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Article

Cation location and migration in lanthanum-exchanged NaY zeolite

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ABSTRACT

LaNH₄Y 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 LaNH₄Y 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 NH₄⁺ cations on the zeolite acidity were studied using infrared spectroscopy and NH₃ temperature-programmed desorption, and the mechanism of rare-earth stabilization of the Y zeolite is described.

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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(H₂O)_n³⁺, 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 $80\text{ }^\circ\text{C}$ for 1 h, filtered, and washed, to give $\text{LaNH}_4\text{Y-1}$. This sample was calcined at $600\text{ }^\circ\text{C}$ 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 $\text{LaNH}_4\text{Y-2}$ 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 $0.02^\circ/10\text{ s}$ with $2\theta = 4^\circ\text{--}80^\circ$. 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 $U_{\text{iso}}(\text{T}) = U_{\text{iso}}(\text{Si, Al}) = 0.019\text{ \AA}^2$, $U_{\text{iso}}(\text{O}) = 0.038\text{ \AA}^2$, and $U_{\text{iso}}(\text{extra-framework atoms}) = 0.063\text{ \AA}^2$ to avoid correlation problems.

The structure was refined in the 2θ range $7^\circ\text{--}80^\circ$ because of the large asymmetry in the diffraction peak at $2\theta = 6.3^\circ$. 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 re-

finement, all the profile and structural parameters were refined simultaneously to obtain optimal fits and satisfactory structural models.

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 $350\text{ }^\circ\text{C}$, evacuated for 2 h ($1 \times 10^{-3}\text{ Pa}$), 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 $500\text{ }^\circ\text{C}$ for 1 h in a N_2 stream with a ramp rate of $10\text{ }^\circ\text{C}/\text{min}$, and then cooled to $100\text{ }^\circ\text{C}$. After NH_3 adsorption stability was achieved, the $100\text{--}500\text{ }^\circ\text{C}$ 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 $2\theta = 11.8^\circ$ 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 $K = I_{11.8^\circ}/I_{12.4^\circ}$ 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 $2\theta = 11.8^\circ$, as shown in

Fig. 1. XRD patterns of zeolite samples. (1) $\text{LaNH}_4\text{Y-1}$; (2) LaY-1 ; (3) $\text{LaNH}_4\text{Y-2}$; (4) LaY-2 .

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
$\text{LaNH}_4\text{Y-1}/\text{LaY-1}$	1.81	14.12	17.44	66.63	$\text{Na}_{8.1}\text{La}_{11.6}\text{Al}_{58}\text{Si}_{134}\text{O}_{384}$
$\text{LaNH}_4\text{Y-2}/\text{LaY-2}$	0.66	13.01	16.55	69.78	$\text{Na}_{3.1}\text{La}_{10.8}\text{Al}_{51}\text{Si}_{141}\text{O}_{384}$

Fig. 1, thus $K = 0$, which indicates that La cations did not migrate into sodalite cages. Furthermore, as the ion-exchange process progressed, the K value gradually increased and reached a maximum for the LaY-2 sample.

3.2. X-ray structure refinement

The XRD data for the $\text{LaNH}_4\text{Y-1}$, LaY-1 , $\text{LaNH}_4\text{Y-2}$, and LaY-2 samples were refined using the Rietveld method of whole pattern fitting. Table 2 shows the final framework structural data, and the bond lengths and bond angles related to the refined structure are summarized in Table 3.

The structure refinement results (Table 2) show that in the $\text{LaNH}_4\text{Y-1}$ sample almost all the La cations were located in supercages. After calcination, 8 La cations migrated into Si' positions of the sodalite cages and 3.2 La cations were located at SiI . There were no obvious changes in the La cation distribution after the second NH_4^+ ion exchange. When the samples underwent a second calcination, there were 10.5 La cations located at Si' positions and 0.9 La cations at SiI positions, suggesting that most La species occupied Si' positions.

The bond length and bond angle data in Table 3 show that the La cations in Si' positions are coordinated to O3 atoms: $\text{LaNH}_4\text{Y-1}$ ($\text{La-O2} = 3.086 \text{ \AA}$), LaY-1 ($\text{La-O2} = 3.083 \text{ \AA}$, $\text{La-O3} =$

Table 3

Interatomic distances ($\text{\AA}$) and angles ($^\circ$) of the zeolite samples.

