Evidence for Superoxo Species on a Silver Surface

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An electron energy loss spectroscopic study has shown the presence of superoxo species besides two peroxo species on the surface of polycrystalline silver, an observation of much significance to catalysis.

A proper understanding of the nature of the adsorbed molecular oxygen species on silver surfaces is of vital importance to catalysis involved in the oxidation of ethylene.[1] Studies based on electron spectroscopy have established the occurrence of parallel adsorbed peroxo-type (O_2^{2-}) molecular oxygen species on Ag surfaces besides atomic oxygen.[2–5] There has, however, been no clear evidence for the formation of superoxo (O_2^-) species although such species have been invoked in the mechanism of oxidation of ethylene on Ag catalysts.[1] In this communication we report the first definitive evidence for the occurrence of the superoxo species in addition to the peroxo species on the surfaces of polycrystalline silver, based on our investigations employing vibrational electron energy loss spectroscopy (e.e.l.s.).

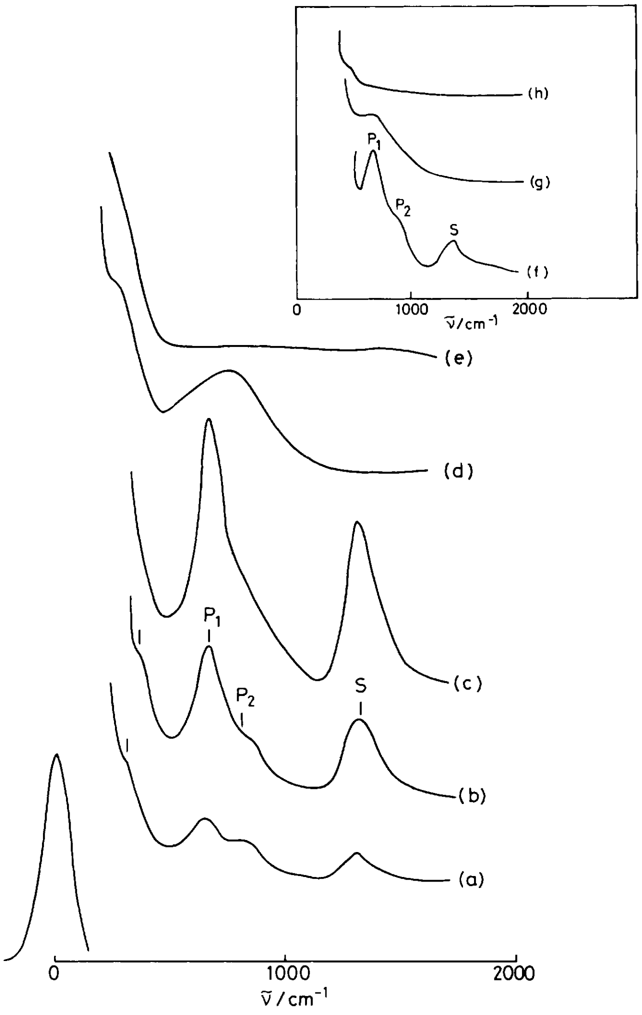

Figure 1. Vibrational electron energy loss spectra of oxygen adsorbed on a polycrystalline Ag surface at different exposures and temperatures. The inset shows another independent set of results on the temperature dependence of the adsorbed species. S and P stand for superoxo and peroxo species respectively. (a) O_2, 50 L (Langmuir; 1 L = Torr s), 80 K; (b) O_2, 1000 L, 80 K; (c) O_2, 2000 L; (d), (c) warmed to 150 K; (e), (c) warmed to 200 K. Inset: (f) O_2, 1000 L, 80 K; (g), (f) warmed to 150 K; (h), (f) warmed to 230 K.

Electron energy loss spectra of oxygen adsorbed on the surface of a clean foil of polycrystalline silver (>99.99% purity) at 80 K are shown in Figure 1 at different exposures. The spectra show distinct bands at 645, 805, and 1320 cm^{-1}, the intensity of the bands increasing with increase in exposure. The temperature dependence of these vibrational bands is also shown in Figure 1. While the 1320 cm^{-1} band disappears at 150 K, the 645 and 805 cm^{-1} bands persist. The bands at 645 and 805 cm^{-1} are in the range associated with the parallel adsorbed peroxo species described in the literature;[2,3] a band around 240 cm^{-1} is seen to be due to the metal–oxygen stretching mode.

The 1320 cm^{-1} band can only arise from a molecular species which is less strongly bound to the surface than the peroxo species. Based on the O–O stretching frequency–bond order relation, we estimate the O–O bond order of the 1320 cm^{-1} species to be close to 1.5. We therefore assign the 1320 cm^{-1} band to the perpendicular adsorbed superoxo species (designated by S in Figure 1). Such a species is indeed known in the chemistry of dioxygen transition metal complexes;[6] thus, Fe and Co co-ordinate oxygen in the superoxo form giving an O–O stretching frequency in the region 1300—1350 cm^{-1}.

We suggest that the bands at 645 and 805 cm^{-1} in Figure 1 are both due to peroxo-type species and we designate these bands as P_1 and P_2 respectively. The Ag (110) surface shows a single band at 640 cm^{-1} due to the peroxo species.[2] The presence of two peroxo species with bands at 610 and 880 cm^{-1} has recently been found in the case of polycrystalline copper;[7] Cu(110) surface however shows a single peroxo species at 660 cm^{-1} just as the Ag (110) surface.

The present study establishes the formation of peroxo as well as superoxo species on a polycrystalline Ag surface. The superoxo species could be favoured by the polycrystalline nature of the surface with a high proportion of the (111) planes due to the face-centred cubic structure of Ag.

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