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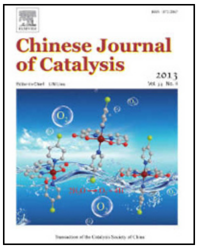

Article

Cation location and migration in lanthanum-exchanged NaY zeolite

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ABSTRACT

$LaNH_4Y$ and LaY zeolites were prepared using a double-exchange double-calcination method by La exchange of NaY zeolite. The distribution of the La cations was determined by powder X-ray diffraction with Rietveld refinement. The results indicate that the La cations are initially located in supercages, and then their hydration shells are stripped off and they migrate to small sodalite structures located at SI′ during heating and dehydration. The changes in the T–O–T angles show significant distortion of the flexible framework and instability in $LaNH_4Y$ obtained using a one-exchange one-calcination process. For La cations located at SI′ and coordinated with O3, the T–O3 bond distance increased, which indicates that the rare-earth cations not only restrain framework dealumination, suppressing condensation of the unit cell, but also have an effect on the T–O3 bond distance, increasing the unit cell volume. The role of the rare-earth species is to ensure the hydrothermal stability of the zeolite in order to control the acid site density and catalytic activity. The effects of La cations and NH_4^+ cations on the zeolite acidity were studied using infrared spectroscopy and NH_3 temperature-programmed desorption, and the mechanism of rare-earth stabilization of the Y zeolite is described.

1. Introduction

Rare-earth (RE)-containing Y-type zeolites (REY) play an important role in fluid catalytic cracking processes, and many studies [1–3] have been performed on the location, migration, and coordination states of RE cations and their effects on the acid properties of zeolites. It is generally accepted that RE cations and water molecules form hydrated RE ions, $RE(H_2O)_n^{3+}$, which are restricted to supercages in the ion-exchange process. During heating and dehydration, the hydration shells of the RE ions are stripped off, and the ions migrate to small cages [4]; this boosts the zeolite stability and catalytic activity as a result of coordination between the cations and the framework oxygen atoms.

The positions of RE cations in a Y zeolite strongly affect the structural stability and acid properties. Although there have been many studies [5–8] on the distribution of RE cations in Y zeolites, very little attention has been devoted to studying the location, migration, and structural changes of the cations in ion-exchange processes for the preparation of REY zeolites. To understand the variations in acidity with zeolite structure in the ion-exchange process, it is necessary to investigate the migration and location of RE species in REY zeolites.

NaY zeolites are inactive in acid catalytic reactions. HY-type zeolites from ammonium-ion-exchanged NaY zeolites have good catalytic activity but poor structural stability. Y zeolites modified with RE elements have high catalytic activities and appropriate stabilities. In industry, RE zeolites are prepared from commercial NaY-type zeolites using a conventional double-exchange double-calcination method. To gain a full under-

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standing of the cation locations, migration, and framework structural changes, the positions, occupations, and coordination of extra-framework cations in the Y zeolites were determined using powder X-ray diffraction (XRD) with Rietveld refinement. Furthermore, zeolite samples were characterized using infrared (IR) spectroscopy and NH_3 temperature-programmed desorption (NH_3-TPD).

2. Experimental

2.1. Sample preparation

The NaY zeolite and NH_4Cl solution were mixed under stirring. A certain amount of $LaCl_3$ aqueous solution was added, and the mixture was kept at 80 °C for 1 h, filtered, and washed, to give $LaNH_4Y$-1. This sample was calcined at 600 °C for 2 h, and the zeolite sample LaY-1 was obtained using a one-exchange one-calcination process.

The ion-exchange treatment with NH_4Cl solution and calcination were repeated, giving $LaNH_4Y$-2 and LaY-2 samples.

Table 1 summarizes the chemical compositions of the samples, determined by atomic absorption spectrophotometry, and the corresponding unit cell compositions. Charge balance is one of the basic principles in zeolite compositions. The unit cell compositions listed in Table 1 show that the sum of the cationic charges is less than the total number of Al atoms; the extra negative charge is neutralized by H^+ to achieve charge balance.