Sample	$\text{LaNH}_4\text{Y-1}$	LaY-1	$\text{LaNH}_4\text{Y-2}$	LaY-2
T-O1	1.903(5)	1.799(5)	1.728(4)	1.669(5)
T-O2	1.636(4)	1.542(4)	1.689(4)	1.586(5)
T-O3	1.772(4)	1.885(6)	1.738(4)	1.702(5)
T-O4	1.446(3)	1.446(4)	1.545(4)	1.594(5)
Average	1.689	1.668	1.675	1.638
O1-T-O2	115.1(2)	111.7(3)	111.7(2)	111.9(3)
O1-T-O3	121.0(1)	104.9(1)	111.2(1)	116.3(1)
O1-T-O4	118.9(1)	115.5(1)	107.0(1)	113.5(1)
O2-T-O3	106.0(1)	95.8(2)	101.6(1)	97.9(2)
O2-T-O4	93.2(2)	110.4(1)	104.5(1)	108.2(1)
O3-T-O4	98.0(2)	116.8(3)	120.5(2)	107.8(3)
Average	108.7	109.2	109.4	109.3
T-O1-T	119.6(1)	138.0(1)	133.3(1)	135.0(1)
T-O2-T	145.4(1)	163.1(0)	152.1(1)	158.7(0)
T-O3-T	137.1(2)	132.1(2)	136.1(1)	137.9(2)
T-O4-T	159.3(0)	152.8(0)	137.5(1)	147.9(0)
La-O2	3.086(9)	3.083(9)	3.106(7)	2.892(9)
La-O3		2.407(9)	2.549(8)	2.419(7)

$2.407 \text{ \AA}$), $\text{LaNH}_4\text{Y-2}$ ($\text{La-O2} = 3.106 \text{ \AA}$, $\text{La-O3} = 2.549 \text{ \AA}$), and LaY-2 ($\text{La-O2} = 2.892 \text{ \AA}$, $\text{La-O3} = 2.419 \text{ \AA}$). One possible explanation for the location of La cations at Si' is the fact that this position has relatively stable six-coordination [14]. In the

Table 2

Final structural models of the zeolite samples.

Atom	Position	Atomic parameter	Zeolite samples			
			$\text{LaNH}_4\text{Y-1}$	LaY-1	$\text{LaNH}_4\text{Y-2}$	LaY-2
T(Si, Al)	192i	x	0.1315 (4)	0.1341(5)	0.1299(7)	0.1266(6)
		y	-0.0528(5)	-0.0520(6)	-0.0563(4)	-0.0538(4)
		z	0.0369(4)	0.0354(2)	0.03760(5)	0.0355(3)
		$U_{\text{iso}}^a / \text{\AA}^2$	0.019	0.019	0.019	0.019
		occ ^b	1	1	1	1
O1	96h	$x = -y$	0.1196(5)	0.1115(6)	0.1127(5)	0.1085(4)
		z	0	0	0	0
		$U_{\text{iso}} / \text{\AA}^2$	0.038	0.038	0.038	0.038
		occ	1	1	1	1
		$x = y$	-0.0020(3)	-0.0029(5)	-0.0024(3)	-0.0017(4)
O2	96g	z	0.1493(0)	0.1393(0)	0.1431(0)	0.1321(0)
		$U_{\text{iso}} / \text{\AA}^2$	0.038	0.038	0.038	0.038
		occ	1	1	1	1
		$x = y$	0.1673(6)	0.1777(7)	0.1749(4)	0.1704(5)
		z	-0.0266(5)	-0.0264(4)	-0.0330(3)	-0.0291(6)
O3	96g	$U_{\text{iso}} / \text{\AA}^2$	0.038	0.038	0.038	0.038
		occ	1	1	1	1
		$x = y$	0.1787(6)	0.1829(4)	0.1845(3)	0.1820(5)
		z	0.2974(3)	0.3084(6)	0.3189(3)	0.3114(4)
		$U_{\text{iso}} / \text{\AA}^2$	0.038	0.038	0.038	0.038
O4	96g	occ	1	1	1	1
		$x = y = z$	0.2447(4)		0.2358(5)	
		$U_{\text{iso}} / \text{\AA}^2$	0.063		0.063	
			1		1	
		$x = y = z$	0.0754(5)		0.0553(3)	
NH_4	32e	$U_{\text{iso}} / \text{\AA}^2$	0.063		0.063	
		occ	1		1	
		$x = y = z$	0.2715(3)	0.2691(6)	0.3199(4)	0.2636(3)
		$U_{\text{iso}} / \text{\AA}^2$	0.063	0.063	0.063	0.063
		occ	0.354(3)	0.101(6)	0.095(7)	0.027(4)
La	32e	$x = y = z$		0.0710(4)	0.0700(5)	0.0674(3)
		$U_{\text{iso}} / \text{\AA}^2$		0.063	0.063	0.063
		occ		0.254(7)	0.248(6)	0.327(6)

