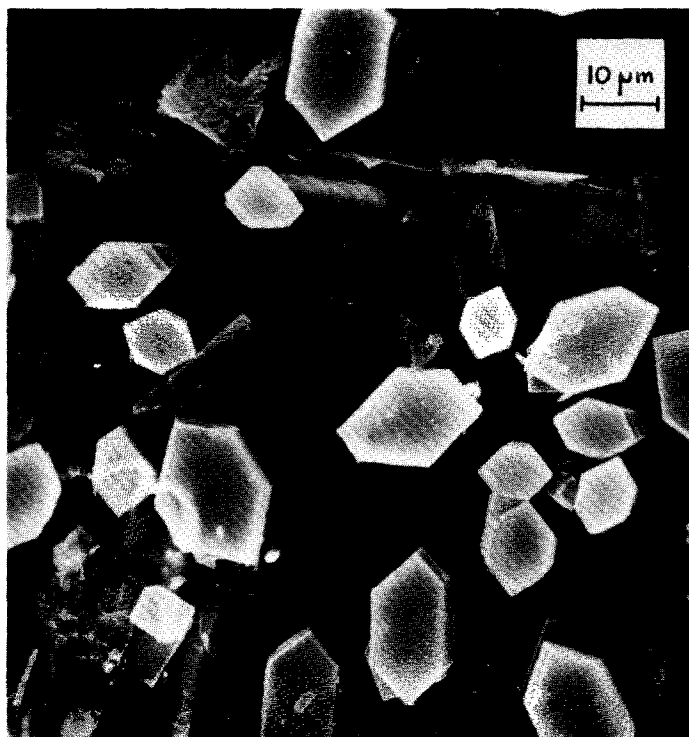


FIG. 2. Scanning electron microscope photograph of catalyst sample 496-6 (Table 1).

where formaldehyde (F) is the product of oxidative dehydrogenation, ether (E) the product of dehydration, and methylal (M) a bifunctional product, leads to the following equivalent conclusions:

- The basal face (010) presents dehydrogenation sites, active only in the presence of  $O_2$  gas.
- The side face (100) is bifunctional in

the presence of  $O_2$ , and presents only dehydration sites in the absence of  $O_2$ .

- The apical faces (001) + (101) are bifunctional with or without  $O_2$ .

*Ethanol reactions.* A standard test mixture: EtOH/ $O_2$ /He 3.6/20/76.4 (molar) was reacted at 291°C and 1 atm. Initial products (low conversion) were acetaldehyde (A), diethyl ether (E), ethylene, and water, with the selectivities shown in Table 4.

In spite of the high values of acetaldehyde selectivity, significant changes of ether selectivity seem to parallel the percentage of apical faces (a). Ethylene selectivity changes were smaller and not clearly correlated with face percentages. This is consistent with our previous observations on unsupported  $\alpha$ - $MoO_3(2)$ : on these crystallites with a very small a% (less than 4%), no diethylether could be detected. Moreover, ether formation was confined to apical faces in the case of methanol (see above).

TABLE 3

Methanol Reaction in Absence of Oxygen. Selectivities for Formation of Methylal ( $S_M$ ), and Dimethylether ( $S_E$ )

Sample	$S_M$ (%)	$S_E$ (%)
420-6	38.2	61.8
420-61	38.6	61.4
471-6	45.9	54.1
496-6	45.6	54.4
496-61	50.5	49.5

TABLE 4

Ethanol Oxidation. Selectivities for Formation of Acetaldehyde ( $S_A$ ), Diethylether ( $S_E$ ), and Ethylene ( $S_{C_2H_4}$ )

Sample	$S_A$ (%)	$S_E$ (%)	$S_{C_2H_4}$ (%)
420-6	96.4	1.6	2.0
420-61	96.1	2.4	1.5
471-6	91.4	5.8	2.8
496-6	92.0	4.6	3.4
496-61	93.0	4.5	2.5

The best relative values of intrinsic activities were found ( $A_A^a = 1$ ) by the usual procedure:

Product	Face activity			(III)
	$A^b$	$A^s$	$A^a$	
A	0.6	1	1	
E	0	0	0.2	

Acetaldehyde is formed on all crystal faces with similar rates: oxidative dehydrogenation in the presence of  $O_2$  gas shows little structure sensitivity. Dehydration is structure sensitive.

