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A neutron diffraction and infrared spectroscopy study of the acid form of the aluminosilicate zeolite, chabazite (H-SSZ-13)

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A powder neutron diffraction study of the structure of D-SSZ-13 (R-3m, $a = 13.6046(6)$, $c = 14.829(1)$ Å, $R_p = 3.79\%$, $R_{wp} = 4.79\%$, $\chi_2 = 2.526$) reveals the presence of two distinct acid sites in the unit cell, one on the six-ring at O(2) and one in the eight-ring window at O(1). These sites are also verified by DRIFT spectroscopy, showing two distinct acid sites upon the dehydration of the zeolite.

Keywords: acid site, solid acid, microporous catalyst

1. Introduction

Acid zeolites find widespread use as catalysts for hydrocarbon conversions in gasoline manufacture [1,2] and other processes such as methanol to olefin reactions [3]. The precise locations of the Brønsted acid sites that are believed to be responsible for such catalysis have been reported in a limited number of systems, including H-SAPO-37 [4], H-Y [5–8], and H-SAPO-34 [9], but there is a pressing need to obtain data on other systems in order that the factors controlling acidity in zeolites might be better understood. In the present work, we describe the structure of the acid form of the high silica, aluminosilicate zeolite, chabazite, known as SSZ-13 [10], and compare its structure with that of its silicoaluminophosphate analogue, H-SAPO-34 [9]. The dehydration of the zeolite was followed using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy with water acting as a probe molecule to test the acidity of the zeolite.

2. Experiments and results

The acid form of SSZ-13 was supplied in its as-synthesized form by Dr. Stacey Zones of Chevron Research and Technology Center. Its preparation has been described elsewhere [10]. The template-containing starting material was calcined at 593 K, ion-exchanged with NH_4NO_3, and finally recalcined to produce the acid form. The latter was deuterated by exposure to D_2O vapor at 353 K and then dehydrated for the neutron diffraction measurements. The Si/Al ratio was determined to be 16 by ^{29}Si MAS NMR. Neutron diffraction data were collected at 5 K using the powder diffractometer, DUALSPEC, at Chalk River Laboratories, Canada. The data were collected at $\lambda = 1.5043$ Å, between 5 and 120° in 2θ. Diffraction data were analyzed by the Rietveld method [11] using the GSAS package [12].

The starting model used for the refinement of the D-SSZ-13 structure was based upon the framework structure of chabazite in space group R-3m. Two acid sites were found during the course of the refinement, one at O(1) in the eight-ring window and the other at O(2) in the six-ring (figure 1). The positions of the deuterium atoms were initially restrained geometrically using an O–D distance of 1.00 Å, but these restraints were even-

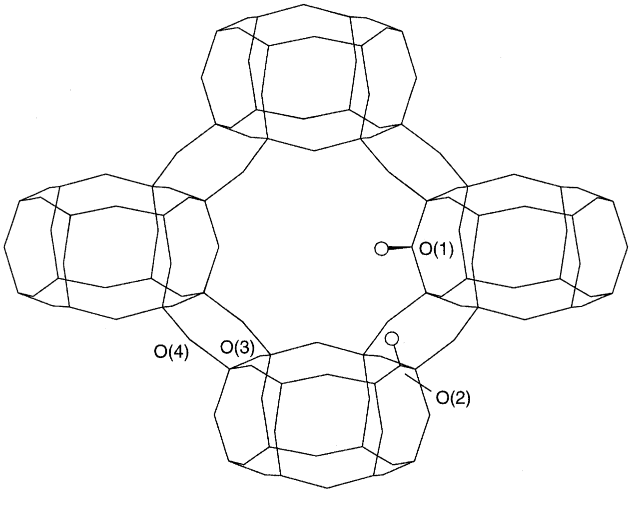

Figure 1. A ball and stick representation of the structure of dehydrated SSZ-13. The figure depicts the hydrogen atoms as spheres while the tetrahedral atoms (Al, Si) and oxygen atoms are omitted for clarity.