^a Isotropic temperature factor. ^b Occupation in atoms (ions) per unit cell.

LaNH₄Y-1 sample, La cations are not coordinated to O3 because there are no La cations at SI' positions.

The average T–O distances in the samples are 1.689, 1.668, 1.675, and 1.638 Å. The expected T–O distance is about 1.64 Å, calculated from the ionic radii and average unit cell compositions obtained from chemical analysis (Si–O = 1.61 Å, Al–O = 1.74 Å); however, the average T–O distances deviate from this expected value, except for the LaY-2 sample, so there may be some unknown factor affecting the T–O bonds during the ion-exchange process. According to Scherzer's results [15], the influence of the cations on the T–O bond lengths can be determined from the variations in the bond lengths. A comparison of the T–O3 bond length with those for T–O1, T–O2, and T–O4 in our samples shows that T–O3 is indeed longer, except in the case of LaNH₄Y-1. In LaNH₄Y-1, because of the La cations located at SI', attraction between La and oxygen increases. The unit cell parameter is also closely related to the T–O bond distances; elongation of the T–O3 bond distance might enlarge the unit cell parameters.

The average O–T–O angles are 108.7°, 109.2°, 109.4°, and 109.3° for LaNH₄Y-1, LaY-1, LaNH₄Y-2, and LaY-2, respectively; these are consistent with those reported in previous papers [4,7,16]. The variations in the T–O–T angles indicate distortion of the flexible framework; the change from 119.6° to 159.3° for LaNH₄Y-1 shows the largest framework distortion and structural instability.

3.3. IR spectra in OH stretching region

Figure 2 shows the OH stretching region in the IR spectra of the samples. The band at 3739 cm⁻¹ is assigned to terminal Si–OH groups of the silica-alumina framework and amorphous Si–OH phases, probably generated in the dealumination processes [17]. The band at 3669 cm⁻¹ corresponds to Al–OH groups of extra-framework Al (EFAL) species [18] and that at 3620 cm⁻¹ is characteristic of acidic bridging OH groups located in supercages [19]. The absorption at 3669 cm⁻¹ for LaY-1, LaNH₄Y-2, and LaY-2 is comparable to that for LaNH₄Y-1, which indicates that the zeolites were dealuminated by calcination. The absorption at 3620 cm⁻¹ corresponding to OH groups in zeolite supercages is not observed; this may be because alkali

Fig. 2. IR spectra in OH stretching region of different zeolite samples.

line Na cations shield some of the acid sites. LaNH₄Y-1 shows a shoulder at 3575 and 3550 cm⁻¹, which could indicate the presence of OH groups linked to La species in supercages. The band at 3521 cm⁻¹ in the spectra of LaY-1, LaNH₄Y-2, and LaY-2 is characteristic of OH groups associated with La located in sodalite cages [17]; this reveals that the La ions that are originally located in supercages migrate to small cages after calcination.

3.4. NH₃-TPD

The NH₃-TPD curves of the zeolite samples are shown in Fig. 3. The low-temperature zone of the desorption peak is ascribed to weak acid sites, and the high-temperature zone corresponds to strong acid sites. The stronger the bonding force between the NH₃ molecules diffused into the zeolite channels and the acid sites, the higher the desorption energy that is needed; in this case, acid sites are strong.

