Oxygen Species resulting from the Adsorption of Gaseous Oxygen on a Copper(II)-exchanged Y-Type Zeolite

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Summary Of the two peaks in the temperature-programmed desorption of a copper(II)-exchanged Y-type zeolite, one, at 603 K, was the desorption of oxygen adsorbed in a non-dissociated form and another, at 773 K, resulted from the desorption of lattice oxygen induced by the adsorption of gaseous oxygen

IN attempts to clarify the adsorption-desorption behaviour of oxygen over metal ion-exchanged zeolites, the copper(II)-exchanged Y-type zeolite (CuNaY) was shown to give two oxygen-desorption peaks in the range 373—823 K upon the adsorption of oxygen at 373—673 K [1,2] Using labelled oxygen molecules we have characterized, experimentally and in more detail, the adsorption states of oxygen in CuNaY.

A sample of CuNaY was prepared by the conventional ion-exchange of NaY (Linde, SK-40). The exchange level was 73%. The apparatus used in the present work was essentially the same as previously reported[3] except that the desorption was monitored by **a** quadrupole mass spectrometer (Nichiden Varian TE-600). After being mounted in a temperature-programmed desorption (T.P.D.) sample tube, the sample was subjected to the following pretreatment at 823 K; evacuation for 1 h, exposure to oxygen at 100 Torr, and re-evacuation for 30 min. Oxygen adsorption was then performed by introducing oxygen for 1 h at 523 K, followed by evacuation at the same temperature for 60 min. The programmed heating was started at a rate of 5 K min^{-1}.

The desorption chromatograph of oxygen from CuNaY showed two distinct peaks with maxima at 603 and 773 K, in agreement with the results of earlier work.[1] The slight variation of the desorption temperatures from those in the previous paper[1] may be due to the use of different samples. It is evident that Cu^{II} ions in the zeolite contribute to the appearance of these two desorption peaks, since no peak was observed from NaY in this region. The desorption chromatograph obtained following the adsorption of $^{18}O_2$ (^{18}O atomic fraction = 99·1%) at 100 Torr, is shown in the Figure (A). The desorption peak at the lower temperature consisted of $^{18}O_2$ only, whereas most of the oxygen molecules desorbed in the range 673—823 K was $^{16}O_2$ despite the absence of $^{16}O_2$ in the adsorbed gas. This result suggests that desorption of lattice oxygen has occurred and that this was induced by the adsorption of gaseous oxygen.

To characterise further this behaviour, an equimolar mixture of $^{16}O_2$ and $^{18}O_2$ was adsorbed at 70 Torr. The result is shown in the Figure (B). In the desorption at 603 K the ratio of desorbed $^{16}O_2$ and $^{18}O_2$ was 1 : 1 and the amount of detected $^{16}O^{18}O$ molecules was very small and the same level as that in the Figure (A). It is concluded that there is no isotope effect in the adsorption–desorption of oxygen at the lower temperature desorption and that oxygen adsorbates exist in a non-dissociated form on CuNaY. In the desorption at *ca.* 773 K, $^{16}O_2$ molecules were mainly desorbed in the same manner as shown in Figure (A). Without the adsorption of oxygen at 523 K, of course, there was no desorption peak in the range 373—823 K. It is beyond doubt, therefore, that this desorption peak resulted from the adsorption of gaseous oxygen. As mentioned previously, the desorption of $^{16}O_2$ upon adsorption of $^{18}O_2$ suggests that the adsorbed oxygen did not desorb, but that the lattice oxygen desorbed. The atomic fraction of ^{18}O in oxygen molecules desorbed at 673—823 K was very small. This indicates the presence of an extremely large amount of lattice oxygen exchangeable with adsorbed oxygen and/or a difference between the entrance of adsorbed oxygen and the exit of desorbed oxygen. The conclusion by Antoshin *et al.*[4] that the structural oxygen in CuNaY is equivalent with respect to the isotopic exchange reaction supports the former suggestion. Examples of the latter mechanism are observed in the behaviour of oxygen over zinc oxide[5] and bismuth molybdate.[6] Although the mechanism cannot be clarified yet, the above phenomenon is very interesting and useful when considering the nature of metal ion-exchanged zeolites and the catalytic activity towards the oxidation of hydrocarbons. It is perhaps worth noting that the repetition of the adsorption–desorption cycle, including oxygen-18, resulted in the increasing quantities of $^{16}O^{18}O$ and $^{18}O_2$ molecules in the higher temperature desorption.

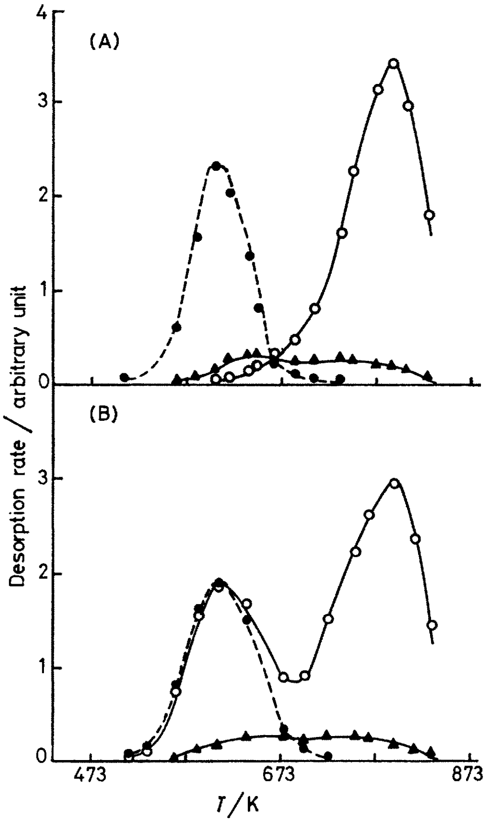

FIGURE. Temperature-programmed desorption chromatogram of oxygen following the adsorption of (A) only $^{18}O_2$ molecules or (B) an equimolar mixture of $^{18}O_2$ and $^{16}O_2$ at 523 K for 1 h on a copper(II)-exchanged Y-type zeolite. ● $^{18}O_2$, ○ $^{16}O_2$, ▲ $^{16}O^{18}O$.

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