In the absence of oxygen, with the test mixture: EtOH/He 3.6/96.4 (molar) at  $215^\circ C$  and 1 atm after 1 h on stream, selectivities stabilized at the values shown in Table 5.

Selectivity changes of aldehyde and ether are larger than in the presence of oxygen (Table 4); ethylene selectivity is still small, and no correlation was attempted for this product. The best fit of experimental data is obtained with the following set of relative intrinsic activities ( $A_A^a = 1$ ):

Product	Face activity			(IV)
	$A^b$	$A^s$	$A^a$	
A	0.12	0	1	
E	0	0.93	0.19	

To summarize, in the presence of oxygen gas, acetaldehyde is formed on all faces

with similar rates, whilst ether is formed on apical faces only. In the absence of  $O_2$ , acetaldehyde formation on basal and side faces strongly decreased, ether formation appearing on side faces. These results agree qualitatively with our previous observations on "large" unsupported  $MoO_3$  crystals (2); the larger ratio  $A_A^a/A_A^b$  (44 instead of 10 here) is due to an underestimation of  $a\%$  in large crystals, as mentioned above. As in the case of methanol, the basal face (010) is monofunctional (dehydrogenation) and much more active in the presence of  $O_2$  gas. The side face (100) dehydrogenates in the presence of  $O_2$ , dehydrates in the absence of  $O_2$ , and the apical faces are bifunctional with or without  $O_2$ . The results as a whole may be understood as follows. We have proposed (2) an interpretation founded on the structural units expected on the different faces from the known structure of  $\alpha$ - $MoO_3$  (6): orthorhombic system, space group  $Pbnm-D_{2h}^{16}$  ( $a = 3.962 \text{ \AA}$ ;  $b = 13.858 \text{ \AA}$ ;  $c = 3.697 \text{ \AA}$ ).

The dehydrogenating active sites may be identified as  $Mo=O$  bonds sticking out of the surface (7), and the dehydrating sites to exposed  $Mo$  cations (Lewis acid). In the presence of oxygen,  $Mo=O$  groups exist on both (010) and (100) faces, but Lewis centers on (100) faces only: this last face is bifunctional (dehydrogenation-dehydration) and catalyzes the formation of methylal, instead of formaldehyde. In the absence of  $O_2$ , the (100) face is reduced and be-

TABLE 5

Ethanol Reaction in Absence of Oxygen. Selectivities for Formation of Acetaldehyde ( $S_A$ ), Diethylether ( $S_E$ ), and Ethylene ( $S_{C_2H_4}$ )

Sample	$S_A$ (%)	$S_E$ (%)	$S_{C_2H_4}$ (%)
420-6	88.6	9.7	1.7
420-61	86.1	11.2	2.6
471-6	84.0	14.0	2.0
496-6	85.2	13.1	1.7
496-61	79.0	19.4	1.6

comes monofunctional (dehydration); the activity of the (010) face (dehydrogenation) is almost totally suppressed. It was shown that this face abstracts hydrogen but cannot oxidize it to water: H accumulates in the bulk of the crystal and forms a bronze  $H_xMoO_3$  (8). Similar interpretations could be applied to apical (001) and (101) faces.

It is clear that the structure-sensitivity of alcohol reactions on  $\alpha$ - $MoO_3$  observed on "large" unsupported crystals (1, 2) is also found on "small" graphite-supported crystals; the slight discrepancies between the two types are due to the underestimation of apical faces in bulk catalysts. The catalytic effect of these faces has been illustrated here.

This structure sensitivity is due to the crystal face catalytic specificity which is correlated with the crystal structure. In the present case the effects are particularly favored by the strong anisotropy of the crystal structure, and by the existence, for the alcohols, of different reaction pathways (dehydrogenation and dehydration) with not too different rates.

Extensions of this type of work to other oxide catalysts and other reactions are in progress.

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