From Fig. 3(a), it is easy to see that the LaNH₄Y-1 and LaNH₄Y-2 samples have stronger NH₃ desorption signals. This is attributed to decomposition of NH₄⁺ in the LaNH₄Y zeolite rather than to adsorption and desorption related to the acidity. Based on further analysis of the desorption peaks at around 190 and 258 °C in Fig. 3(a) and the literature [20,21], we believe that the desorption peak at 190 °C arises from physical desorption of NH₃ on the zeolite surface and randomly dispersed NH₄⁺ on the zeolite, and the peak at 258 °C is attributed to decomposition of NH₄⁺ filling zeolite supercavities. In the LaNH₄Y-1 sample, La cations occupy supercavities, so there are fewer NH₄⁺ ions, and ammonia desorption is therefore weak.

Figure 3(b) shows that the acid amount and strength of LaY-2 are higher than those of LaY-1; this may be related to the presence of Na and EFAL, because the presence of Na species would reduce the strong acid amount [22] and EFAL would increase the weak acid content.

Fig. 3. NH₃-TPD curves of different zeolite samples.

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Graphical Abstract

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Cation location and migration in lanthanum-exchanged NaY zeolite

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Lanthanum cations are initially distributed in supercages and then migrate to SI' located inside sodalite cages during heating and dehydration.

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La交换NaY分子筛中的离子定位和迁移规律

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摘要: 以NaY分子筛为原料, 采用二次交换二次焙烧工艺, 制得了 LaNH_4Y -1, LaY -1, LaNH_4Y -2和 LaY -2四种分子筛样品. 采用粉末X射线衍射结合Rietveld结构精修确定了La离子在分子筛中的分布. 结果表明, 在离子交换过程中, La离子首先定位于分子筛超笼里; 经焙烧脱水后, La离子迁移到分子筛方钠石笼并定位在SI'位置. T-O-T键角的变化表明, LaNH_4Y -1表现出最大的骨架扭曲性和结构不稳定性. La离子定位在SI'位置与O3配位, 增加了T-O3的键长, 表明稀土离子不仅通过控制骨架脱铝抑制晶胞收缩, 还可能通过影响T-O3键长使晶胞增大. 在REY分子筛中, 稀土的主要作用是稳定分子筛结构, 从而调节其酸性和催化活性. 采用红外光谱和 NH_3 程序升温脱附考察了La离子和 NH_4^+ 对分子筛酸性的影响, 并总结了稀土离子稳定Y型分子筛的机理.

关键词: LaY型分子筛; Rietveld结构精修; 镧离子迁移; 骨架结构; 热稳定性

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1. 前言

稀土(RE)改性的Y型分子筛(REY)在流化催化裂化中应用最为广泛, 一直以来人们对RE离子进入分子筛的位置、迁移方向、配位状态及其对分子筛酸性的影响进

行了大量的研究^[1-3]. 普遍认为, RE离子与水分子很容易形成稀土水合离子 $\text{RE}(\text{H}_2\text{O})_n^{3+}$, 在离子交换过程中分散在分子筛超笼. 再在焙烧过程中脱除水合外层并迁移到小笼^[4], 与骨架氧原子形成配位, 提高了分子筛的稳定性和催化活性.

RE阳离子在Y型分子筛中的定位状况对分子筛的结构稳定性和酸性有显著影响. 尽管有关RE离子在Y型分子筛分布情况的报道较多^[5-8], 但是有关NaY离子交换法制备REY过程中稀土的移动和定位以及分子筛结构的变化规律尚未见报道. 为了探求离子交换各阶段Y型分子筛结构和酸性的变化, 研究离子交换制备REY过程中离子定位和迁移规律十分必要.

NaY型分子筛对酸催化的反应没有活性, 只有经过 NH_4^+ 交换制成HY型分子筛才具有较高的催化活性, 但HY结构稳定性较差; 通过引入RE离子制成REY型分子筛, 可使其活性和稳定性增加. 在制备REY分子筛时, 工业上广泛采用二次交换二次焙烧的工艺, 为了深入了解在这一过程中稀土离子在Y型分子筛中的定位、迁移规律以及分子筛结构的变化, 本文研究了La离子交换NaY制备LaY的过程, 通过X射线多晶衍射(XRD)进行全谱拟合, 确定了分子筛的结构信息及非骨架离子的定位和分布, 并通过红外光谱(IR)和氨程序升温脱附(NH_3 -TPD)对分子筛进行了表征.

