

Location and Reducibility of Ni Ions in HEU-Type Zeolites

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Received July 31, 1992; in revised form February 8, 1994; accepted February 11, 1994

Starting from a well-characterized natural clinoptilolite (sample HC), the following samples were prepared by ionic exchange with the corresponding cations: NaHC, KHC, CaHC, and MgHC. These samples were exchanged with Ni²⁺ to obtain the samples NiNaHC, NiKHC, NiCaHC, and NiMgHC. Using absorption spectrometry, NH₃ adsorption, thermoprogrammed reduction, and Mössbauer spectrometry we studied the reduction of iron in HC, the cationic composition and adsorption of NH₃ in NaHC, KHC, CaHC, MgHC, NiNaHC, NiKHC, NiCaHC, and NiMgHC, and the thermoreduction in Ni-exchanged samples.

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INTRODUCTION

Catalysis is by far the most important field in the application of zeolites; consequently, the research activity in this area is very intense. In the past three decades, efforts in the study and use of zeolites as catalysts were fundamentally directed toward developing products for the petrochemical industry (1-3), but it is now recognized that the use of zeolites as catalysts in different processes in organic chemistry must be further developed (4, 5).

The chemical reactivity of small metal particles included in the cavities and channels of zeolites and its analogs is of considerable practical interest in the preparation of catalysts (6, 7) for hydrocarbon conversion (3, 8).

For the entrapment of metal particles in zeolites the most important method of preparation involves the ionic exchange of the cation of the metal of interest in the zeolite, calcination, and the reduction of the cationic species with hydrogen (7, 9). The most important features related to the reduction of cations in zeolites are location of the cations, nature of the cations, the reducing agent, influence of cocations, etc. (7, 8, 10).

The preparation and characterization of metallic Ni particles entrapped in zeolite supports by reduction of Ni ions previously exchanged in the zeolite channels and

cavities have been the subject of numerous studies in the past few years for the development of catalytically active phases (6, 7, 11). The aim of the present paper is the study of the influence of Ni²⁺ location in the channels of HEU-type structures and the role of cocations (Na, K, Ca, and Mg) in achieving Ni²⁺ reducibility. The reducibility of Fe present in the zeolite matrix has also been studied.

EXPERIMENTAL

The clinoptilolite natural zeolite was obtained from the deposit of Castillas, Havana, Cuba (labeled HC), with the corresponding elemental composition SiO₂, 66.8%; Al₂O₃, 13.1%; Fe₂O₃, 1.3%; Na₂O, 0.6%; K₂O, 1.9%; CaO, 3.2%; MgO, 1.2%; and H₂O, 12.1%; and a phase composition 85% clinoptilolite and 15% calcite (1-5%), feldspar (0-1%), montmorillonite (2-3%), quartz (1-3%), and volcanic glass. The characterization methods are reported elsewhere (12-14).

The sample HC was refluxed five times during 2 hr in a 3 M solution of NaCl, KCl, CaCl, and MgCl (liquid solid ratio = 2 ml/g) to obtain NaHC, KHC, CaHC, and MgHC. These samples were refluxed five times during 2 hr with 1 M solution of Ni(NO₃)₂ (liquid solid ratio = 2 ml/g) to obtain NiNaHC, NiKHC, NiCaHC, and NiMgHC. The cationic composition of all the specimens was determined by acid leaching (8 hr at 100°C) with HCl (37%) and analysis of the obtained liquors by atomic absorption with a Pye Unicam SP-1900 spectrophotometer.

Adsorption was carried out by a volumetric technique (15), using NH₃ as the adsorbate phase, at 300 K, in the pressure range between 100 and 100,000 Pa. At this T-P range the isotherm does not show hysteresis effects, because capillary condensation of NH₃ does not take place, owing to the physical properties of this gas; i.e., its boiling point is 240 K. Each isotherm consisted of 10 experimental points, and the attainment of equilibrium for each experimental point required about 12 hr; the resulting data were fitted, using a PC program (16), to the Dubinin adsorption isotherm (17),

$$\ln n_a = \ln n_a^0 - \{(RT/E)^n \ln (P_0/P)^n\},$$

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where n_a is the magnitude of adsorption, n_a^0 is the maximum adsorption magnitude, E is the characteristic energy of adsorption, P is the equilibrium pressure, P_0 is the vapor pressure of the adsorbate at the experimental temperature, and n is an empirical parameter.

