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CHARACTERIZATION OF THE STRUCTURE AND PERFORMANCE OF Ce^{3+} EXCHANGED LIX MOLECULAR SIEVES

KARAKTERIZACIJA STRUKTURE IN LASTNOSTI Ce^{3+} IZMENJALNIH LIX MOLEKULARNIH SIT

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In order to prepare CeLiX zeolite molecular sieves with different Ce^{3+} exchange degrees, LiX zeolite molecular sieves were modified by Ce^{3+} via a cation-exchange method. These sieves were characterized with the FT-IR, XRD, SEM, BET and XRF techniques. The adsorption isotherms of N_2 and O_2 were measured with a gas-adsorption analyzer at 25 °C. The results show that the Ce^{3+} can replace the extra-framework lithium element. The introduction of Ce^{3+} did not change the original crystal structure, and the small spherical powder structure remained unchanged after the modification. The distribution of particle size was uniform with a particle diameter near 4 µm. The exchange percentage of the Ce^{3+} increased with the exchange times. After three rounds of exchange, the exchange percentage reached 61.2 %. The pore size distribution of the LiX zeolite was 2–6 nm before modification, while this value changed to a 7-nm medium-size pore after modification. The introduction of Ce^{3+} can significantly improve the adsorptive selectivity of the LiX zeolite for O_2/N_2 separation. The adsorptive selectivity of the CeLiX was greater than 1 after three rounds of exchange, which indicated the product was oxygen-adsorbent molecular sieves.

Keywords: LiX molecular sieve, cation exchange, adsorptive selectivity, O_2/N_2 separation

Avtorji prispevka so pripravljali CeLiX zeolitna molekularna sita z različnimi stopnjami izmenjave Ce^{3+} kationov. LiX zeolitna molekularna sita so modificirali s pomočjo kationske izmenjevalne metode. Izdelana sita so nato okarakterizirali s tehnikami FT-IR, XRD, SEM, BET in XRF. Adsorpcijske izoterme N_2 in O_2 so merili s plinskim adsorpcijskim analizatorjem pri 25 °C. Rezultati analiz so pokazali, da lahko Ce^{3+} zamenja zunanje ogrodje elementa litija (Li). Uvajanje Ce^{3+} kationov ni spremenilo originalne kristalne strukture in tudi struktura drobnih krogličnih delcev je ostala po modifikaciji nespremenjena. Velikostna porazdelitev delcev je bila enovita s premerom delcev blizu 4 µm. Procentualni delež izmenjave kationov Ce^{3+} je naraščal s časom izmenjave. Po treh krogih izmenjave je procentualni delež izmenjave dosegel 61,2 %. Pred modifikacijo LiX zeolita je bila velikost por 2–6 nm, po modifikaciji pa se je spremenila na povprečno 7 nm. Uvajanje Ce^{3+} kationov lahko pomembno izboljša adsorptivno selektivnost LiX zeolita za ločitev O_2 od N_2. Adsorptivna selectivnost CeLiX je bila večja kot 1 po treh krogih izmenjave, kar kaže na to, da je produkt primeren kot kisikovo adsorpcijsko molekularno sito.

Ključne besede: LiX molekularno sito, kationska izmenjava, adsorptivna selektivnost, O_2/N_2 separacija

1 INTRODUCTION

Molecular sieves have wide industrial applications. They are common catalytic materials, adsorptive separation materials and ion-exchange materials. Microporous molecular sieves play an increasingly prominent role in petroleum chemicals, fine chemicals and daily-use chemical industries.[1–4] The extra-frame cation in molecular sieves can be easily exchanged. The extra-frame cation balances the negative charge of the molecular sieve frame and is usually located in the pore or cage of the molecular sieve. The quantity and the location of the extra-frame cation in molecular sieves have a strong impact on the performance of the molecular sieve, such as the catalytic and adsorptive performance. One or several cations can modify the zeolite molecular sieve with outstanding performance via the ion-exchange method.

