

A Stable Dioxygen Species on Silver Single Crystals and Model Silver Catalysts

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Substantial amounts of a dioxygen species which is stable at room temperature can be generated at clean silver surfaces; the concentration of this species is relatively insensitive to surface structure, but it can be enhanced by the presence of subsurface oxygen.

Silver is a unique catalyst for the heterogeneous selective oxidation of ethylene to ethylene oxide, and the technological importance of this reaction has prompted much basic research. On the basis of i.r. studies on supported Ag catalysts, Sachtler *et al.*¹ suggested that the catalytically active epoxidising species was chemisorbed dioxygen [O₂(a)]. Such species have been produced on alkali-doped Ag single crystals,^{2,3} but recent observations⁴ on Ag powders have cast doubt on the validity of the Sachtler mechanism. Thus Backx *et al.*⁴ concluded that the catalytically active species was adsorbed *atomic* oxygen [O(a)], and that the concentration of O₂(a) species detectable by e.s.r. spectroscopy⁵ was too low to account for the observed activity. We report here on the first observation of a chemisorbed dioxygen species at the surface of a pure Ag(111) single crystal surface at room temperature and low pressure. The concentration of this species is about 800 times higher than that inferred from the e.s.r. work on powders; furthermore, its concentration can be significantly enhanced by the pressure of subsurface (dissolved) oxygen.

Experiments were carried out in an ultra-high vacuum apparatus which was linked to a small high-pressure reaction cell. Specimen preparation and operating procedures have been described elsewhere.² After generating a clean, well ordered (111) surface in UHV (LEED–Auger analysis) the specimen was inserted into the reaction cell and dosed with O₂ at 3–300 Pa and 300 K. It was then returned to the UHV chamber and the oxygen thermal desorption spectrum recorded; some experiments were carried out with ¹⁸O₂ or mixtures of ¹⁸O₂ with ¹⁶O₂.

Oxygen chemisorption occurred with a very low sticking probability, no uptake being detectable until the exposure exceeded 10⁵ L (1 L = 1.33 × 10⁻⁴ Pa s). The adsorption rate followed Langmuir kinetics, saturation occurring after a total exposure of ca. 5 × 10⁶ L; this corresponds to a sticking probability of ca. 2 × 10⁻⁷. The desorption spectra show two maxima, one at 580 K (Δ*H*_a ca. 130 kJ mol⁻¹) and one at 380 K (Δ*H*_a ca. 95 kJ mol⁻¹). The former corresponds to the species O(a), well known from earlier single crystal studies. The latter is a new feature which closely resembles that due to the dioxygen species previously only found at low O₂ exposures and in the presence of alkali. Isotope scrambling studies with a 2:1 mixture of ¹⁸O₂ and ¹⁶O₂ clearly reveal that the 380 K feature is due to a dioxygen species (*i.e.* one in which the

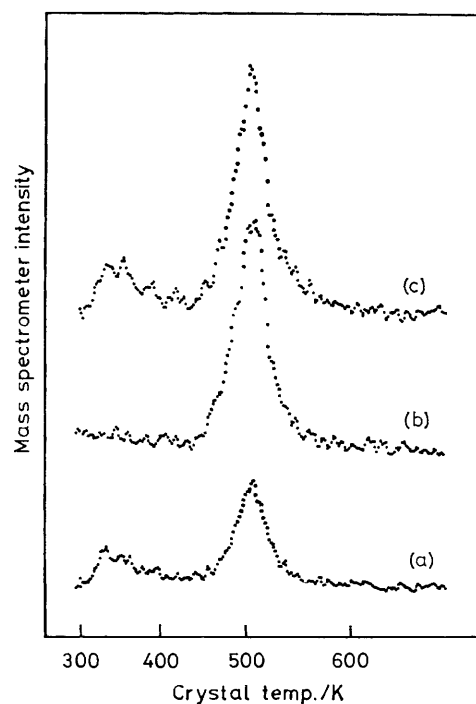


Figure 1. Oxygen desorption spectra from Ag(111) following O₂ chemisorption at 300 K using a 2:1 ¹⁸O₂/¹⁶O₂ mixture: (a) ¹⁶O¹⁶O spectrum, (b) ¹⁸O¹⁶O spectrum, (c) ¹⁸O¹⁸O spectrum.

integrity of the O–O bond is preserved) while at the same time confirming the atomic nature of the species desorbing at 580 K (Figure 1). At saturation coverage, the population of O₂(a) is 16% of that of O(a), suggesting that the e.s.r. observations detect only a fraction of the adsorbed dioxygen. It is important to recognise that the O₂(a) species reported here is quite distinct from that observed by Backx *et al.* on Ag(110);⁶ this latter entity was stable only at temperatures below 173 K.

Similar experiments were carried out on Ag-on-alumina model catalysts prepared by vacuum evaporation to yield an Ag particle size of ca. 200 Å. The sticking probability of oxygen on these materials was ca. 10³ higher than on the Ag(111)

specimen, but once again the desorption spectra showed the presence of both O(a) and O₂(a) species. The relative amount of O₂(a) was significantly greater on the model catalyst (29% more) as compared with the single crystal, so the possibility exists that O₂(a) is preferentially adsorbed at defect sites or sites with low metal atom co-ordination numbers. This was investigated by examining the uptake of O₂ by the Ag(111) specimen after the latter had been subjected to extensive surface damage by Ar⁺ bombardment. No significant enhancement of the O₂(a) population ensued, ruling out such structural effects. However, it was found that the O₂(a) concentration was significantly increased (ca. 60%) by deliberately diffusing oxygen into the bulk metal before the adsorption run. The higher dioxygen concentration on the model catalyst therefore probably reflects the higher levels of subsurface oxygen that can be attained with these high surface area specimens. Isotope scrambling experiments established that O(a) underwent exchange with dissolved oxygen, but there was no detectable exchange of this bulk oxygen with O₂(a).

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