Influence of Surface Structure on the Interaction of Allyl Iodide with MoO_3 Catalysts

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Interaction of allyl iodide with MoO_3 catalysts presenting different crystal habits shows that acrylaldehyde formation is correlated with the presence of the (100) MoO_3 face; consequences of this result on the mechanism of propene oxidation are discussed.

Molybdenum is a component of the well known bismuth–molybdenum oxide catalyst for mild oxidation of propene to acrylaldehyde.[1] It is now postulated that molybdenum sites are responsible for oxygen insertion in the hydrocarbon species.[2,3] Therefore several studies have been devoted to the role of the single MoO_3 phase in this mechanism.

As depicted in Figure 1, platelet-like MoO_3 crystallites usually mainly expose the basal (010) face which is the natural cleavage plane of this layered compound. Volta *et al.* have shown in previous studies[4,5] that the crystal habit of MoO_3 samples depends on their preparation and they concluded that propene oxidation on MoO_3 is a structure-sensitive reaction: selectivity for acrylaldehyde has been correlated with the development of the (100) face.

The propene oxidation mechanism includes several steps:[3,6]

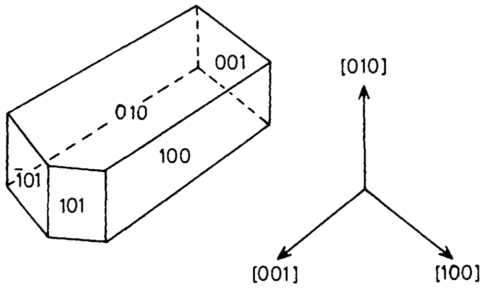

Figure 1. Crystal habit of MoO_3.

Table 1. Interaction of allyl iodide with various MoO_3 catalysts. Comparison with selectivity for propene mild oxidation.

	Sample					
	(a) [mainly (010) oriented]	(b) [developed (100), (101), and $(10\bar{1})$ faces]	(c) [85% (010), 10% (100)]	(d) [61% (010), 18% (100)]	(e) [mainly (010) oriented]	(f) [mainly (100) oriented]
Products[a]						
Acrylaldehyde	–	+	–	+	–	+
CO_2	–	–	+	+	–	+
Activity[b]/10^{-10} mol g^{-1}						
Acrylaldehyde	96	450	206	341	22	54
CO_2	107	104	88	65	15	17
% Selectivity[c]						
Acrylaldehyde	32	73	32	61	34	53
Ethanal	23	13	18	12	6	22
CO_2	35	13	48	35	53	25

[a] Interaction of allyl iodide at 300 °C (+ : detected; – : not detected) in static conditions. [b] Oxidation of allyl iodide in dynamic conditions at 300 °C, $O_2:C_3H_5I:N_2$ = 76:1:680 Torr. (The activity is expressed per gram of catalyst.) [c] Oxidation of propene at 380 °C, $O_2:C_3H_6:N_2$ = 100:100:560 Torr.

(i) the initial rate-limiting step, which is well recognized, involves the activation of propene molecules with abstraction of a hydrogen atom yielding a π-allyl intermediate on a cationic site acting as a Lewis acid; (ii) the subsequent steps including oxygen insertion are still under discussion. Haber and Serwicka[7] recently claimed that the selective insertion of oxygen occurs on the (010) basal plane whereas propene should be activated on side crystal planes [*i.e.* (100) and other planes perpendicular to the basal (010) face]. In order to make the first step easier, the generation of allyl intermediates on the catalyst surface by using allyl iodide[8] and other allyl compounds has been proposed.[1,7,9] Allyl compounds may therefore be used to investigate the relative importance of the oxygen insertion step in the overall structure-sensitive mechanism of mild oxidation of propene.

