Mechanism of the Silver-catalysed Heterogeneous Epoxidation of Ethylene

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Chemisorbed atomic oxygen is the crucial surface species which selectively oxidises ethylene to ethylene oxide; adsorbed dioxygen plays no direct role in this reaction.

Silver is a uniquely effective catalyst for the heterogeneous selective oxidation of ethylene to ethylene oxide, and this reaction has been the subject of many mechanistic studies. Sachtler et al.[1] obtained evidence from i.r. spectroscopy and

site-blocking experiments with chlorine which suggested that adsorbed *dioxygen* [O_2(a)] is the surface species responsible for epoxidation; CO_2 + H_2O formation was ascribed to chemisorbed *atomic* oxygen [O(a)]. This view has received support from e.s.r. studies,[2] and indeed it has guided much of the thinking in this field. However, some authors have argued in favour of adsorbed *atomic* oxygen being the catalytically active species which generates both ethylene oxide and (CO_2 + H_2O): the question is still the subject of active debate. Thus, Force and Bell[3,4] argue in favour of the latter view as do Backx *et al.*;[5] Cant and Hall[6] used the deuterium kinetic isotope effect to arrive at yet a third mechanism: it was proposed that O_2(a) is the common precursor for both ethylene oxide and (CO_2 + H_2O). This is also the conclusion favoured by Akimoto and co-workers.[7]

Here we report the first observation of ethylene oxide production from C_2H_4 + O_2 by a single crystal Ag(111) surface under highly controlled conditions. It is also demonstrated that the stable dioxygen species (already shown to be characteristic of clean Ag[8]) plays no direct role in the epoxidation reaction. Experiments were carried out in an ultra-high-vacuum chamber linked to a high pressure reactor cell; the former contained facilities for surface characterisation. This arrangement permitted rapid cycling between *in situ* surface analysis and reactant gas dosing at much higher pressures. In a typical experiment an atomically clean, well-ordered surface was generated (Ar^+ bombardment, annealing at 700 K, low energy electron diffraction–Auger analysis) and then saturated with oxygen at 300 K (300 Pa for 60 s). A controlled dose of ethylene was then applied (30 Pa for 10—500 s) followed by temperature programmed reaction (t.p.r.) spectroscopy (8 K s^{-1}) using a computer controlled mass spectrometer. Up to 8 ion signals could be followed simultaneously; this permitted unambiguous identification of product species and greatly increased the reliability of the reaction data.
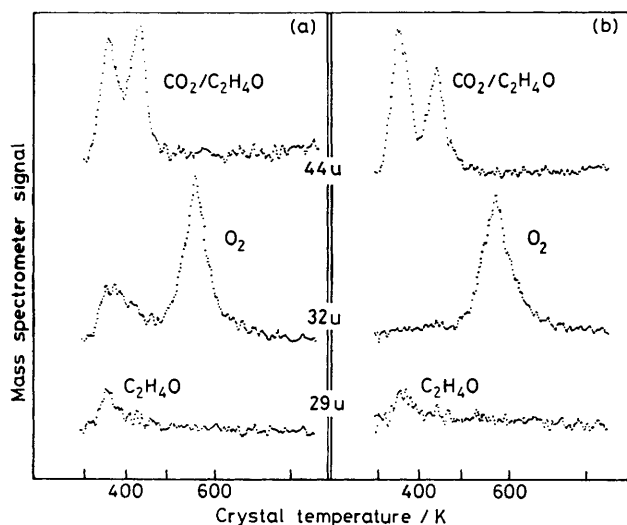
In the absence of dissolved oxygen it was found that the only observable reaction was complete combustion → CO_2 + H_2O; the chemisorbed species [O_2(a)] was unreactive towards ethylene under these conditions. However, when the specimen surface was pre-conditioned by heating at *ca.* 425 K for *ca.* 1 h in a 6:1 mixture of oxygen and ethylene, it became active for selective oxidation. Auger spectroscopy revealed that this procedure led to the accumulation of a substantial amount of dissolved or subsurface oxygen in the selvedge region. (No detectable build up of carbon occurred; it is thought that the role of ethylene is to prevent excessive oxidation of the Ag surface.) For low ethylene doses (10^3 Pa s) the t.p.r. spectra displayed two new sets of features. A weak set at 360 K gave signals at 44, 43, 42, 29, and 15 u. These correspond to the desorption of a mixture of 35 ± 12% ethylene oxide with acetaldehyde (the latter is due to surface-catalysed isomerisation of the former[9]); they account for about 10% of the carbon containing products. The activation energy to desorption is 90 kJ mol^{-1}. A very strong feature at 450 K dominated the 44 and 28 u spectra and is due to CO_2; much weaker signals were also observed for fragment ions characteristic of MeCHO, $MeCO_2H$, and (CO_2H)$_2$. It seems likely that these are intermediates in the further oxidation of ethylene oxide to CO_2 + H_2O.[9]

Figure 1(a) shows typical results for the production of CO_2 and (ethylene oxide + MeCHO) monitored at 44 and 29 u. Also shown is the 32 u spectrum due to desorption of unreacted oxygen. The low temperature peak is due[8] to O_2(a) and the high temperature peak is due to O(a). If the surface was prepared in an identical fashion, but the dioxygen species removed by desorption at 450 K prior to C_2H_4 dosing, the result shown in Figure 1(b) was obtained. It can be seen that the yield of ethylene oxide is unaffected by the absence of chemisorbed dioxygen.

We conclude that chemisorbed atomic oxygen and the presence of subsurface oxygen are necessary and sufficient conditions for the catalytic epoxidation of C_2H_4 by Ag. Chemisorbed dioxygen, though present at the surface at reaction temperature, does not appear to play a direct role in the reaction mechanism.

Figure 1. (a) T.p.r. spectra from Ag(111) (surface preparation described in the text) dosed with oxygen and ethylene at 300 K. (b) As (a) but with the dioxygen species removed by desorption at 450 K prior to C_2H_4 dosing. The 29 u signal is the CHO^+ fragment from ethylene oxide + MeCHO.

References

1 P. A. Kilty and W. M. H. Sachtler, *Catal. Rev. Sci. Eng.*, 1974, **10**, 1.
2 S. Tanaka and T. Tamashina, *J. Catal.*, 1975, **40**, 140.
3 E. L. Force and A. T. Bell, *J. Catal.*, 1975, **38**, 440.
4 E. L. Force and A. T. Bell, *J. Catal.*, 1975, **40**, 356.
5 C. Backx, J. Moolhuysen, P. Greenen, and R. A. van Santen, *J. Catal.*, 1981, **72**, 364.
6 N. W. Cant and W. K. Hall, *J. Catal.*, 1978, **52**, 81.
7 M. Akimoto, K. Ichikawa, and E. Echigoya, *J. Catal.*, 1982, **76**, 333.
8 R. B. Grant and R. M. Lambert, *J. Chem. Soc., Chem. Commun.*, 1983, 58.
9 R. B. Grant and R. M. Lambert, manuscript in preparation.