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On the Reaction Specificity of MoO_3 Faces: the Role of $Mo_{18}O_{52}$ as a Precursor for MoO_3 Propylene Oxidation Catalysts

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Electron microscopy shows that crystals of $Mo_{18}O_{52}$ are oxidised under activation or catalytic conditions to MoO_3 crystallites with highly developed (100) and (101) or $(10\bar{1})$ faces with a subsequent improvement in the selectivity of propylene oxidation to acrolein.

The different faces of a crystal can exhibit different catalytic properties and this has been demonstrated in the case of MoO_3 for partial oxidation of propylene,[1—4] but-1-ene, and but-2-ene.[5] Studies on graphite-supported MoO_3 catalysts and on unsupported MoO_3 microcrystals have shown that the (100) MoO_3 face is specific for allylic oxidation, and this has been explained by the unusual structure of this face. It has been proposed that the crystallographic fit observed between the support (graphite) and the active phase (MoO_3) is responsible for the unusual development of the (100) MoO_3 crystal face in comparison with naturally grown MoO_3 crystals.[6] This has been extended to other catalytic oxide systems for which reaction specificity has been observed.[6]

This communication reports that $Mo_{18}O_{52}$, which exhibits a sub-structure of the MoO_3 type, can generate, as a nucleation matrix during activation with a propylene–air mixture, MoO_3 crystallites with highly developed (100), (101), or $(10\bar{1})$ faces, coupled with a subsequent improvement in the selectivity of propylene oxidation to acrolein.

$Mo_{18}O_{52}$ exhibits a structure which can be regarded as MoO_3 layers cut into strips.[7] Figure 1 shows the arrangement of the MoO_6 octahedra along the (010) MoO_3 cross-section and the configuration of the (100) $Mo_{18}O_{52}$ surface. It can be described as a stair structure with (010) MoO_3 terraces built of six MoO_6 octahedra in the [100] MoO_3 direction and eighteen MoO_6 octahedra in the [001] MoO_3 direction. The [010] $Mo_{18}O_{52}$ ledge consists of (100) MoO_3 kinks (three MoO_6 octahedra) and (001) MoO_3 kinks (one MoO_6 octahedron) so that the [010] $Mo_{18}O_{52}$ direction is parallel to the [103] of MoO_3. This structure has molybdenum corner atoms with low co-ordination [intersection of the (010) MoO_3 terraces with the (001) and (100) MoO_3 kinks].

$Mo_{18}O_{52}$ crystals were prepared in a sealed quartz tube from powdered MoO_3 and Mo metal heated at 700 °C in the presence of I_2.[8] Preparation conditions were chosen to favour the synthesis of $Mo_{18}O_{52}$ only, free of any other molybdenum oxides such as MoO_3, Mo_9O_{26}, Mo_8O_{23}, Mo_4O_{11}, and MoO_2. The structure of the solid was then determined by *X*-ray diffraction and electron microscopy [transmission and scan-

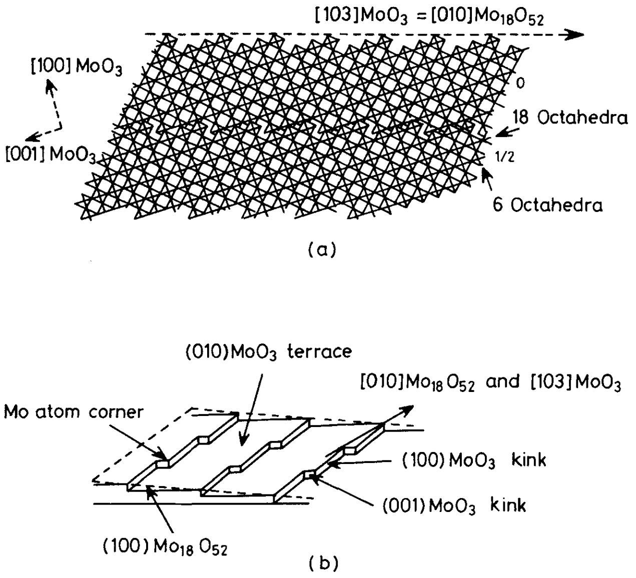

Figure 1. (a) Structure of $Mo_{18}O_{52}$ along the (010) cross-section of MoO_3. (b) Configuration of the (100) $Mo_{18}O_{52}$ surface.

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Table 1. Catalytic activity of MoO_3 and $Mo_{18}O_{52}$ samples in propylene oxidation (T = 375 °C, O_2–C_3H_6–N_2 = 150–100–510 Torr; flow rate 1 cm^3 s^{-1}).

