

A STUDY OF THE REDOX BEHAVIOUR OF COPPER IONS IN ZEOLITES X AND Y BY TEMPERATURE PROGRAMMED REDUCTION

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Temperature Programmed Reduction (TPR) has been used to study the redox behaviour of copper ions in X and Y zeolites. Two distinct Cu^{II} to Cu^{I} reduction processes are discernible in both X and Y zeolites. These two processes have been assigned to the reduction of Cu^{II} ions occupying sodalite and supercage sites; a small fraction of the Cu^{II} ions, assumed to occupy hexagonal prism sites, remain unreduced. At 773 K in nitrogen, autoreduction of both sodalite and supercage Cu^{II} occurs in X zeolite, while only supercage Cu^{II} ions are autoreduced in Y zeolite. The reductions are reversible in Y zeolite, but some CuO is formed in X which is subsequently reduced by a third process. Activation energies (kJmol^{-1}) were obtained as follows: Cu^{II} to Cu^{I} (sodalite cages) 84 ± 13 , Cu^{II} to Cu^{I} (supercages) 64 ± 10 and CuO to Cu^{0} (X type zeolite) 49 ± 7 .

Introduction

Recent temperature programmed reduction (TPR) studies [1] have shown that the technique can be successfully applied as a "finger print" method for the characterisation of catalysts.

We have studied here the reduction of cupric ions in zeolites X and Y. Previous studies [2, 3] of the type-Y system by isothermal techniques showed that the reduction of Cu^{II} to Cu^{I} occurred by two distinct processes, although a TPR study [4] of the same system did not resolve them. In view of the conditions used in the above study, it seems likely that TPR under milder conditions would yield more detail of the reduction mechanisms involved.

The TPR of (Cu, Na)-X-50 was also studied here to enable a comparison to be made of the redox behaviour of copper in zeolites of different Si/Al ratios. We also report some work on the autoreduction of Cu^{II} in both X and Y zeolites, where TPR is able to shed light on the locations of the ions involved.

Experimental

Apparatus and procedure

The apparatus and procedure used were similar to those described previously [1]. The reducing gas was 4% hydrogen in nitrogen. The samples (200 mg) were held on a sinter (20 mm diameter) in a glass reactor. The reactor was held in a stirred air oven which could be heated linearly at rates up to 20 K min^{-1} . The rate of hydrogen consumption was monitored *via* a katharometer.

Materials

Samples of zeolite Y (LINDE, SK—40) and zeolite X (BDH) were ion exchanged in aqueous copper nitrate solution. Excess nitrate was used to produce (Cu, Na)-Y-68 and the appropriate amounts of nitrate to produce (Cu, Na)-Y-32 and (Cu, Na)-X-50. It has been shown [3, 5] that these methods produce Cu^{II} ion exchanged zeolites. Cylinder gases (BOC and PK MORGAN) were purified by passage over activated charcoal and magnesium perchlorate.

Sample pretreatment

Each sample was pretreated in the reactor under flowing nitrogen or air. The temperature was raised from ambient to 773 K at 30 K min^{-1} , held for 10 minutes then rapidly lowered to 325 K under flowing gas.

Qualitative tests for Cu^{I} , Cu^0 , and CuO

Samples were exposed to carbon monoxide at room temperature, and flushed with nitrogen. The samples were then prepared as nujol mulls and their IR spectra recorded. Absorption at 2145 cm^{-1} was taken as evidence for the presence of Cu^{I} [6]. The presence of the metal or oxide was indicated in some samples by the appearance of characteristic lines in the powder X-ray diffraction patterns.

Results

(Cu, Na)-Y-68, Air pretreated samples

Ten samples were subjected to TPR at heating rates from 2.8 to 17.7 K min^{-1} . A typical spectrum, presented in Fig. 1, consists of two peaks separated by about 100 K. The total amount of hydrogen consumed was $1.00 \cdot 10^{-4} \text{ mol}$, corresponding to 0.47 mol of hydrogen per mol of Cu^{II} in the sample. Before and after the TPR the samples were tested for CuO , Cu^{I} and Cu^0 as described above. The test for Cu^{I} was positive for the reduced samples; all other tests were negative.

