Preparation and Characterization of Excessively Copper Ion-exchanged Mordenite

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Repeated ion exchanges of mordenite with copper ions bring about excess loading of copper ions, this is not paralleled in the cases of nickel and chromium ions; an i.r. study shows that a hydroxy-bridged polymer of the copper ion is formed.

Zeolites are crystalline aluminosilicates containing three-dimensonsal arrays of SiO_4 and AlO_4 tetrahedra. Owing to the presence of aluminium atoms in the zeolite lattice, there is a net charge in the lattice, and compensating cations, typically sodium, are required to balance the anionic framework charge; other cations are relatively easily exchanged with these cations.[1] Schoonheydt *et al.*[2] found that copper and nickel ions were exchanged nonstoicheiometrically in X- and Y-type zeolites; a similar phenomenon was reported by Namba and Yashima.[3] Iwamoto *et al.*[4] reported high catalytic activity of excessively copper ion-exchanged ZSM-5 zeolite for direct decomposition of NO. Further, Suzuki *et al.*[5] found that the catalytic activity of a nickel ion-exchanged zeolite was markedly improved by treatment with aqueous NaOH; they attributed the enhanced activity to small nickel oxide aggregates in the zeolite. As the catalytic and electronic properties of zeolites are influenced by the variety, amount, and distribution of the exchangeable cations, the preparation of specific ion-exchanged zeolites and their structural characterization is of considerable importance in understanding these properties. We have investigated the ion exchange properties of mordenite, which has one-dimensional cylindrical channels running parallel to the *c*-axis, and have found that repeated ion exchange by copper ions was nonstoicheiometric, unlike the cases of nickel and chromium ions, and the product exhibits a characteristic i.r. peak at 3350 cm^{-1}, which has not been reported previously in a zeolite system.

The starting materials for ion exchange experiments were the sodium forms of mordenite TSZ-644 (NaM, TOSOH Corp., Si/Al 10). A sample was ion-exchanged using aqueous $CuCl_2\cdot6H_2O$ (0.3 M; pH 4.1) (Nacalai Tesque Inc.). Contact between the phases was maintained for 1 h at 363 K. Samples containing different amounts of copper ion were prepared by repeating the exchange process several times. After filtration, the zeolite was washed several times to remove excess absorbed ions, and then air-dried at 373 K for approximately 2 h. The same procedure was repeated for the preparation of Ni^{II}- and Cr^{III}-mordenites, using an aqueous solution of $NiCl_2\cdot6H_2O$ (0.3 M; pH 5.1) or $Cr(NO_3)_3\cdot6H_2O$ (0.3 M; pH 2.97). The copper or nickel ion-loaded mordenites were re-exchanged with NH_4Cl (1 M) at 363 K until there were free copper or nickel ions. In the case of the chromium ion-exchanged mordenites, a solution of $HClO_4$ (~30%) was used instead of NH_4Cl. The liberated copper or nickel ions were determined by chelatemetric titration and the exchange capacities were calculated. The quantity of chromium ion was determined by colorimetry.

To obtain i.r. spectra (JASCO, IR-810 spectrometer) a self-supporting disc (20 mm diameter) was prepared by compressing 50 mg of the sample under a pressure of 400 kg cm^{-2}. The sample was mounted in an *in situ* cell similar to that used previously.[6]

Table 1 shows the relation between the extent of exchange and the number of exchanges for copper, nickel, and chromium ions; it was assumed that one divalent or trivalent ion can be exchanged for two or three sodium(I) ions. In the case of copper ions the extent of exchange increases with an increasing number of exchanges; its value exceeds 100% for

Table 1. Relation between the extent of ion exchange and the number of exchanges.

	Exchange times				
Ion	1	3	5	10	15
	Extent of exchange/%				
Cu^{2+}	83	101	122	187	215
Ni^{2+}	71	79	80	82	83
Cr^{3+}	52	53	57	58	58

