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Co^2 Ion Exchange in Zeolite NaA

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TECHNICAL NOTE

Co^{2+} Ion Exchange in Zeolite NaA

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ABSTRACT

$^{60}Co^{2+}$ ion exchange at room temperature (20°C) from aqueous cobalt chloride solution with zeolite NaA either hydrated or heated at 150 and 600°C has been studied. In all samples a fast Co^{2+} uptake is found in which 2 meq Na^+ ions/g of zeolite are replaced by cobalt ions. This process is stable and no desorption is observed. These results are quite different from those obtained in previous work with zeolite NaY which showed that sorption was followed by a desorption process.

INTRODUCTION

It has been shown that zeolite "aqueous" chemistry may vary depending on the exchangeable cation. For example, Mn^{2+} and Zn^{2+} ions adopt quite different coordination environments within the zeolite (1).

In a previous work (2) the shape of the Co^{2+} sorption curves against time was discussed for zeolites dehydrated at 150°C. A fast sorption uptake followed by a desorption process was observed, and an equilibrium

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state was then reached. It was inferred that when Co^{2+} ions in aqueous solution are exchanged by sodium ions from zeolite NaY, Co^{2+} ions first occupy the tetrahedrally coordinated sites in the sodalite cages and then the octahedrally coordinated sites in the large cavity. The Co^{2+} ion behavior was explained by the location and coordination of cobalt and by its mobility in the Y zeolite network. Hence, the size of the windows between sodalite cages and large cavities is expected to play a determinant role during the process. The differences between the structures of NaA and zeolites NaY should, therefore, bring new data to understand Co^{2+} sorption in zeolites. Although both zeolites are built from sodalite cages, zeolite A has smaller large cavities (11.4 Å diameter instead of 12.4 Å). In zeolite A, the windows to enter into the large cavities have a diameter of 4.2 Å (8 oxygen atoms), and for zeolite Y these windows are 8 Å (12 oxygen atoms). The Si/Al ratio for zeolite A (1) is lower than for zeolite Y (3.2).

The aim of the present paper is to study the Co ion-exchange behavior in zeolite NaA and to compare the results with those obtained in zeolite Y.

EXPERIMENTAL

Materials and Equipment

Synthetic powder zeolite 4A (less than 50 mesh) in the Na form was treated for 8 days in a 5 N NaCl solution. Cobaltous chloride solution (2), 0.05 N, labeled with ^{60}Co (^{60}Co-labeled solution), was utilized for the cobalt ion-exchange process in the zeolite NaA.

^{60}Co was obtained by neutron irradiating cobalt nitrate for 1 hour in a Triga Mark III reactor with a neutron flux of 10^{12}–10^{13} n/cm^2·s. The irradiation was carried out in a fixed irradiation system. Co^{2+} ion exchange with sodium ions of the zeolite NaA was determined by γ-spectroscopy analyses of ^{60}Co. It was measured either with a NaI(Tl) well detector coupled to a monochannel Picker analyzer or with a Ge/hyperpure solid-state detector coupled to a 2048 channel pulse height analyzer.

All zeolite samples were studied by x-ray diffraction with a Siemens D500 diffractometer with a copper anode x-ray tube. The K_α radiation was obtained with a diffracted beam monochromator. The thermal stability of the exchanged zeolites was also studied by treating the samples at 600°C and obtaining the corresponding x-ray patterns.

Cobalt Uptake Curves

Cobalt ion exchange at room temperature (20°C) was studied in hydrated zeolite NaA and in the same zeolite heated at 150 and 600°C in vacuum.

Each uptake curve was obtained by introducing 200 mg of the zeolite into an Erlenmeyer flask (50 mL capacity) and adding 20 mL of the previously prepared ^{60}Co labeled solutions. After 5 minutes of contact time under occasional stirring, the liquid was separated from the solid by centrifugation and the activity of an aliquot (5 mL) was measured. Fresh solution (20 mL) was then added to the solid left in the bottom of the centrifuge tube, and the above described process was repeated for the chosen time intervals.

RESULTS AND DISCUSSION

The composition of the NaA zeolite used in this work was determined to be $Na_{12}Si_{12}Al_{12}O_{48}\cdot 32H_2O$. The zeolite NaA cation sites per gram of zeolite are 5.58 meq. All the exchanged zeolites were characterized by x-ray diffraction. The integrity of the zeolite network was maintained in all samples.

Co^{2+} Ion Exchange in Dehydrated Zeolite 4A

Curves a and b of Fig. 1 show the ion-exchange behavior of Co^{2+} by the NaA zeolites dehydrated at 600 and 150°C; a fast sorption of Co^{2+} and no desorption were observed. A higher sorption of Co^{2+} was found for zeolite NaA if compared with NaY (1). The maximum Co^{2+} uptake was 2 meq of Co^{2+}/g of zeolite.