Solid	Conversion of C_3H_6/% g^{-1}	Selectivities			
		CO_2	Acrolein	Ethanal	Propanal
$Mo_{18}O_{52}$[a]	1.640	38	42	13	7
MoO_3[b]	0.015	55	37	5	3
Activated $Mo_{18}O_{52}$[c]	0.423	12.5	73	12.5	2

[a] Surface area = 2.4 m^2 g^{-1}. [b] Surface area = 0.03 m^2 g^{-1}. [c] Activated under O_2–C_3H_6–N_2 (150–100–510 Torr) mixture for 20 min at 475 °C; flow rate 0.07 cm^3 s^{-1}.

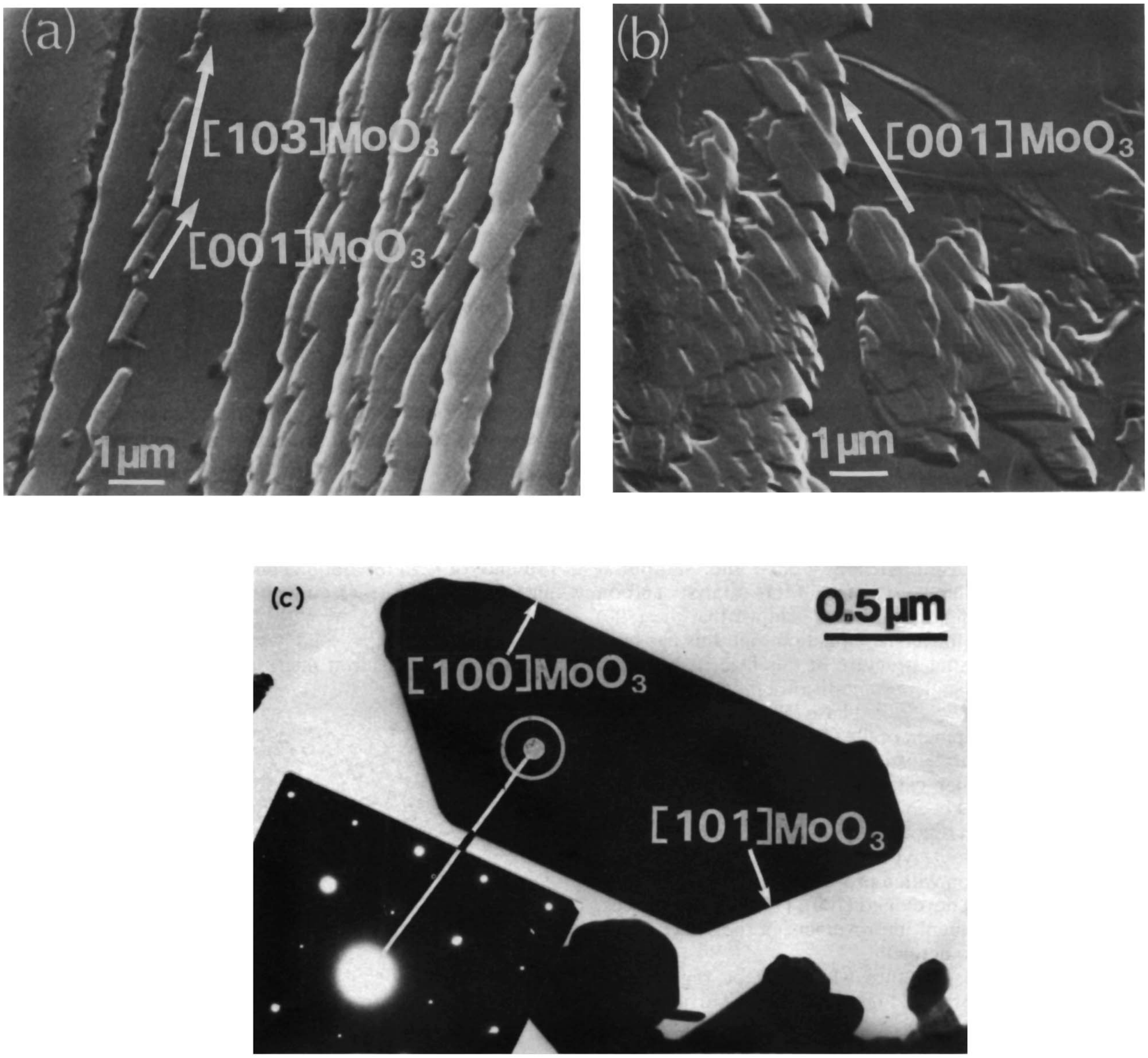

Figure 2. Electron microscopy of the solids. Surface of $Mo_{18}O_{52}$ (a) after 16 h catalysis at 375 °C and (b) after 63 h catalysis at 375 °C. (c). MoO_3 crystallite observed after activation of $Mo_{18}O_{52}$ at 475 °C.

ning electron microscopy (t.e.m. and s.e.m.) and reflection high energy electron diffraction (r.h.e.e.d.)] before and after activation under an air–propylene mixture at 475 °C for 20 min (composition O_2–C_3H_6–N_2 = 150–100–510 Torr) with a rapid attainment of temperature and also after catalytic propylene oxidation, using both activated and untreated $Mo_{18}O_{52}$ as catalysts, at 375 °C using the same gaseous mixture for different periods of time. The bulk reoxidation of $Mo_{18}O_{52}$ to MoO_3 was estimated by i.r. spectroscopy after these different treatments.