The temperature-programmed reduction (TPR) experiments were carried out in a conventional apparatus using thermal conductivity (TC) detection (18). The procedure used for the measurement was as follows: A 0.25-g sample was placed in a U-shaped quartz cell and heated from room temperature to 823 K at 10 K/min in a flow of air (20 cm³/min) and maintained at this temperature for 4 hr, followed by cooling to room temperature. Then the air flow was switched to a reductive hydrogen argon mixture (molar ratio, 7:3; flow rate, 25 cm³/min) previously deoxygenated and dried over Pd/Al₂O₃ and Ca-LTA zeolite cartridges. After stabilization of the TC cell, the temperature was increased at 10 K/min to 1273 K, and the hydrogen consumption was monitored and integrated over the whole temperature range. Water evolved during reduction was collected in a Ca-LTA zeolite trap placed just ahead of the TC cell. For quantitative measurements the TC signal was calibrated against a high-purity V₂O₅ sample which was stoichiometrically reduced to V₂O₃ at 800 K (18).

⁵⁷Fe Mössbauer spectra were obtained in a Wissel constant-acceleration spectrometer in transmission geometry with a ⁵⁷Co source in a Rh matrix. The sample thickness was calculated to obtain an iron surface density of about 15 mg/cm²; the isomer shift parameters are reported relative to iron nitroprussite, and the Mössbauer parameters were calculated from the spectra with the help of a computer program (19).

RESULTS AND DISCUSSION

Figure 1 shows the thermoreduction profile of the HC sample, indicating the presence of two reduction peaks. To examine closely these two effects encountered in TPR work we recorded the Mössbauer spectra of two samples reduced at different temperatures (650°C (HC₁) and

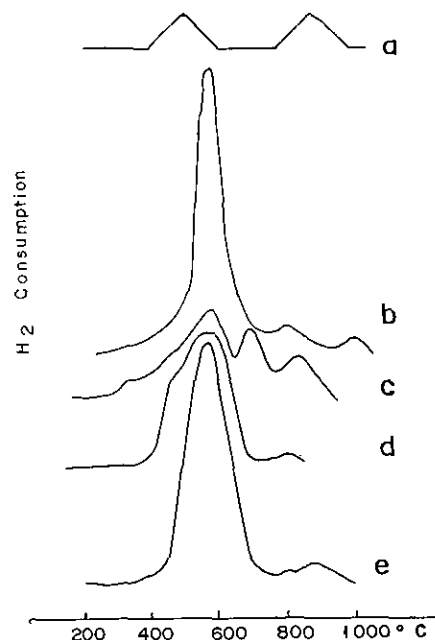


FIG. 1. Thermoreduction profiles of: (a) HC, (b) NiKHC, (c) NiCaHC, (d) NiMgHC, and (e) NiMaHC.

1000°C (HC₂)) and the sample in its natural form. The calculated Mössbauer parameters are reported in Table 1.

In previous papers on the state of iron in zeolites (20, 21) it was shown that Fe³⁺ is located in HC samples on two different sites: site 1 ($\delta_1 = 0.56$ mm/sec, $\Delta_1 = 0.93$ mm/sec) with octahedral coordination, and site 2 ($\delta_2 = 0.55$ mm/sec, $\Delta_2 = 0.35$ mm/sec) with tetrahedral coordination. Fe³⁺ in the octahedral site is in the form of Fe(H₂O)₆³⁺ in extraframework positions, and the tetrahedral Fe³⁺ resides on aluminum sites in the zeolite framework (20) (no Fe²⁺ was found in this sample).

The Mössbauer data taken on sample HC₁ indicate the presence of Fe²⁺ in sites 3 and 4 ($\delta_3 = 1.06$ mm/sec and $\delta_4 = 1.11$ mm/sec), i.e., 88% of the present Fe³⁺ was reduced to Fe²⁺ at 650°C, and the remaining Fe³⁺ is located in tetrahedral sites. The subsequent reduction of Fe²⁺ to Fe⁰ ($\delta_0 = 0.17$ mm/sec) occurs at 900°C; 32% of

TABLE 1
Mössbauer Parameters of Natural and Thermoreduced HC Samples

Sample	δ_0^a	δ_1	δ_2	δ_3	δ_4	Δ_1^b	Δ_2	Δ_3	Δ_4	A_0^c	A_1	A_2	A_3	A_4
HC	—	0.56	0.55	—	—	0.93	0.35	—	—	0	40	60	0	0
HC ₁	—	—	0.54	1.06	1.11	—	0.46	1.25	1.83	0	0	12	33	55
HC ₂	0.17	—	—	1.06	1.04	—	—	1.23	1.89	40	0	0	32	28

Note. Errors for δ and Δ are 0.02 and 0.04 mm/sec, respectively.

^a In mm/sec.

^b In mm/sec.

^c In %.

TABLE 2
Cationic Composition^a of HC, NaHC, KHC, CaHC,
and MgHC

Sample	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
HC	0.2	0.4	0.8	0.7
NaHC	1.6	0.3	0.1	0.0
KHC	0.2	1.7	0.0	0.1
CaHC	0.2	0.3	1.0	0.5
MgHC	0.1	0.3	0.2	1.4

Note. The error in the determination of the cationic composition is 0.1 meq/g.