When a reduced sample was subjected to the 'air pretreatment' process, and the TPR repeated, identical results were obtained. Thus, the total amount of hydrogen consumed in the TPR of the re-oxidised sample was $9.29 \cdot 10^{-5} \text{ mol}$.

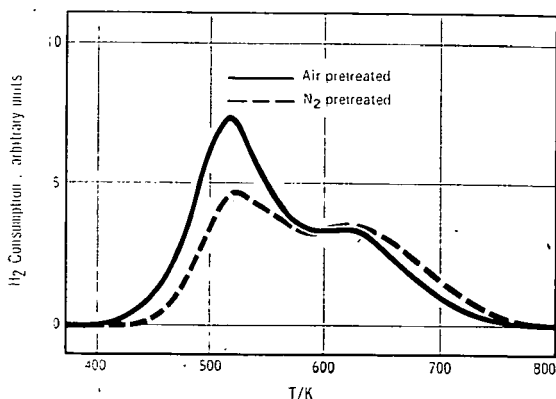


Fig. 1. TPR spectra of (Cu, Na)-Y-68.
 $\beta = 13.5 \text{ K min}^{-1}$, 4% H_2/N_2

(Cu, Na)-Y-68, Nitrogen pretreated samples

Four samples were subjected to TPR at heating rates from 9.3 to 17.9 Kmin⁻¹. A typical spectrum is shown in Fig. 1. As for the air pretreated sample the spectrum consists of two peaks indicating the two separate reduction processes. However, the amount of hydrogen consumed in this reduction ($7.24 \cdot 10^{-5}$ mol) is only 70% of that consumed by the air pretreated sample. It can be seen from Fig. 1 that this difference is due to a diminution of the amount of hydrogen consumed in the low temperature reduction. Tests indicated the presence of Cu^I in samples both before and after reduction. No Cu⁰ or CuO was detected.

When the reduced sample was subjected to the air pretreatment, the TPR results obtained were the same as those obtained for samples that had received only the air pre-treatment. Thus, the re-oxidised sample on subsequent TPR, consumed $9.47 \cdot 10^{-5}$ mol of hydrogen.

(Cu, Na)-Y-32, Air pretreated sample

A single 400 mg sample was subjected to TPR. The spectrum, shown in Fig. 2, consists of two peaks. The total amount of hydrogen consumed was $9.61 \cdot 10^{-5}$ mol.

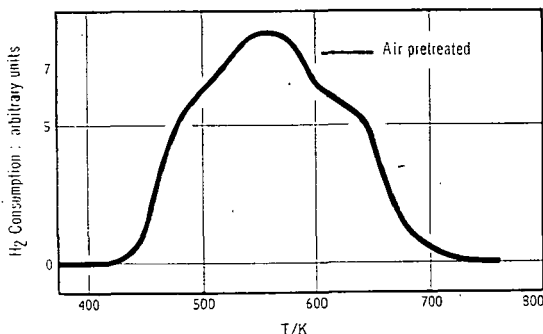


Fig. 2. TPR spectrum of air pretreated (Cu, Na)-Y-32. $\beta = 13.5$ Kmin⁻¹, 4% H₂/N₂. 400 mg of zeolite were used

(Cu, Na)-X-50, Air pretreated samples

Six samples were subjected to TPR at heating rates from 3.0 to 18.0 Kmin⁻¹. A typical spectrum is presented in Fig. 3. Again two reduction processes are observed, most of the hydrogen being consumed in the high temperature reduction. The total amount of hydrogen consumed was $9.82 \cdot 10^{-5}$ mol. Tests indicated the presence of Cu^I and Cu⁰ in the reduced samples.

The above processes were not found to be reversible. Thus, after the reduced samples were subjected to the air pretreatment, tests showed the absence of Cu⁰ and Cu^I but gave clear evidence of CuO. A typical TPR spectrum for these samples is shown in Fig. 4. A third low temperature reduction is clearly discernible. The total amount of hydrogen consumed in this reduction was $1.24 \cdot 10^{-4}$ mol.