2. 实验部分

2.1. 样品的制备

将NaY与 NH_4Cl 溶液打浆混合, 加入一定量 LaCl_3 溶液, 在80 °C交换1 h. 然后将分子筛浆液抽滤, 水洗, 即得 $\text{LaNH}_4\text{Y-1}$ 样品. 再将其在600 °C焙烧2 h, 得到分子筛样品LaY-1.

将LaY-1样品再次同上进行离子交换和焙烧, 所得样品分别记为 $\text{LaNH}_4\text{Y-2}$ 和LaY-2.

由原子火焰光谱法测定分子筛样品的化学组成, 计算得到分子筛样品的晶胞组成, 结果见表1. 可以看出, 阳离子的电荷总和小于Al的原子总数, 多余负电荷被 H^+ 中和从而整体保持电荷平衡.

2.2. 样品的结构精修

使用Scintag公司XDS 2000型X射线粉末衍射仪表征样品的晶体结构, 扫描速率 $0.02^\circ/10\text{ s}$, 扫描范围 $2\theta = 4^\circ\text{--}80^\circ$. 使用GSAS软件包对样品进行结构精修. 分子筛的初始骨架结构模型来自文献[4,9,10], 采用实验值作为晶胞参数的初值, 化学分析值作为原子的占有率初值. 由于热效应对分子筛原子的温度因子影响不大^[11], 可以在拟合中固定, 并取 $U_{\text{iso}}(\text{T}) = U_{\text{iso}}(\text{Si}, \text{Al}) = 0.019\text{ \AA}^2$, $U_{\text{iso}}(\text{O}) = 0.038\text{ \AA}^2$, $U_{\text{iso}}(\text{非骨架原子}) = 0.063\text{ \AA}^2$.

结构精修选取 $2\theta = 7^\circ\text{--}80^\circ$ 的衍射数据, 由于 $2\theta = 6.3^\circ$ 处显示出较大的不对称性. 峰形函数选取

Pseudo-Voigt, 精修参数包括零点漂移、晶胞参数、背底函数以及峰形参数GU, GV, GW, LX和LY, 之后对原子坐标及占位进行修正, 最后所有参数同时进行精修, 得到最佳拟合和满意的结构模型.

2.3. 样品的表征

FT-IR谱测定在布鲁克TENSOR 27型红外光谱仪上进行, 取10 mg左右的粉末样品压成薄片, 固定在红外池中, 经真空净化(350 °C, $1 \times 10^{-3}\text{ Pa}$) 2 h后, 降至室温录谱.

用 NH_3 -TPD法测定分子筛样品的酸强度分布. 准确称取分子筛样品0.10 g装入样品管, 接入 NH_3 -TPD系统中, 在 N_2 中以 $10\text{ }^\circ\text{C/min}$ 从室温程序升温至500 °C, 稳定后降至100 °C后吸附 NH_3 , 吸附饱和后记录100–500 °C的 NH_3 -TPD谱.

3. 结果与讨论

3.1. 样品的XRD物相

图1为四种分子筛样品的XRD谱. 可以看出, 所有样品均保留了完整的骨架结构, 没有观察到 La_2O_3 或其他有关La的衍射峰, 表明La离子已经进入分子筛结构中, 或者以晶粒小于4 nm的微粒高度分散在分子筛表面, 而未被检测出^[12].

研究表明^[13], 稀土离子在超笼和方钠石笼中的分布可与XRD谱图中(311)晶面($2\theta = 11.8^\circ$)和(222)晶面($2\theta = 12.4^\circ$)衍射峰强度相关联, 它反映了稀土离子的迁移. 由此可以定义一个参数 $K = I_{11.8^\circ}/I_{12.4^\circ}$, K 值愈大表示稀土进入方钠石笼越多, 反之亦然. 由图1可见, 在LaY-1样品中, $2\theta = 11.8^\circ$ 处没有衍射峰, K 值为0, 表明La离子没有进入到分子筛的方钠石笼. 随着离子交换的进行, K 值逐渐增加, 在LaY-2样品上达到最大值.

