Temperature-programmed Desorption Spectra of Oxygen from Transition Metal Ion-exchanged Y-Type Zeolites

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Summary Temperature-programmed desorption spectra of oxygen from several metal ion-exchanged Y-type zeolites show that oxygen is adsorbed on them in various states and in various amounts depending on the metal ion species exchanged; $Cu^{II}Y$, an exceedingly active catalyst for oxidation, adsorbs markedly large amounts of oxygen which reflects on the importance of such adsorbed oxygen in the catalytic oxidation reactions.

Catalytic activities of metal ion-exchanged Y-type zeolites (M–Y) towards oxidation reactions were reported recently.[1,2] In order to understand the mechanism of these reactions, we investigated adsorption of oxygen on M–Y by means of a temperature-programmed desorption (TPD) technique.

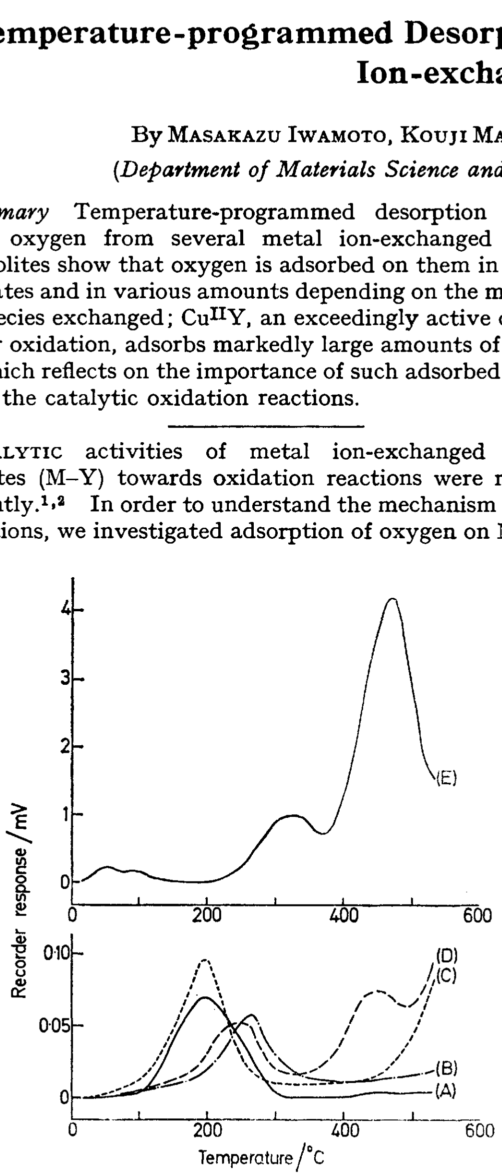

Figure. TPD chromatograms of oxygen from several transition metal ion-exchanged Y zeolites: A, $Na^{I}Y$; B, $Ni^{II}Y$; C, $Mn^{II}Y$; D, $Co^{II}Y$; and E, $Cu^{II}Y$.

Samples of M-Y were prepared by ion-exchange of $Na^{I}Y$ (Linde, SK-40) with aqueous metal sulphate solutions. The exchange levels were 55, 70, 60, and 62%, respectively, for $Mn^{II}Y$, $Co^{II}Y$, $Ni^{II}Y$, and $Cu^{II}Y$. After being mounted in a TPD cell,[3] samples were subjected to the following pretreatments at 500 °C: evacuation for 2 h, exposure to 100 Torr of oxygen for 1 h, and re-evacuation for 15 min. Oxygen adsorption was then performed by introducing 100 Torr of oxygen at 500 °C, followed by cooling to 10 °C at a rate of 3·3 °C min^{-1} under the same atmosphere. At 10 °C, the samples were evacuated for 15 min and subjected to programmed heating (5 °C min^{-1}). Desorbed oxygen was detected by a thermal conductivity cell.

Typical desorption spectra are shown in the Figure. The desorption temperatures and the desorption peak areas vary extensively with the type of sample used. In the range of 100—500 °C, $Cu^{II}Y$ shows two specifically large desorption peaks with maxima at 320 and 460 °C. In contrast, far weaker peaks are observed for other samples: two peaks (245 and 450 °C) and an ascent above 500 °C for $Co^{II}Y$, a peak (195 °C) and an ascent above 450 °C for $Mn^{II}Y$, and one peak for each of $Ni^{II}Y$ (260 °C) and $Na^{I}Y$ (195 °C). The desorption spectra are thus characteristic of the metal ion species exchanged in the zeolite. Therefore, it seems probable that oxygen adsorbates involved in these systems are bound directly to metal ions. However, it is difficult to identify the oxygen adsorbates at this stage. Only in the case of the O_2–$Na^{I}Y$ system, the corresponding adsorbate is assignable to the superoxide ion O_2^- on the basis of the observations made by other workers that O_2^- formed on Na^+ in the zeolite at lower temperatures, which was identified by e.s.r. spectroscopy, was completely eliminated when heated at $>$ 150[4] or 300 °C.[5]

The total amount of desorbed (or adsorbed) oxygen at 100—500 °C, as calculated from the peak areas of desorption spectra, was 1·08, $3{\cdot}76 \times 10^{-2}$, $3{\cdot}44 \times 10^{-2}$, $2{\cdot}14 \times 10^{-2}$, and $1{\cdot}58 \times 10^{-2}$ $cm^3 g^{-1}$, respectively, for $Cu^{II}Y$, $Co^{II}Y$, $Mn^{II}Y$, $Na^{I}Y$, and $Ni^{II}Y$. In the case of $Cu^{II}Y$, the amount of desorbed oxygen corresponds to 0·047 molecules per Cu^{2+} ion. The order is in agreement with our previous result obtained by a pulse adsorption technique.[2] Although the reason for the large difference in oxygen adsorption capacity of $Cu^{II}Y$ is not clear yet, it is interesting to note that $Cu^{II}Y$ showed distinct catalytic activity during an earlier investigation.[1] This reflects on the importance of adsorbed oxygen in catalytic oxidation reactions.

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