Specificity of MoO_3 Crystalline Faces in Propene Oxidation

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Summary Oxidation of propene on oriented and non-oriented 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[1] is of importance.

Many studies of catalysis by metals have tried to correlate selectivity with structural parameters;[2] for example, in ethylene hydrogenation the (100) face of nickel crystallites is practically inactive, while the (111) and (110) faces are much more active.[3] In the case of catalysis by oxides, in spite of some encouraging attempts,[4–6] 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.[7] We now report results on the specificity of MoO_3 crystalline faces for this reaction.

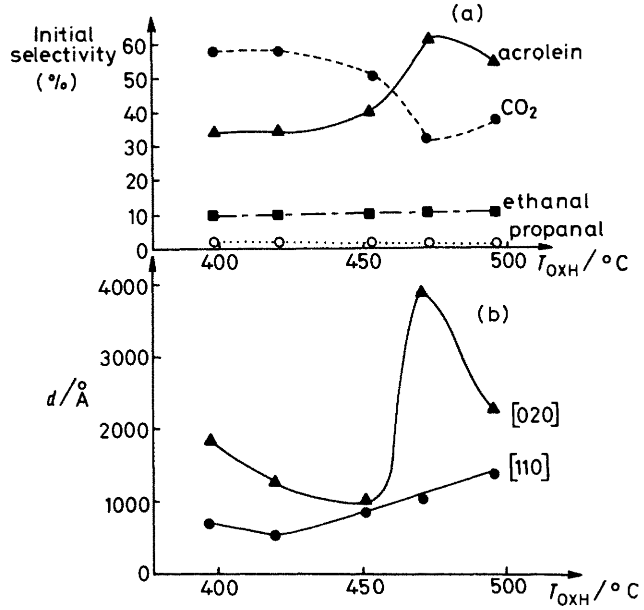

Figure 1. (a) Initial selectivity and (b) MoO_3 crystallite diameter *d* in the oxidation of propene *vs.* T_{OXH}.

Five MoO_3-graphite supported catalysts have been prepared by oxy-hydrolysis, at different temperatures (T_{OXH}), of an $MoCl_5$ intercalation graphite compound as described elsewhere,[7] and their reactivity for propene oxidation at low conversion is compared.† Previous work has shown that the MoO_3 catalysts are oriented with (020) MoO_3 planes parallel to (001) graphite planes.[7] 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_{OXH} increases, a slow but regular growth of the MoO_3 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_2 (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_3 area calculated from the MoO_3 concentration‡ and the size of the MoO_3 crystallites (curve b). The difference between 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.

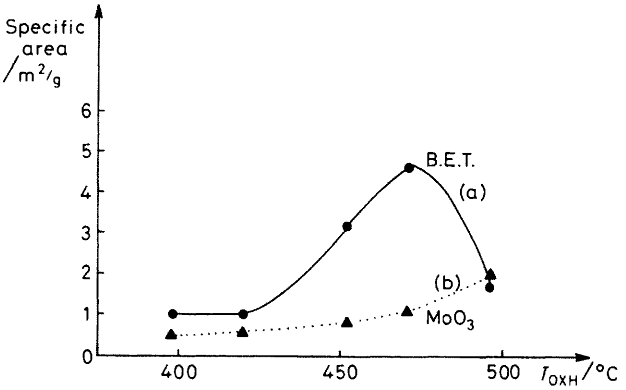

Figure 2. (a) B.E.T. surface area and (b) MoO_3 area calculated from MoO_3 concentration.

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

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† Experimental conditions (ref. 7): *T* 375 °C; $P(O_2)$ 100 Torr; $P(C_3H_6)$ 100 Torr; $P(N_2)$ 560 Torr; conversion < 1%.

‡ The MoO_3 concentration was obtained from the i.r. spectra of the solids (ref. 7).

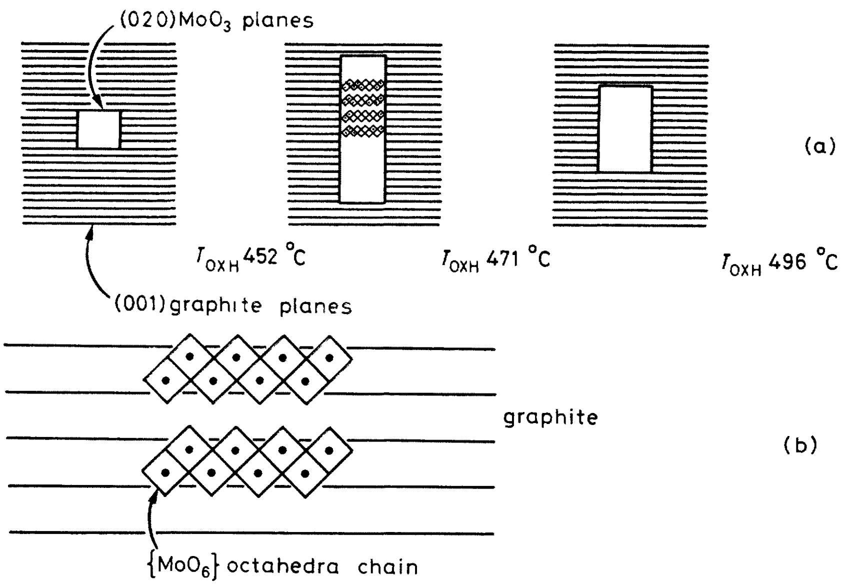

FIGURE 3. (a) Change in catalyst with increase in T_{OXH} and (b) arrangement of MoO$_3$ crystallites relative to graphite.

TABLE

	Initial selectivity for propene oxidation (%)		
	Acrolein	CO$_2$	Ethanal
(020) MoO$_3$ crystallites	4	94	1
Non-oriented MoO$_3$ crystallites	10	86	4

were composed of (020) oriented and non-oriented MoO$_3$ crystallites.§ (020) MoO$_3$ crystallites are less selective for acrolein than the corresponding non-oriented ones (Table) which have more acrolein sites in the [020] direction.

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§ (020) MoO$_3$ crystallites were prepared by L.E.T.I., C.E.N.G.,, Grenoble, France. The particle size of the two solids was 63—100 μm. Catalytic conditions were the same as in ref. 7.

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