Change of Thermal Desorption Behaviour of Adsorbed Oxygen with Water Coadsorption on Ag^+-doped Tin(IV) Oxide

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Summary Water coadsorption markedly changed the desorption spectrum of oxygen adsorbed on Ag^+–SnO_2; the broad desorption plateaus above 610 K were transformed into a sharp peak at 570 K.

HYDROXYLATION of oxide surfaces upon exposure to water vapour[1] can affect surface properties such as catalytic behaviour and adsorptivity. However, little is known about its influence on the nature of adsorbed oxygen; it may not exert any influence[2] in most cases. Two instances have been reported so far in which water strongly modifies the nature of oxygen adsorbates: (i) two oxygen species desorbing at 593 and 743 K on Cu^{2+}-exchanged Y zeolite were changed into a single species that was desorbed at 663—673 K,[3] and (ii) O^{2-} species desorbing at 853 K on SnO_2 were converted into hydroxyl groups, resulting in the concurrent desorption of oxygen and water at 893 K.[4] We report here a more drastic instance of the change of oxygen adsorbates under the influence of water.

An Ag^+-doped SnO_2 sample was prepared from α-stannic acid gel obtained from tin(IV) chloride, followed by ion-exchange with silver acetate. The amount of Ag^+ exchanged was $0\cdot213$ mmol g^{-1} or $3\cdot55$ mol%. The resultant Ag^+-exchanger was calcined at 1073 K for 5 h in air. The temperature programmed desorption (T.P.D.) technique was employed to examine the adsorbed species, the apparatus being essentially the same as described elsewhere.[4,5] The sample ($0\cdot5$ g) was pretreated at 1073 K for 2 h in a stream of 10% oxygen and 90% helium, and then cooled to room temperature in the same stream for oxygen adsorption. The succeeding T.P.D. run was carried out at temperatures up to 1073 K at a uniform heating rate of 10 K min^{-1} in flowing helium with a flow rate of 30 cm^3 min^{-1}. Individual desorption spectra of oxygen and water were obtained by employing two thermal conductivity detectors and a cold trap placed between them.

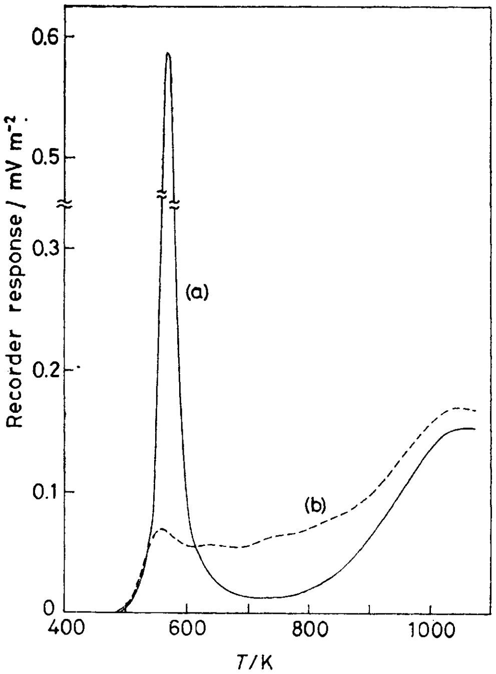

FIGURE 1. Influence of water coadsorption on the T.P.D. spectrum of oxygen: (a) water ($9\cdot16$ μmol m^{-2}) was coadsorbed at room temperature; (b) no adsorbed water.