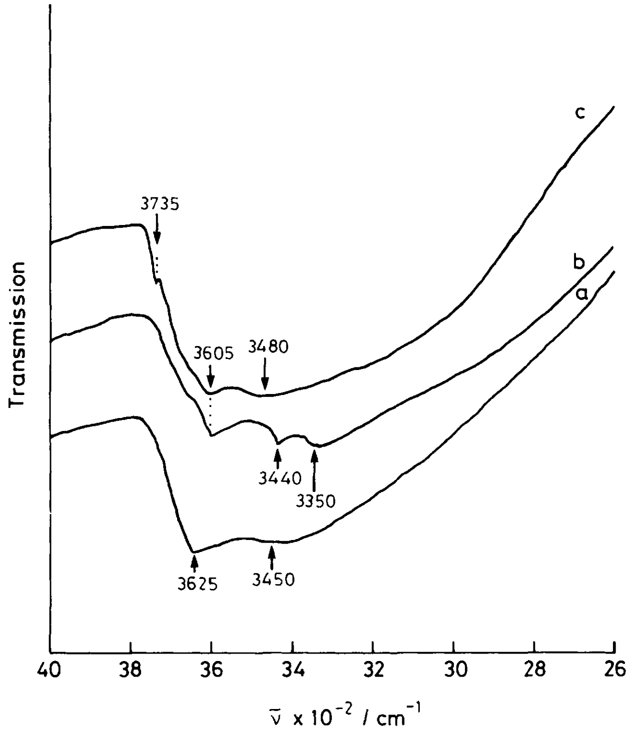

Figure 1. I.r. spectra of (a) CuM-27, (b) CuM-150, and (c) NiM-84 (the number indicates the % exchange).

three exchange treatments and reaches 215% (abbreviated as CuM-215) for fifteen exchange treatments. It is apparent that the extent of exchange by copper ions is much higher than expected from consideration of the stoicheiometry when two sodium ions in mordenite are exchanged with one copper ion. *X*-ray diffraction data of CuM-215 are similar to those of NaM, *i.e.*, the framework is not destroyed in the ion exchange process. On the other hand, for nickel ions, the extent of exchange is 71% for a single exchange treatment, reaching 80% for five treatments, and scarcely changes with further exchange treatment, *i.e.*, nonstoicheiometric exchange is not observed in this case. In the case of chromium ions, the extent of exchange is 52% for a single exchange treatment and 58% for fifteen treatments. These facts indicate that the nonstoicheiometric ion exchange is specific for copper ions under our experimental conditions.

The i.r. spectra of CuM-27, CuM-150, and NiM-84 are shown in Figure 1, after treatment *in vacuo* at 373 K. The peak at 3735 cm^{-1} has been attributed to silica-type hydroxy groups present either as lattice terminators or siliceous impurities.[7,8] The peaks at 3625 and 3605 cm^{-1} are tentatively attributed to cation deficiencies which lead to introduction of hydrogen into the structure.[7,8] The peaks at 3450, 3440, or 3480 cm^{-1} are caused by physically adsorbed water; these peaks disappear after evacuation at 673 K (not shown here) and are analogous to those of other zeolites.[7,8] The peak at 3350 cm^{-1} appears in CuM-150 and in CuM-215, but not in CuM-27, NiM-84, and CrM-58 (not shown here). This peak has not been observed previously and is characteristic of nonstoicheiometrically copper ion-exchanged mordenites. Ferraro *et al.*[9] assigned peaks at about 3300—3400 cm^{-1} in copper(II) complexes to the bridging OH stretching vibration. Tarte[10] also reported the OH vibration in basic copper salts in this region. Taking into account these considerations and our results, we conclude that hydroxy-bridged polymers are formed in this system, *i.e.*, polynuclear complexes of the type $[Cu_x(OH)_y]^{(2x - y)+}$. The maximum extent of exchange for chromium ions is 58%, irrespective of a larger hydrolysis constant than that of copper ions, which excludes the possiblility that the exchange process is mainly a surface reaction or that the basic salts are precipitated when excess copper ion is exchanged. This is supported by the facts that the characteristic OH stretching vibration of excessively ion-exchanged Cu-mordenite does not coincide with that of $Cu(OH)_2$ and that the exchanged copper ions can be re-exchanged with an NH_4Cl solution (1.0 M), as with nickel ions; the coprecipitated basic salt may give rise to the same OH stretching vibration as $Cu(OH)_2$ and may not be re-exchanged with NH_4^+ ion. Thus, it is concluded that the polynuclear complexes of the type $[Cu_x(OH)_y]^{(2x - y)+}$ give rise to excess loading of transition metal cations in the zeolite compared with that predicted from the stoicheiometry. The differences in ion exchange properties between copper and nickel ions are attributable to the difference in the magnitude of the hydrolysis constants,[11] corresponding to the pH value of each solution in our experiment. On the other hand, the exchange capacity of chromium ions does not exceed 100%, irrespective of the large hydrolysis constant of the chromium ion; this may be due to the presence of a relatively large quantity of the large OH-bridged polynuclear species of chromium ions, which would not be exchanged in the pores, in aqueous solution. As the mordenite type zeolite has elliptical one-dimensional channels running parallel to the *c*-axis, it is expected to act as a one-dimensional material. Thus, excessively metal ion-exchanged mordenites should have noteworthy catalytic and electronic properties, and this is being investigated.

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