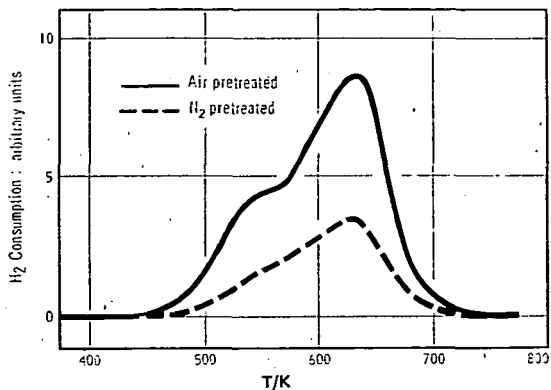


Fig. 3. TPR spectra of (Cu, Na)-X-50.
 $\beta = 13.0 \text{ Kmin}^{-1}$, 4% H_2/N_2

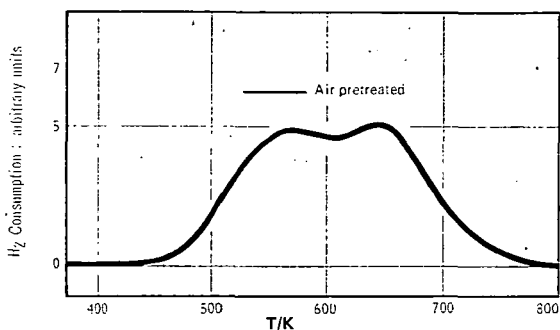


Fig. 4. TPR spectrum of (Cu, Na)-X-50 reduced
 and reoxidised. $\beta = 13.7 \text{ Kmin}^{-1}$, 4% H_2/N_2

(Cu, Na)-X-50, Nitrogen pretreated samples

Three samples were subjected to TPR at heating rates from 12.9 to 17.9 Kmin^{-1} . A typical spectrum is shown in Fig. 3. Both reduction processes are apparent. The total amount of hydrogen consumed by the sample $4.18 \cdot 10^{-5} \text{ mol}$. Tests showed the presence of Cu^{I} before reduction and Cu^{I} and Cu^0 after reduction. The sample reduced at 13.5 K min^{-1} was subjected to the air pretreatment and investigated. Tests showed that Cu^{I} and Cu^0 were removed, but that CuO was produced. Subsequent TPR gave the same three peaks as found for the re-oxidised, air pretreated sample (Fig. 4). The amount of hydrogen consumed was $1.58 \cdot 10^{-5} \text{ mol}$, an increase of 25% over the amount consumed by the re-oxidised, air pretreated sample.

Reaction orders and activation energies

Under the conditions used here, the reduction processes were taken as first order in both Cu^{II} concentration [2] and hydrogen concentration [10]. Thus the equation [10]:

$$2 \ln T_m - \ln \beta + \ln [\text{H}_2]_m = E/RT_m + \text{constant}$$

may be used to derive values for the apparent activation energies of the reduction processes (T_m and $[H_2]_m$ are the temperatures and hydrogen concentrations at the rate maxima respectively and β is the linear heating rate).

The reduction processes in (Cu, Na)-Y-68 were found to have activation energies (kJmol^{-1}) of 84 ± 13 (high temperature process) and 64 ± 10 (low temperature process). The same values were found for the analogous processes in (Cu, Na)-X-50. The low temperature process in (Cu, Na)-X-50, Fig. 4, was found to have an activation energy of $49 \pm 7 \text{ kJmol}^{-1}$.

Discussion

The qualitative analyses for Cu^{I} , Cu^0 and CuO indicate that the reduction of air pretreated (Cu, Na)-Y-68 produces only Cu^{I} under conditions used here. Moreover, a previous study [3] showed that after reaction using more drastic reducing conditions only 6.5% of the copper in this system was reduced to Cu^0 . Thus, the TPR spectra for the air-pretreated (Cu, Na)-Y-68 show that about 94% of the Cu^{II} is reduced exclusively to Cu^{I} by two separate reduction processes.

These findings are in accord with the results of a previous study [2] although at the hydrogen pressures used, $P_{H_2} > 13.3 \text{ kNm}^{-2}$, the reduction was found to be zero order in hydrogen. However, a recent TPR study [4] of this system, using hydrogen concentrations of the order of 80 kNm^{-2} , was only able to distinguish a single reduction process of Cu^{II} to Cu^{I} . Our result that about 6% of the Cu^{II} ions remain unreduced is consistent with the small percentage of ions occupying positions in hexagonal prisms. Furthermore our results showing two distinct reduction processes are in accord with the distribution of the remaining ions between the sodalite units and the supercages [7, 8].