Figure 1 shows the T.P.D. spectra of oxygen from the sample (a) with and (b) without coadsorbed water. Spectrum (b) consists of a small peak at 560 K and a few very broad plateaus above 610 K, with an increase above 870 K. The peak at 560 K seems to correspond to the 503 K oxygen species on silver which it was suggested included both O_2^- and O^-,[2] although the peak temperature is somewhat higher. However, the spectrum above 610 K was different from spectra on silver and on pure SnO_2[4], indicating a certain modification of the adsorbent properties of SnO_2 by Ag^+-doping. When water was coadsorbed on this oxygen-containing surface at room temperature, the oxygen desorption spectrum drastically changed as shown in spectrum (a); the higher temperature region significantly decreased whereas the 570 K peak markedly increased. The number of desorbed oxygen atoms up to 1073 K was $3\cdot00 \times 10^{18}$ and $3\cdot08 \times 10^{18}$ atoms m^{-2} for curves (a) and (b), respectively. It is certain, therefore, that the 570 K species arose from the higher temperature species. The amount of 570 K oxygen (up to 670 K) was $1\cdot40 \times 10^{18}$ atoms m^{-2} or $1\cdot20 \times 10^{19}$ atoms g^{-1}, which is approximately one-tenth the amount of Ag^+ ions added. On the other hand, the number of unoccupied surface metal sites would be of the same order as those on the pure SnO_2 and Ag surfaces, although in the present instance it is not known if tin predominates over silver or *vice versa*. It has been calculated that there are $4\cdot69 \times 10^{18}$ and $1\cdot31 \times 10^{18}$ sites m^{-2} for the cleaved (110) plane of SnO_2 and for the Ag surface with an equilibrium plane distribution,[6] respectively. Comparison of these values strongly indicates that the 570 K species are not attributable to any bulk materials like Ag_2O, but to some adsorbed species within a monolayer.

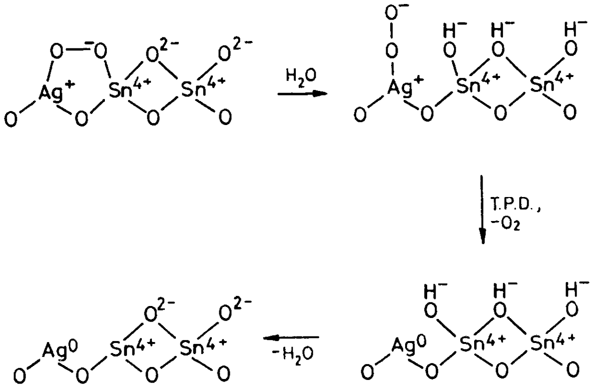

FIGURE 2. Proposed mechanism for the change of oxygen adsorbates with water coadsorption.

This kind of modification of oxygen adsorbates resulting from water coadsorption was not observed in the case of undoped SnO_2.[4] Similar experiments on three kinds of Ag catalyst, self-supported and supported on silica and γ-alumina, did not show such modification either (see also ref. 2).

X-Ray diffraction analysis of the sample submitted to the oxygen adsorption pretreatment did not show the presence of any metallic silver, nor a bulk binary compound. When the sample was heated at 1073 K for 3 h in helium, however, the growth of silver crystallites was identified. It is most likely, therefore, that the silver atoms doped exist as Ag^+ ions after the oxygen pretreatment, presumably owing to formation of a surface binary compound, although the details are unknown at present. Further evidence for this was the change in the T.P.D. spectra of water itself.[7] The spectrum of water coadsorbed on the oxygenated surface was quite different from that on pure SnO_2. The amount of surface hydroxyl groups desorbing above 600 K markedly decreased on doped SnO_2, probably because of the blocking of water adsorption sites (Sn^{4+}) on SnO_2 by the Ag^+ doping and also by preadsorbed oxygen. However, pretreatment at 1073 K in helium, which resulted in the crystallization of silver as just mentioned, led to water desorption analogous to that from pure SnO_2. On the basis of these observations, we propose the mechanism in Figure 2 as a possibility for the change of the oxygen adsorbates influenced by water coadsorption. An atomic species like O^- may be an alternative to the molecular species bridged to Ag^+ and Sn^{4+}.

Irrespective of the exact mechanism, the change of the oxygen adsorbates is of great interest in the sense that they are transformed into a weakly bonded and relatively uniform species by water adsorption. Studies on the catalytic activity or selectivity of the water-treated surface are in progress.

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