Six MoO_3 catalysts presenting different crystal habits and different catalytic behaviour for propylene oxidation have been compared with respect to their interaction with allyl iodide: (a) Merck MoO_3 powder with crystallites exposing mainly the (010) face; (b) MoO_3 powder prepared by oxidation of the $Mo_{18}O_{52}$ suboxide with crystallites presenting highly developed (100), (101), or $(10\bar{1})$ faces;[10] (c) and (d) MoO_3 crystallites supported on graphite with different surface faces repartitioned as previously measured[4,11] and quoted in Table 1; (e) macroscopic (010) oriented vapour-grown single-crystals with less than 10% of side planes;[12] (f) macroscopic (100) oriented polycrystalline MoO_3 prepared by molybdenum oxidation.[13] The structure characterization of the samples (a)—(d) has already been largely described.

Catalysts (mass 20 mg) were submitted to an initial oxygen treatment at 400 °C in the reactor for standardisation. After outgassing at 250 °C (10^{-8} mbar; 1 bar = 10^5 Pa), 1 µl of allyl iodide was introduced on the catalyst according to reference 8 and products formed at different temperatures by interaction of the reagent with the MoO_3 catalysts were analysed by mass spectrometry. In order to limit the formation of propene, hexa-1,5-diene, and benzene which have been related[8] to the homogeneous decomposition of allyl iodide, experiments were started at a fairly low temperature (260 °C) with a reactor volume as small as possible. The lack of reaction has been confirmed in blank experiments carried out without catalyst or in the presence of the support alone (graphite). A second series of experiments was performed by direct oxidation of allyl iodide in dynamic conditions on the same catalysts (mass 250 mg) at 300 °C with the composition $O_2:C_3H_5I:N_2$ = 76:1:680 Torr. The activity for the transformation of allyl iodide to acrylaldehyde and CO_2 is reported per gram of catalyst in Table 1. The selectivity for acrylaldehyde formation in propene oxidation is also given for comparison.

It appears that acrylaldehyde formation by interaction of allyl iodide with MoO_3 is limited to catalysts with a greater proportion of the (100) face [catalysts (b), (d), and (f)]. On the (010) oriented MoO_3 catalysts [(a) and (e)], acrylaldehyde is not detected, even at higher reaction temperatures, while CO_2 is only detected on the most active catalysts, (c), (d), and (f).

The experiments of allyl iodide oxidation in dynamic conditions confirm the difference observed for the direct oxidation of allyl iodide to acrylaldehyde and CO_2 depending on the proportion of the (100) and (010) MoO_3 faces. It is noteworthy that there is a linear correlation between the ratio acrylaldehyde : CO_2 produced *vs.* the ratio %(100) : %(010) face for catalysts (c) and (d), as observed for mild propene oxidation on these catalysts.[5] Table 1 shows also that catalysts presenting a high selectivity for acrylaldehyde formation in propene oxidation and simultaneously a high development of the side (100) MoO_3 face are the same as those which give acrylaldehyde by interaction with allyl iodide.

However, to what extent is the structure and the surface chemistry of the catalysts modified by the interaction with allyl iodide? We tried to answer this question by i.r. and *X*-ray photoelectron spectroscopy (x.p.s.) of the highly active catalyst (b) and found that there is no alteration of the i.r. spectrum of the catalyst after oxidation with propene or allyl iodide. No iodine was detected by x.p.s. Moreover, the x.p.s. study of the two solids showed two similar spectra with well resolved Mo 3d doublets (the binding energy is typical of the Mo^{6+} state) without any shoulder on the low binding energy side, characteristics of an eventual reduction of MoO_3.

In previous studies, it has been shown that the reaction of mild oxidation of propene to acrylaldehyde occurs specifically on the (100) MoO_3 face. It was therefore inferred that the initial rate determining step of hydrogen abstraction leading to allyl intermediates is structure sensitive. Insofar as allyl iodide allows the reaction to really by-pass the initial rate-determining step and then to generate π-allyl intermediates whatever the crystal face, the present study shows that allyl intermediates are readily transformed into acrylaldehyde on MoO_3 catalysts exposing mainly the (100) face and that the oxygen insertion step preferentially occurs on this (100) face.

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