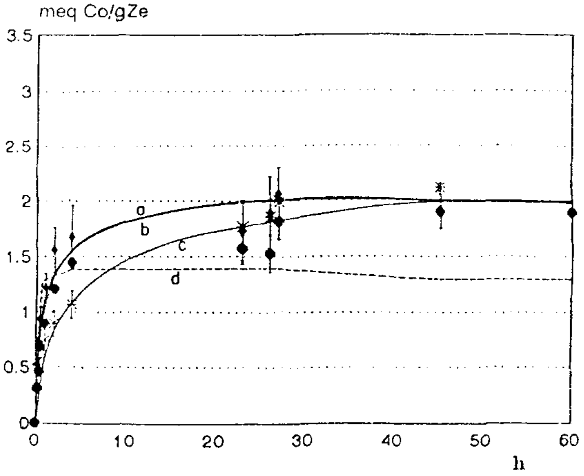

FIG. 1 Ionic exchange behavior of Co^{2+} by zeolites: (a) zeolite NaA dehydrated at 600°C, (b) zeolite NaA dehydrated at 150°C, (c) hydrated zeolite NaA, (d) hydrated zeolite Y.

According to Riley et al. (3), in dehydrated zeolite NaA the Co^{2+} ions lie on a threefold axis so as to protrude somewhat into the large central cavity of the zeolite. At this position bonds to three equivalent zeolite framework oxygen atoms are formed. For hydrated zeolite NaA (1), the four Co^{2+} ions per unit cell are located at two sites: one cobalt ion resides in the sodalite unit where it is coordinated by a regular octahedron of water molecules, the other three Co^{2+} ions are distributed in equivalent sites on unit cell threefold axes in the large cavities. These conclusions agree with those observed by Egerton et al. (4) who found by magnetic studies that in hydrated CoA the ions exist as hexaquo complexes: $Co(H_2O)_6^{2+}$ and, on dehydration, cobalt atoms change from octahedral to tetrahedral coordination. They suggested as well that when zeolite A was dehydrated, the cobalt would then be coordinated to the three nearest framework oxygens and to the oxygen of a residual water molecule in pseudotetrahedral coordination.

On the other hand, Wichterlova et al. (5) pointed out that Co^{2+} in hydrated zeolite Y is coordinated in a hexa-aquo complex with octahedral symmetry in the large cavity, and probably the Co^{2+} ion is not fixed in a discrete position of the zeolite skeleton. In this way, when Co^{2+} was exchanged in dehydrated zeolite Y, a desorption process was observed before the equilibrium was reached since ion exchange takes place together with the hydration process.

Then, in our case, for partially dehydrated cobalt-exchanged zeolite A, Co^{2+} ions are fixed to discrete positions of the zeolite skeleton as described before (5). On the other hand, in the maximum uptake, Co^{2+} is found in the sodalite cages and in the large cavities of zeolite A which have smaller windows than the zeolite Y. Hence, in zeolite A it is difficult to transfer the cations from the large cavity sites, and, therefore, in A zeolite no desorption process is observed.

Hydrated Zeolite

Curve c of Fig. 1 shows the ion-exchange behavior of Co^{2+} by hydrated zeolite NaA. In this case the slope of the sorption curve is smaller, showing that the diffusion process is slower than for dehydrated zeolite A. For hydrated zeolite NaA, the maximum Co^{2+} uptake was again 2 meq of Co^{2+}/g of zeolite, but for zeolite Y the sorption was 1.2 meq of Co^{2+}/g zeolite (2). This behavior may be explained by the different Si/Al ratio, among other factors. Zeolite Y contains 31% less aluminum atoms than A zeolite. The maximum Co^{2+} capture in zeolite Y (Curve d) is close to 1.3 meq/g of zeolite which is, also, 31% lower than 2 meq/g of zeolite.

CONCLUSIONS

The following points emerge from this study.

1. Cobalt ion exchange in zeolite NaA (2 meq/g) is higher than cobalt ion exchange (1.5 meq Co/g zeolite) in zeolite NaY.
2. Cobalt desorption process is not present in Co zeolite A as it has been observed in zeolite Y (2).
3. This paper confirms the results obtained in a previous paper (2), i.e., during the ion-exchange experiments, the coordination of Co^{2+} varies as does its location in the zeolite skeleton (1, 3).
4. The final cobalt uptake from the aqueous cobalt chloride solution by the zeolite NaA is independent of the hydration state of the zeolite (2 meq Co^{2+}/g). The opposite behavior for zeolite Y has been observed elsewhere (2).

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