Surface Oxygen Species on Isotopically Labelled Oxide Surfaces

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Summary Isotopic labelling of surface oxide ions has been used to show that radical ions such as $(O^-)_S$ and $(O_2^-)_S$ can exist on the surface of MgO as isolated ions and are not part of complex molecular ions which involve surface oxide ions.

THE application of e.s.r. to surface studies has made considerable advances in the identification of adsorbed oxygen species and in particular isotopic labelling of the adsorbed oxygen with ^{17}O (nuclear spin 5/2) has confirmed that $(O_2^-)_S$,[1] $(O^-)_S$,[2,3] and $(O_3^-)_S$[4,5] can exist on oxide surfaces. However, *g*-tensor measurements and calculations of the unpaired spin density distribution do not eliminate the possibility that unlabelled and therefore unseen lattice oxide ions may be involved to form a complex species. Reaction of O^- with a lattice oxide ion would give $(O_2^{3-})_S$ which has been suggested as chemically favourable;[6] such a species could not be unambiguously distinguished from $(O^-)_S$ with the presently available data. We show here that by labelling the oxide ions of the surface with ^{17}O it can be clearly established that monatomic species such as $(O^-)_S$ exist on an oxide surface in an uncomplexed form.

High surface area (*ca.* 80 m^2 g^{-1}) MgO samples were prepared by decomposition of the carbonate *in vacuo* as described previously.[7] The surface oxide ions were then exchanged by irradiation and thermal treatment in an oxygen atmosphere containing 71 atom % of ^{17}O. At the end of the treatment measurement of the isotopic composition of the gas phase indicated that 20% of the $^{16}O^{2-}$

surface ions should have been replaced by $^{17}O^{2-}$ assuming that the exchange was limited to the first layer of oxide ions. Adsorbed oxygen was removed by heating at 300 °C *in vacuo* and the samples then were used.

The isotopic labelling of the surface was confirmed by u.v. irradiation of the samples *in vacuo*. A sample with ^{16}O oxide ions gives an axially symmetric line with $g_\perp = 2{\cdot}0355$ and $g_\parallel = 2{\cdot}002$ previously identified with the V^-_S centre[4,8] (an O^- ion adjacent to a cation vacancy on the surface); the doped sample gives a six-line hyperfine spectrum with $A_\parallel = 302$ MHz and $A_\perp = 29$ MHz arising from interaction with O^- labelled with ^{17}O.[9] The intensity of the hyperfine spectrum relative to the line corresponding to $^{16}O^-$ indicates that about 14% of the surface oxygen ions are replaced by ^{17}O in reasonably good agreement with the gas-phase measurements.

U.v. irradiation of samples in the presence of excess of hydrogen leads to the formation of electrons trapped on the surface [F^+_S(H) centres]. These centres react strongly with N_2O to give $(O^-)_S$ and O_2 to form $(O_2^-)_S$. Careful comparison of the e.s.r. spectra of these radical ions on $Mg^{16}O$ and $Mg^{17}O$ indicated no significant differences. In particular, there was no evidence of hyperfine structure that would be associated with unpaired spin density on oxide lattice ions. This result establishes that the simple atomic species can be observed on oxide surfaces and that there is no significant interaction of the unpaired electron with the oxide lattice ions. Reactions of the adsorbed species with lattice oxide ions to form O_2^{3-} or O_3^{2-} as suggested by Symons[6] do not appear to occur to MgO. Similar experiments on isotopic labelling of the surface ions are being carried out on more catalytically active oxides which contain less strongly bound lattice ions.

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