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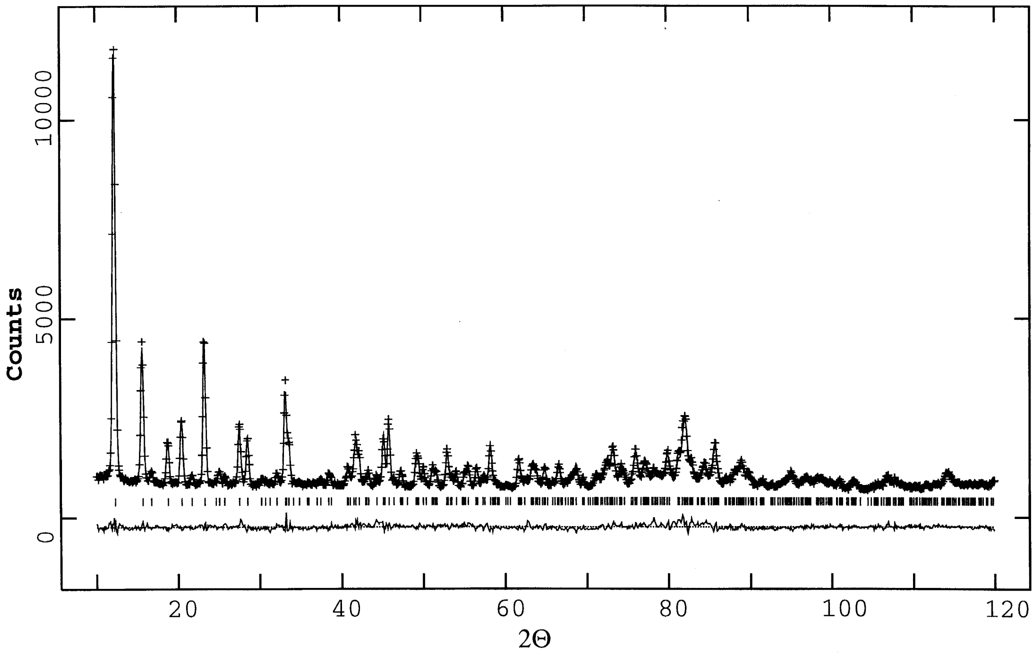

Figure 2. Final observed, calculated and difference profile plots for the neutron refinement of dehydrated SSZ-13.

tually relaxed and both the coordinates and the occupancies of the deuterons were allowed to refine independently. Isotropic temperature factors were refined for two atom types, while those for the deuterium atoms were fixed at the value reported by Czjzek et al. for zeolite H-Y [2]. The bond lengths and key bond angles from the final refinement (figure 2) are reported in table 1.

The fractional occupancy for the deuteron at O(1) was found to be 4.0% (or 1.44 atoms per unit cell) and the O–D distance 1.04 Å ; the corresponding values for O(2) was 8.3% (or 1.49 atoms per unit cell) and 0.93 Å. The deuteron at O(2) was found to tilt towards the center of the six-ring at an angle of 45° from the plane of the Si–O–Al bridge, at a distance of 2.64 Å from the other oxygen of the six-ring (O(3)); this geometry may be stabilized by weak hydrogen bonding, leading to weaker acidity at this site. By contrast, the deuteron at O(1) lies only 19° off its corresponding plane and points towards the center of the supercage.

Infrared spectra were recorded on a Nicolet 850 spectrometer equipped with a DTGS-KBr detector, a diffuse reflectance cell, and a Harrick in situ cell in which the sample was heated (in 50°C steps until 300°C, at a constant rate of 2°C/min, with a 30 min equilibration period at each temperature step). In a typical experiment, 100 scans were accumulated with a 4 cm^{-1} resolution. In the spectra, two narrow peaks at 3603 and 3579 cm^{-1}, characteristic of bridging hydroxyl groups, are present and increase in intensity as the sample is dehydrated; also present is a peak at 3730 cm^{-1} with a lower energy shoulder, which is typical of silanol groups in high silica zeolites (figure 3). The presence of the two bridging hydroxyl peaks cannot be attributed to the splitting of a doubly degenerate mode since their intensities are clearly different, but can reasonably be ascribed to the presence of two types of bridging Brønsted acid sites with different acidities. They are strikingly similar to the features observed in H-SAPO-34 (where they are referred to as the high frequency (HF) and low frequency (LF) bands) and, following ref. [9], we therefore tentatively assign them to the Brønsted acid sites at O(1) and O(2), respectively. Also as in H-SAPO-34 [13], four features can be distinguished upon vacuum treatment at room temperature, a peak at 3670 cm^{-1} and three broad bands at 2879, 2403, and 1610 cm^{-1} (last peak not shown in figure 3). These four peaks have exactly the same behavior: their intensities decrease regularly up to 300°C. Following the analysis in ref. [13], these peaks can be assigned to hydronium ions adsorbed to one or two framework oxygens. Also in this hydrated state is a broad peak at 3540 cm^{-1} which shifts to higher frequencies when the sample is dehydrated. It is likely that this peak is due to water molecules hydrogen bonding to the