3.2. XRD结构精修

对 $\text{LaNH}_4\text{Y-1}$, LaY-1, $\text{LaNH}_4\text{Y-2}$ 和LaY-2四种样品进行Rietveld全谱拟合, 表2为样品最终的结构参数, 表3为分子筛骨架与非骨架离子相关的键长和键角.

由表2可见, 在样品 $\text{LaNH}_4\text{Y-1}$ 中, La离子全部定位于分子筛的超笼SII位置, 焙烧后8个La离子定位在方钠石笼SI'位置, 3.2个La离子定位在SII位置. 经二次 NH_4^+ 交换后, La离子分布情况没有发生明显变化; 样品再次焙烧后, 10.5个La离子定位在方钠石笼SI'位置, 0.9个La离子定位在SII位置, 即大部分La离子定位在SI'位置.

如表3所示, $\text{LaNH}_4\text{Y-1}$, LaY-1, $\text{LaNH}_4\text{Y-2}$ 和LaY-2样品中La–O2键长分别为3.086, 3.083, 3.106和2.892 Å. LaY-1, $\text{LaNH}_4\text{Y-2}$ 和LaY-2的La–O3键长分别为2.407,

2.549和2.419 Å, 表明迁移到SI'位置的La离子与骨架O3形成了配位, 一种可能的原因是由于SI'位置有着比较稳定的六配位条件^[14]. 在LaNH₄Y-1中, SI'位置没有La离子的存在, 因此也就没有形成配位.

四种样品的T-O平均键长分别为1.689, 1.668, 1.675和1.638 Å. Si-O = 1.61 Å, Al-O = 1.74 Å, 结合晶胞组成和离子半径, 可以计算得到T-O = 1.64 Å左右, 除LaY-2以外样品的T-O键长均与计算值有所差异, 这可能是由于稀土离子交换过程中某些不确定因素对T-O键的影响. 根据Scherzer等^[15]的研究结果, 骨架外离子也会对T-O键产生影响并通过键长的变化探测, 比较T-O1, T-O2, T-O3和T-O4发现, 除LaNH₄Y-1外, 其他三种样品中T-O3的键长最大, 这是由于La离子占据了SI'位置与通过对O3原子的吸引而增加了T-O3键长. T-O的键长与晶胞参数密切相关, T-O3键长的延伸可能使晶胞增大.

O-T-O平均键角分别为108.7°, 109.2°, 109.4°和109.3°, 与文献一致^[4,7,16]. T-O-T键角的变化表明分子筛骨架结构具有一定的扭曲, 而LaNH₄Y-1的结构中T-O-T键角从119.6°变化到159.3°, 表明LaNH₄Y-1具有最大的骨架扭曲性和结构不稳定性.

3.3. 羟基区红外的测定

图2为四种样品羟基区的IR谱. 3739 cm⁻¹为硅铝骨架末端的Si-OH和分子筛脱铝后形成的Si-OH的吸收带^[17]; 3669 cm⁻¹为非骨架铝形成的Al-OH的吸收带^[18]; 3620 cm⁻¹为定位于分子筛大笼里的酸性羟基的特征吸收带^[19]. 与LaNH₄Y-1比较, LaY-1, LaNH₄Y-2和LaY-2在3669 cm⁻¹出现吸收峰, 表明分子筛经过焙烧处理后骨架脱铝. LaNH₄Y-1和LaY-1没有出现与大笼羟基有关的吸收峰(3620 cm⁻¹), 可能与分子筛中碱性阳离子Na有关, 屏蔽了一部分酸性中心. LaNH₄Y-1中3550和3575 cm⁻¹处的吸收带可能与分散在分子筛超笼的La离子形成的羟基基团有关. 在LaY-1, LaNH₄Y-2和LaY-2样品中3521 cm⁻¹的吸收峰为定位在小笼的稀土组分相关的羟基吸收带^[17], 表明分子筛经过焙烧处理后, La离子从大笼迁移到了小笼.

