J.C.S. CHEM. COMM., 1980

## Specificity of MoO<sub>3</sub> Crystalline Faces in Propene Oxidation

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Summary Oxidation of propene on oriented and nonoriented catalysts shows a specificity for the reaction of the  $MoO_3$  crystalline faces; catalytic sites for acrolein formation are located in the [020] direction.

At present much industrial research into olefin oxidation is focused on increasing the selectivity of formation of mild oxidation products, with an increasing demand for new processes using very selective catalysts. Consequently, knowledge of the factors which govern selectivity<sup>1</sup> is of importance.

Many studies of catalysis by metals have tried to correlate selectivity with structural parameters;<sup>2</sup> for example, in ethylene hydrogenation the (100) face of nickel crystallites is practically inactive, while the (111) and (110) faces are much more active.<sup>3</sup> In the case of catalysis by oxides, in spite of some encouraging attempts,<sup>4-6</sup> no clear correlation has yet been shown between the orientation of oxide crystallites and their catalytic properties in mild oxidation reactions. We have established such a connection for oriented  $MoO_3$ -graphite catalysts in propene oxidation.<sup>7</sup> We now report results on the specificity of  $MoO_3$  crystalline faces for this reaction.



FIGURE 1. (a) Initial selectivity and (b)  $MoO_3$  crystallite diameter d in the oxidation of propene vs.  $T_{OXH}$ .

Five  $MoO_3$ -graphite supported catalysts have been prepared by oxy-hydrolysis, at different temperatures  $(T_{0XH})$ , of an  $MoCl_5$  intercalation graphite compound as described elsewhere,<sup>7</sup> and their reactivity for propene oxidation at low conversion is compared.<sup>†</sup> Previous work has shown that the  $MoO_3$  catalysts are oriented with (020) MoO<sub>3</sub> planes parallel to (001) graphite planes.<sup>7</sup> The size of the  $MoO_3$  crystallites in the [020] and [110] directions has been measured by analysis of the profile of the corresponding X-ray lines. When  $T_{0XH}$  increases, a slow but regular growth of the MoO<sub>2</sub> crystallites is observed in the [110] direction, together with a more pronounced growth in the [020] direction which has a maximum at 470 °C (Figure 1, b). This is connected with a selectivity maximum for acrolein formation and a corresponding minimum for CO<sub>2</sub> (Figure 1, a). Figure 2 shows a plot of the Brunauer-Emmett-Teller (B.E.T.) area of the catalysts against  $T_{OXH}$  (curve a), which is compared with the MoO<sub>3</sub> area calculated from the  $MoO_3$  concentration<sup> $\ddagger$ </sup> and the size of the  $MoO_3$  crystallites (curve b). The difference between



FIGURE 2. (a) B.E.T. surface area and (b)  ${\rm MoO}_3$  area calculated from  ${\rm MoO}_3$  concentration.

the two curves corresponds to the area of the graphite support. An increase in this area is observed simultaneously with the growth of the  $MoO_3$  crystallites in the [020] direction. A model showing the evolution of the catalysts which is consistent with the X-ray crystallographic study and scanning electron microscopy observations on the one hand, and the catalytic study on the other, is proposed in Figure 3, a. The structure of the  $MoO_3$  crystallites and their orientation relatively to the graphite structure is represented in Figure 3, b. It appears, by consideration of Figure 1, that acrolein sites are located in the [020] direction at the end of the parallel  $\{MoO_6\}$  octahedra chains which form the framework of the laminar structure of  $MoO_3$ . These sites have no specificity for ethanal and propanal production.

The specificity for the reaction of  $MoO_3$  crystallite faces was confirmed by comparison of the catalytic results obtained in the oxidation of propene on two catalysts which

<sup>†</sup> Experimental conditions (ref. 7): T 375 °C; P(O<sub>2</sub>) 100 Torr; P(C<sub>3</sub>H<sub>6</sub>) 100 Torr; P(N<sub>2</sub>) 560 Torr; conversion < 1%

 $<sup>\</sup>ddagger$  The MoO<sub>3</sub> concentration was obtained from the i.r. spectra of the solids (ref. 7).



FIGURE 3. (a) Change in catalyst with increase in  $T_{OXH}$  and (b) arrangement of MOO<sub>3</sub> crystallites relative to graphite.

T	ABLE			
	Initial propend Acrolein	Initial selectivity for propene oxidation (%) Acrolein CO <sub>2</sub> Ethanal		
(020) $MoO_3$ crystallites Non-oriented $MoO_3$ crystallites	$\frac{4}{10}$	94 86	1 4	

were composed of (020) oriented and non-oriented MoO<sub>3</sub> crystallites.§ (020) MoO<sub>3</sub> crystallites are less selective for acrolein than the corresponding non-oriented ones (Table) which have more acrolein sites in the [020] direction.

(Received, 21st December 1979; Com. 1321.)

§ (020) MoO3 crystallites were prepared by L.E.T.I., C.E.N.G.,, Grenoble, France. The particle size of the two solids was 63-100  $\mu$ m. Catalytic conditions were the same as in ref. 7.

<sup>1</sup>G. C. A. Schuit, *Chim. Ind.* (*Milan*), 1969, **51**, 1037. <sup>2</sup>G. Dalmai-Imelik, C. Leclercq, J. Massardier, A. Maubert-Franco, and A. Zalhout, Proc. 2nd Int. Conf. on Solid Surfaces, Kyoto, 1974.

<sup>1</sup> G. Dalmai-Imelik and J. Massardier, Proc. VIth Int. Cong. on Catalysis, The Chemical Society, London, 1976.
<sup>3</sup> G. Dalmai-Imelik and J. Massardier, Proc. VIth Int. Cong. on Catalysis, The Chemical Society, London, 1976.
<sup>4</sup> J. Haber and B. Grzybowska, J. Catal., 1973, 28, 489.
<sup>5</sup> M. Ai and S. Suzuki, Bull. Chem. Soc. Jpn., 1974, 47, 3074.
<sup>6</sup> E. Bordes and P. Courtine, J. Catal., 1973, 57, 236.
<sup>7</sup> J. C. Volta, W. Desquesnes, B. Moraweck, and G. Coudurier, Kinet. Catal. Lett., 1979, 12, 241.