^a In meq/g.

Fe²⁺ remains on tetrahedral sites, and 28% on octahedral sites.

Table 2 reports the ionic composition of the samples NaHC, KHC, CaHC, MgHC, and HC. The reported data clearly show that Na⁺ and K⁺ are selectively exchanged in HC; i.e., the cationic composition of NaHC involves 80% of Na⁺, vs 84% of K⁺ for KHC. For the bivalent cations Ca²⁺ and Mg²⁺ the degree of exchange is lower (50% of Ca²⁺ in CaHC and 70% of Mg²⁺ in MgHC), in accord with the selectivity rules for ionic exchange in HEU-type zeolites (22).

Table 3 reports the data corresponding to the ionic exchange of Ni²⁺ in NaHC, KHC, CaHC, and MgHC. In all samples Ni²⁺ exchanges with the appropriate cation, i.e., Na⁺ for NiNaHC, K⁺ for NiKHC, etc.

Adsorption data are shown in Table 4; the reported values for the maximum adsorption capacity (n_a^0) for NaHC, KHC, CaHC, and MgHC samples are related to the positions occupied by these cations in the HEU-type zeolite channels. The penetration of gases in this structure is through a series of intersecting channels: channels A (10-member ring) and B (8-member ring) are parallel to each other and parallel to the *c*-axis of the monoclinic C-centered unit cell of the HEU-type zeolite. On the other hand, C channel (8-member ring) lies along the *a*-axis of

TABLE 3
Cationic Composition^a of NiNaHC, NiKHC, NiCaHC, and
NiMgHC Samples

Sample	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Ni ²⁺
NiNaHC	0.4	0.2	0.2	0.1	1.1
NiKHC	0.0	1.2	0.0	0.1	0.8
NiCaHC	0.1	0.2	0.8	0.4	0.6
NiMgHC	0.1	0.4	0.3	0.7	0.7

Note. The error in the determination of the cationic composition is 0.1 meq/g.

^a In meq/g.

TABLE 4
Parameters of the Dubinin Isotherm for the Adsorption of
NH₃ at 300 K Calculated by a Computer Program by Fitting of
Experimental Data

Sample	a_0 (mmole/g)	E (kJ/mole)
NaHC	5.5	25
NiNaHC	5.9	22
KHC	4.2	20
NiKHC	5.5	18
CaHC	5.8	26
NiCaHC	4.9	19
MgHC	6.3	28
NiMgHC	4.6	20

Note. Maximum adsorption is reported in relation to dehydrated adsorbent, i.e., mmole/g of dehydrated adsorbent, and the errors for a_0 and E are 0.05 mmole/g and 1 kJ/mole.

the unit cell, intersecting both the A and the B channels. The most common charge-balancing cations in clinoptilolite are Na⁺, K⁺, Ca²⁺, and Mg²⁺. These cations occupy sites M1 to M4 (25), where M1 is located in channel A and is occupied by Na⁺ or Ca²⁺, and M2 is located in channel B and is fundamentally occupied by Ca²⁺ and Na⁺; K⁺ is located in M3, which is situated in channel C. Finally, Mg²⁺ occupies site M4, located in the center of channel A (23–26).

The maximum adsorption capacity of NaHC is higher than the parameter reported for KHC; this fact is related to the location of K⁺ in site M3, which completely blocks channel C by virtue of its large cationic radius (1.33 Å), whereas Na⁺, located exclusively in M1, does not completely block channels A, B, or C; furthermore, the cationic radius of Na⁺ is lower (0.97 Å). The maximum adsorption capacities reported for CaHC and MgHC samples are higher than those reported for samples NaHC and KHC because these cations are bivalent and occupy half the sites taken up by Na⁺ and K⁺. The relatively high maximum adsorption measured for MgHC is a consequence of its cationic radius (Ca, 0.99 Å; Mg, 0.66 Å) (27).

For the samples NiNaHC and NiKHC the values reported for the maximum adsorption capacities are consistent with the fact that Ni is bivalent, exhibits a low cationic radius (0.69 Å), and tends to occupy sites M1 and M2. In NiCaHC and NiMgHC samples, the low degree of exchange of CaHC and MgHC renders it difficult to interpret adsorption data; nevertheless, the lower maximum adsorption value indicates that Ni²⁺ could be partially located in site M3. The TPR profiles corresponding to samples NiNaHC and NiKHC (Fig. 1) show only one reduction peak; this indicates the existence of a single reduction process. This experimental result is correlated with the location of the reduction reaction in a single site

and with the interference of only one cation (3, 4). In NiCaHC and NiMgHC more than one reduction process is observed, which is related to the interference of different cations present in the samples and to the possible location of Ni^{2+} in the M3 site for these samples.

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