3.4. NH₃-TPD结果

图3为各分子筛样品的NH₃-TPD. 由图可见, 样品的低温脱附峰对应于沸石弱酸位, 高温区则对应于沸石强酸位. 扩散到分子筛孔道内的NH₃分子与酸中心结合力越强, 脱附所需要的能量就越高, 酸中心强度也就越高. 比较而言, LaNH₄Y-1和LaNH₄Y-2脱附峰面积更大, 这是

由于在高温下LaNH₄Y分子筛NH₄⁺发生分解所致, 而非与酸性有关的吸附与脱附. 进一步分析图3(a), 在190和258 °C存在两个脱附峰, 可分别归属于物理吸附在分子筛表面的NH₃和有序分散的NH₄⁺, 以及分子筛大笼中的NH₄⁺, 由于LaNH₄Y-1样品大笼被La离子所占据, NH₄⁺的数量相对较少, 因而其脱附峰较小^[20,21].

还可以看出, LaY-2样品酸量和酸强度均高于LaY-1, 这与Na含量与非骨架铝的存在有关, 因为Na的存在会导致强酸量减少^[22], 非骨架铝的存在会导致弱酸量增加.

3.5. 稀土离子的移动规律

在稀土离子交换过程中, RE(H₂O)_n³⁺首先通过物理吸附作用定位在分子筛的超笼, 继而在焙烧过程中脱去水合外层进入到方钠石笼, 主要占据SI'位, 与骨架O3形成配位. 适度的离子交换度可提高分子筛的催化活性, 过高的离子交换度则会降低其催化活性. 当一个方钠石笼含有一个稀土离子时, 稀土离子可以呈图4(a)的配位状态.

一个稀土离子与三个O3配位代替了三个H⁺, 通过对水的极化作用产生新的H⁺. 在相同的脱水度下, 相同骨架硅铝比的REY分子筛与HY分子筛相比, 酸量减少而酸强度增加. 因此我们认为, 在理论上, HY分子筛中B酸的数目等于骨架中Al原子的数目, 在稀土离子交换的分子筛中, B酸的数目低于骨架中铝原子的数目. 这种推测与文献一致^[19].

另一方面, 当REY的交换度较高时, 每个方钠石笼含有两个或两个以上稀土离子时, 两个稀土离子通过氧桥键相连^[23,24], 从而替代了6个铝羟基上的H⁺, 且在较高的脱水度下, 只新产生了一个H⁺ (图4(b)), 使分子筛稳定性增加, 但活性下降. 因此稀土离子的主要作用是稳定分子筛的结构, 从而达到调节其酸性和催化活性的作用, 与文献结果相似^[25].

稀土稳定Y型分子筛的机理如下^[20,26]. (1)当Y型分子筛不含稀土离子时, 水热处理过程中分子筛结构的崩塌源自两个骨架上相邻铝羟基之间的脱羟基化作用, 使得Al原子脱离骨架形成非骨架铝. 在高硅铝的分子筛中, 所有的酸性位相对独立, 脱羟基化作用较弱, 因而其稳定性较高. (2)当Y型分子筛经过稀土改性后, 稀土离子存在于方钠石笼与三个骨架O3配位成键. 稀土离子替代了铝羟基上的H⁺, 抑制了相邻铝羟基之间的脱羟基化作用; 相反, REY的脱羟基化作用发生在稀土离子上的羟基与相邻铝羟基之间, 从而减少骨架缺位的产生

(图4(c)).

4. 结论

采用二次交换二次焙烧法制备了 LaNH_4Y 和 LaY 分子筛, XRD全谱拟合结果表明, 在离子交换过程中, La 离子首先定位于分子筛超笼; 经焙烧脱水后, La 离子迁移到方钠石笼并定位在 SI' 位置; 再次交换和焙烧后, La 离子几乎全部迁移到分子筛方钠石笼. 这也得到IR光谱和

NH_3 -TPD结果的验证. 定位于 SI' 位置的 La 离子与骨架 O_3 形成配位, 替代了铝羟基上的 H^+ . 当 REY 与 HY 分子筛骨架硅铝比相同时, 则前者的酸量更低, 但酸强度略高. 在稀土改性的 Y 型分子筛中, 稀土的主要作用是稳定分子筛的结构, 从而达到调节其酸性和催化活性的作用. 在水热处理条件下, 分子筛骨架的脱羟基化作用发生在 RE 的羟基与骨架上质子之间, 从而增加了分子筛的稳定性.