2.2. Sample structure refinement

Powder XRD data were collected using a Scintag XDS 2000 X-ray diffractometer at a scan speed of 0.02°/10 s with 2θ = 4°–80°. Structure refinement was performed using the Rietveld method included in the GSAS software package. The starting model of the zeolite framework was derived from several reports [4,9,10], the initial unit cell parameters were determined using XRD, and the initial values of the occupancy factors were obtained by chemical analysis. It has been reported in the literature [11] that the thermal effects on the isotropic thermal parameters of the zeolite framework are small; therefore, the U_{iso} values were fixed in the remaining refinements at $U_{iso}(T) = U_{iso}(Si, Al) = 0.019$ Å^2, $U_{iso}(O) = 0.038$ Å^2, and U_{iso} (extra-framework atoms) = 0.063 Å^2 to avoid correlation problems.

The structure was refined in the 2θ range 7°–80° because of the large asymmetry in the diffraction peak at 2θ = 6.3°. The peak shape parameters of the profile, GU, GV, GW, LX, and LY, were refined after refining the zero shift, lattice parameter, and the background function. Then the atomic coordinates and occupation numbers were refined. In the last stage of the refinement, all the profile and structural parameters were refined simultaneously to obtain optimal fits and satisfactory structural models.

Table 1
Chemical compositions of the zeolite samples.

Sample	Na_2O (wt%)	La_2O_3 (wt%)	Al_2O_3 (wt%)	SiO_2 (wt%)	Unit cell composition
$LaNH_4Y$-1/LaY-1	1.81	14.12	17.44	66.63	$Na_{8.1}La_{11.6}Al_{58}Si_{134}O_{384}$
$LaNH_4Y$-2/LaY-2	0.66	13.01	16.55	69.78	$Na_{3.1}La_{10.8}Al_{51}Si_{141}O_{384}$

2.3. Sample characterization

IR spectra were obtained using a Bruker TENSOR 27 IR instrument. About 10 mg of sample were pressed into a wafer and loaded in the IR absorption cell. Before the spectra were recorded, the samples were heated to 350 °C, evacuated for 2 h (1×10^{-3} Pa), and then cooled to room temperature.

The acid strength distribution was investigated using NH_3-TPD method. An accurately weighed sample (0.10 g) was placed in a sample tube, and the tube was connected to the NH_3-TPD system. Prior to the measurements, the samples were pretreated at 500 °C for 1 h in a N_2 stream with a ramp rate of 10 °C/min, and then cooled to 100 °C. After NH_3 adsorption stability was achieved, the 100–500 °C region of the spectrogram was recorded.

3. Results and discussion

3.1. XRD patterns of samples

The XRD patterns of the four samples (Fig. 1) all showed only peaks corresponding to the Y zeolites; peaks ascribed to lanthanum oxide or other La-based phases were not observed, suggesting that La species had entered the structures of the Y zeolites or were highly dispersed on the zeolite surface. The diameters of the species would be less than 4 nm, so they would not be observed in XRD experiments [12].

The results reported in the literature [13] indicate that the RE species distributions in supercages and sodalite cages are closely related to the intensities of the diffraction peaks centered at 2θ = 11.8° and 12.4°, which are assigned to the (311) and (222) planes of zeolite crystals. This relationship provided a basis for determining RE cation migration, and a parameter $K = I_{11.8°}/I_{12.4°}$ was defined; a higher K value indicates a larger number of RE species located in sodalite cages. In the LaY-1 sample, there is no diffraction peak at 2θ = 11.8°, as shown in

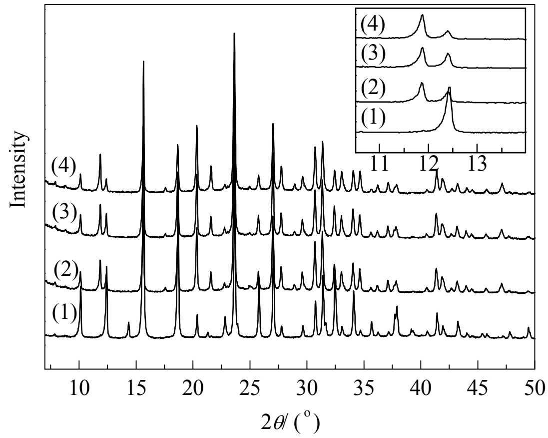

Fig. 1. XRD patterns of zeolite samples. (1) $LaNH_4Y$-1; (2) LaY-1; (3) $LaNH_4Y$-2; (4) LaY-2.