Zeolite molecular sieves can be X-type, Y-type or A-type. The X-type zeolite molecular sieve is the most extensively studied.[5,6] The ion-exchange can adjust the surface charge property and the adsorptive performance of the molecular sieve.[7–9] For example, in most cases, the specific surface area of the zeolite molecular sieve slightly decreases after the ion-exchange of the extra-frame cations. The cations to be exchanged have differences in size, quantity and location in the frame structure. The ion exchange can affect the specific surface area and pore size of the zeolite molecular sieve. This can further affect its adsorptive performance to achieve adsorptive separation.[10] For example, the exchange of cations with a high valence state to low valance state reduces the amount of cations leaving a cavity and increasing the pore size of the zeolite. The exchange of a large-radius cation with a small-radius cation can block the cavity of the zeolite molecular sieve and reduce the effective pore size and change the volume of the crystal cavity and specific surface area. [11]

Chao et al.[12] adopted Li$^+$/alkaline earth ions to modify the X-type zeolite molecular sieve by mixed-cation exchange. After modification, the thermal stability and adsorptive selectivity of the zeolite molecular sieve was improved. The selectivity coefficient of the X-type zeolite molecular sieve for N_2/O_2 was 3.7, while that of the LiX zeolite molecular sieve after 97 % lithium exchange was 10.2. Yang et al.[13] used Ag$^+$ to exchange the LiX molecular sieve and obtained AgX molecular sieves composed of 80 % Li$^+$ and 20 % Ag$^+$. This zeolite molecular sieve showed a significant increase in the N_2 adsorptive volume, but showed a small change in the O_2 adsorptive volume. The Ag$^+$ combined into zeolite molecular sieves could improve the adsorptive volume and selectivity coefficient for N_2/O_2 separation. Weston et al.[14–16] found that the N_2 adsorptive volume of a Li-LSX molecular sieve rapidly increased only when the Li$^+$ exchange level was greater than 75 %.

The LiX zeolite molecular sieve is mainly used for N_2 absorption as an outstanding adsorbent for N_2/O_2 separation. It is widely used in air separation for oxygen and nitrogen production. Andrieux[17] developed an adsorbent with a high oxygen selectivity. Loading the transition element complex on the zeolite substrate results in a high specific surface area, and the transition element in the complex can adsorb the oxygen in the gas mixture and function as an oxygen adsorbent. A study by Jasra et al.[18] showed that a NaX zeolite molecular sieve had better oxygen adsorption performance after exchanging alkaline metal ions with trivalent cations.

Due to the high abundance, low cost and stable valance state of Ce^{3+},[19] Ce^{3+} was used to modify the LiX zeolite molecular sieve and prepare a CeLiX zeolite molecular sieve via a cation-exchange method in this study. The structure and adsorptive property on N_2 and O_2 were also characterized in detail.

2 EXPERIMENTAL PART

2.1 Materials and Instruments

The LiX zeolite molecular sieve (n(Si):n(Al)=1.4, powder, Shanghai Hengye Chemical Ltd.), cerium chloride (analytical grade, Tianjin Guangfu fine-chemical institute), cerium nitrate (analytical grade, Tianjin Chemical No.3 factory).

The composition and structure were characterized by NICOLET 6700 Fourier transform infrared (FTIR) spectrometer from Thermo Fisher Scientific (US), MiniFlex 600 X-ray diffraction (XRF) instrument from Rigaku (Japan), 1530 VP scanning electron microscope from LEO (Germany), ASAP2020 specific surface area and porosity analyzer from Micrometritics (US), SRS3400 X-ray fluorescent spectrometer from Bruke (Germany) and 3H-2000PH gas adsorption analyzer from BSD (China).