It was observed by r.h.e.e.d. and s.e.m. [Figure 2(a,b)] that the $Mo_{18}O_{52}$ crystals used in the catalytic reaction for,

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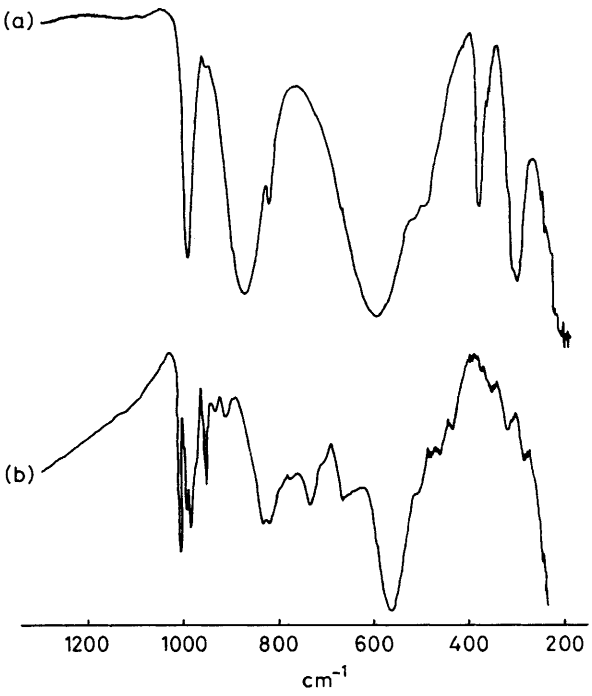

Figure 3. I.r. spectra of the solids. (a) MoO_3; (b) $Mo_{18}O_{52}$. $Mo_{18}O_{52}$ activated at 475 °C has the same spectrum as MoO_3.

respectively, 16 and 63 h at 375 °C were only oxidized on the surface.

As shown schematically in Figure 1(b), the oxidation of the $Mo_{18}O_{52}$ crystal proceeded in steps in the [010] $Mo_{18}O_{52}$ direction {[103] MoO_3 direction} by growth of MoO_3 crystals in the [001] MoO_3 direction with subsequent development of the side (100) and (101) or $(10\bar{1})$ MoO_3 faces. Comparison of Figure 2(a) and (b) shows that the side faces developed with time. No change in the initial i.r. spectrum of $Mo_{18}O_{52}$ was observed after oxidation treatment [Figure (3b)]. Catalytic activity was too low to measure. Crystals of $Mo_{18}O_{52}$ were ground in order to increase the catalytically active area of the grains. The grinding was controlled so that it did not change the structure of the $Mo_{18}O_{52}$ crystals but reduced the $Mo_{18}O_{52}$ grain size. Ground $Mo_{18}O_{52}$ crystals were then activated at 475 °C for 20 min with a rapid rate of temperature increase (16° min^{-1}) in order to accelerate the oxidation process previously observed at 375 °C. The i.r. spectra of this $Mo_{18}O_{52}$ sample now resembled that of MoO_3 [Figure 3(a)] which suggested that $Mo_{18}O_{52}$ had been almost completely oxidized to MoO_3. This was confirmed by *X*-ray analysis. The catalytic activity of the activated $Mo_{18}O_{52}$ sample was compared with that of unactivated $Mo_{18}O_{52}$ and MoO_3 samples at 375 °C, Table 1. A large decrease in propylene conversion was observed after activation, with a simultaneous enhancement in acrolein selectivity. The almost complete reoxidation of $Mo_{18}O_{52}$ to MoO_3 was confirmed by electron microscopy of the activated sample. Examination by s.e.m. and t.e.m. showed the presence of small MoO_3 crystallites of uniform shape (l = 1—2 μm; w = 0.5—1 μm; t *ca.* 0.1—0.2 μm) and the r.h.e.e.d. examination identified the basal (010), side (100), and apical (101) or $(10\bar{1})$ MoO_3 faces [Figure 2(c)]. The shape of the grown MoO_3 crystallites with a strong development of the side crystal faces, especially the (100) face, is thought to be responsible for the improvement in acrolein selectivity after activation. The decrease in propylene conversion is thought to be associated with the fact that there are fewer molybdenum corner atoms with low co-ordination present in comparison with the $Mo_{18}O_{52}$ structure. Further studies are required in order to follow the changes in catalytic behaviour as a function of activation and reaction time. This work demonstrates the common structural features between the $Mo_{18}O_{52}$ nucleation matrix and the MoO_3 active phase which allows growth of MoO_3 crystallites with unusual crystal face development.

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