Table 1
Bond distances and angles for H-SSZ-13 at 5 K

Bond distances (Å)		Bond angles (deg)	
T–O(1)	1.617(5)	T–O(1)–T	144.8(5)
T–O(2)	1.599(5)	T–O(2)–T	149.4(5)
T–O(3)	1.615(5)	T–O(3)–T	147.8(5)
T–O(4)	1.613(5)	T–O(4)–T	150.0(5)
O(1)–D(1)	1.04(3)	out of the plane by 19°	
O(2)–D(2)	0.93(4)	out of the plane by 45°	
O(3)–D(2)	2.64(4)		

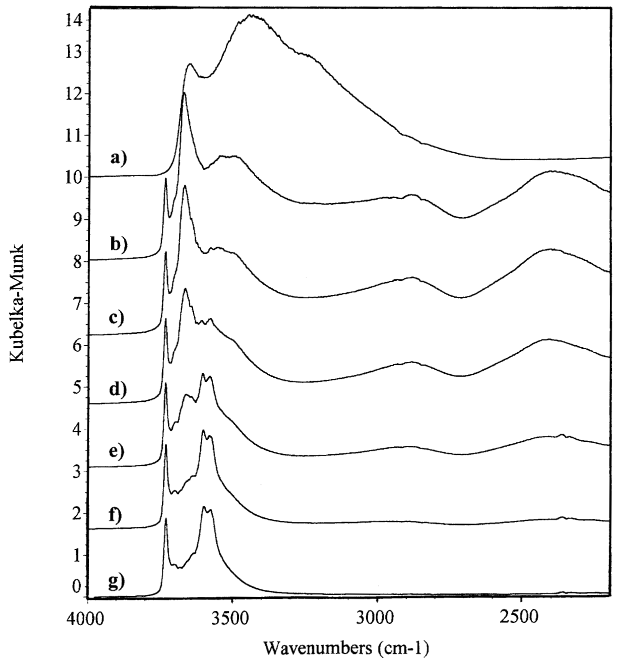

Figure 3. Expanded region of the diffuse reflectance infrared spectra of the dehydration of SSZ-13 recorded at (a) room temperature, (b) room temperature under vacuum (10^{-3} Torr), (c) 100°C (10^{-3} Torr), (d) 150°C (10^{-3} Torr), (e) 200°C (10^{-3} Torr), (f) 250°C 10^{-3} Torr), (g) 300°C (10^{-3} Torr).

protons of acid sites in the zeolite, as was observed in H-SAPO-34 [14].

3. Conclusions

The preference for protonation of O(1) and O(2) shows no correlation with the predictions of quantum chemical calculations [15], which leads us to expect protonation at the oxygens with the smallest T–O–T angles, but the situation may be more complex in H-SSZ-13 due to the narrow range of angles (table 1) and the influence of the hydrogen bonding (see above). It is interesting to compare our findings with the results of recent neutron studies on the silicoaluminophosphate analogue of SSZ-13, H-SAPO-34 [9], where protonation is observed at O(2) and O(4), rather than O(1) and O(2), even though the bond angles are very comparable. However, in the presence of low loadings of water in H-SAPO-34, the proton is removed from O(4) to form a hydronium ion that interacts with O(1) [14]. The presence of a hydronium ion has been observed in the hydrated form of SSZ-13 through infrared spectroscopic methods. A neutron diffraction study of the hydrated form would enable us to determine the relative strengths of the acid sites and what species are present.

Appendix. Supplementary material

Atomic coordinates, occupancies, and temperature factors for the assymetric unit of H-SSZ-13

Atom	Site	x/a	y/a	z/c	Occupancy	U_{iso} ($Å^2$)
Si (1)	36i	0.2273 (4)	0.2277 (4)	−0.3961 (3)	0.9422	0.0136 (11)
Al (1)	36i	0.2273 (4)	0.2277 (4)	−0.3961 (3)	0.0578	0.0136 (11)
O (1)	18g	0.0000	0.7365 (4)	0.5000	1.000	0.0237 (13)
O (2)	18h	0.8786 (2)	0.7572 (4)	0.3703 (4)	1.000	0.0164 (13)
O (3)	18h	0.4716 (4)	0.2358 (2)	0.7134 (3)	1.000	0.0182 (13)
O (4)	18f	0.0000	0.6448 (3)	0.0000	1.000	0.0100 (11)
D (1)	36i	−0.027 (7)	0.650 (4)	0.492 (8)	0.040 (4)	0.0431
D (2)	18h	0.892 (2)	0.784 (5)	0.311 (3)	0.083 (9)	0.0431

Space group, lattice parameters, and profile parameters for H-SSZ-13

space group	R-3m	U	657 (45)
a (Å)	13.6046 (6)	V	−293 (39)
c (Å)	14.8291 (10)	W	263 (7)
zero (deg)	0.3030 (2)	asymmetry parameter	7.0 (1)

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