It is thus tempting to assign the low temperature reduction to the reduction of Cu^{II} ions in the supercage and the high temperature reduction to the reduction of Cu^{II} ions in the sodalite units. However, our results indicate that most Cu^{II} ions are reduced by the low temperature process, whereas the distribution of ions in the dehydrated framework shows that most ions are accommodated in the more stable sodalite positions. This anomaly is further highlighted by the results obtained with (Cu, Na)-Y-32. These results, shown in Fig. 2, show the same two reduction processes exhibited by (Cu, Na)-Y-68. X-ray data, for the dehydrated system, indicate however that Cu^{II} ions occupy only hexagonal prisms and sodalite units; on the basis of the above, therefore, only one reduction process would be expected.

The appearance of two distinct reduction processes of Cu^{II} to Cu^{I} in (Cu, Na)-Y-32 has been attributed to the presence of water in the zeolite framework [2]. We thus suggest that our results are indicative of a partially hydrated zeolite-Y system.

The nitrogen pretreatment of (Cu, Na)-Y-68 was found to reduce about 25% of the Cu^{II} ions to Cu^{I} . This partial autoreduction has been previously reported for this system [9] and a mechanism has been proposed. A comparison of the TPR spectra for the air and nitrogen pretreated samples (presented in Fig. 1) indicates that the Cu^{II} ions involved in the autoreduction are those involved in the low temperature reduction, and here assigned to supercage sites.

The TPR spectrum of air pretreated (Cu, Na)-X-50, shown in Fig. 3, indicates that the reduction occurs by two separate reduction processes, a result similar to that found for the reduction of (Cu, Na)-Y-68. However, in contrast to the results

found for the Y zeolite, the reduction of (Cu, Na)-X-50 results in the production of Cu^0 in addition to Cu^I . It is somewhat surprising, though, that the hydrogen consumption corresponds to only 0.42 mol per mol of Cu^{II} .

It is assumed [10] that the TPR spectrum is not radically altered by the 'hidden' peak due to the reduction of Cu^I to Cu^0 and that the two peaks refer, as suggested for the Y zeolite, to the reduction of Cu^{II} in the sodalite and supercage positions. Thus the TPR spectrum of air pretreated (Cu, Na)-X-50 shows that, in contrast to air pretreated (Cu, Na)-Y-68, most of the Cu^{II} is reduced in the high temperature reduction process which was assigned above to the reduction of ions in sodalite positions. This result is that expected from the distribution of ions in the dehydrated zeolite. The fact that we would expect the air pretreatment to produce a more dehydrated zeolite than would be the case for the Y zeolite is thus consistent with the above.

The nitrogen pretreatment of (Cu, Na)-X-50 resulted in the reduction of Cu^{II} to Cu^I . The hydrogen uptake during the subsequent TPR was only 43% of that absorbed by the sample subjected to air pretreatment. It is thus apparent that far more drastic autoreduction of (Cu, Na)-X-50 takes place than was the case for (Cu, Na)-Y-68 (see above). The TPR spectrum of the nitrogen pretreated sample (see Fig. 3) suggests, as must be expected, that the reduction involves Cu^{II} from both sodalite and supercage positions.

Using the above assignments, the activation energies obtained for the reduction of Cu^{II} to Cu^I in (Cu, Na)-Y-68 are 84 kJmol^{-1} (for Cu^{II} in the sodalite units) and 64 kJmol^{-1} (for Cu^{II} in supercage positions). These can be compared with values of 111 (sodalite) and 70 kJmol^{-1} (supercage) obtained from an isothermal kinetic study [2]. Activation energies measured for the analogous processes in X-zeolite are not significantly different from those measured for (Cu, Na)-Y-68.

The simplest mechanism for these reductions is the reaction between hydrogen and Cu^{II} ions 'in situ' in the sodalite and supercage positions. An alternative mechanism, invoked previously [2], provides that Cu^{II} ions in sodalite positions must migrate to the supercage before reduction can take place. If this process involves an equilibrium between Cu^{II} ions in the two positions, followed by reduction of Cu^{II} in the supercage, then the difference in activation energies (about 20 kJmol^{-1}) is equal to the difference in energy between Cu^{II} ions in the two lattice positions.

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