2.2 Modification of molecular sieve

The LiX zeolite molecular sieve was modified by cation exchange in an aqueous solution. A pre-treated LiX molecular sieve (calcined at 300 °C for 2 h) was continuously mixed with cerium chloride solution under certain conditions via an isothermal magnetic mixer (**Table 1**). The middle product was then filtered, washed, dried and calcined to produce a product after one exchange. This experimental procedure was repeated three times. LiX zeolite molecular sieves with different Ce^{3+} exchange degrees were eventually obtained and denoted as CeLiXn (n represents the times of the exchange).

Table 1: Ion-exchange reaction conditions

Molecular sieve	Raw material	Dosage (g)	Solution concentration (mol·L^{-1})	Solution volume (mL)	Reaction temperature (°C)	Reaction time (h)
CeLiX1	LiX	12	0.1	200	80	3
CeLiX2	CeLiX1	8	0.1	200	80	3
CeLiX3	CeLiX2	4	0.1	200	80	3

3 RESULTS AND DISCUSSION

3.1 Structure of Molecular Sieve Frame

3.1.1 FTIR analysis

Figure 1 shows the adsorption peak at 3500 cm^{-1}, indicating the stretching vibration of the –OH group from free water molecules adsorbed on the surface of a molecular sieve. The adsorption peak at 3500 cm^{-1} is attributed to the crystal water inside the zeolite molecular sieve. The 1000 cm^{-1} and 725 cm^{-1} adsorption peaks are attributed to the asymmetrical and symmetrical stretching vibrations of the tetrahedron inside the zeolite molecular sieve, respectively. These are characteristic of the X-type zeolite.[20] These results show that introducing the cerium ion did not damage the original structure, and the crystal structure remained unchanged.

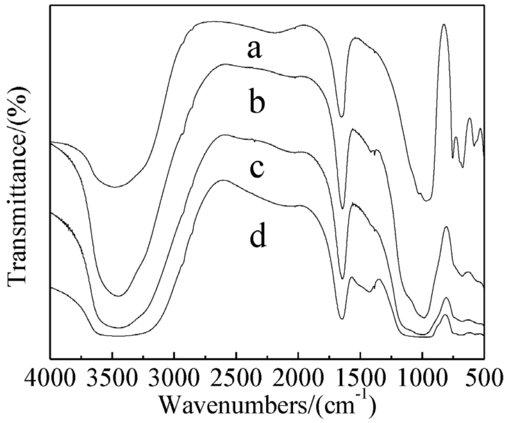

Figure 1: Infrared spectra of zeolite molecular sieve (a for LiX, b for CeLiX1, c for CeLiX2, d for CeLiX3)

The location of the adsorption peaks in the FTIR remains the same before and after the Ce^{3+} modification. The only change was the intensity of some adsorption peaks. The characteristic peaks of the molecular sieves modified by different reaction times have the same location; only the peak strength is inversely proportional to the exchange times. The decrease in peak strength is possibly due to the combination of anions in the cerium salt with Si-OH or Al-OH groups on the surface of the LiX zeolite molecular sieves. This might also be due to the effect of Ce^{3+} itself on the molecular sieves.[10,21]

3.1.2 XRD analysis

Figure 2 shows the XRD spectra of CeLiX zeolite molecular sieve. **Figure 2** compares the LiX zeolite molecular sieve before and after the Ce^{3+} exchange. The diffraction peak of the LiX molecular sieves has a small change on the diffraction angle. Its strength decreases, indicating that the ion exchange has a small impact on the basic structure of zeolite molecular sieves. However, introducing Ce^{3+} decreases the strength of the diffraction peak of the LiX zeolite molecular sieve. This might be due to two reasons. First, cerium chloride is a strong-acid and weak-base salt. The hydrolysis of cerium chloride makes the solution acidic and destroys the silicon aluminum frame of the zeolite molecular sieve. Second, multiple exchanges damage the zeolite molecular sieve. Nonetheless, the XRD spectra of the CeLiX zeolite molecular sieve have a characteristic peak of the LiX zeolite molecular sieve. This indicates that despite some reduction in the integrity of the crystal, introducing Ce^{3+} does not change the original crystal structure of the zeolite, which both have a cubic pattern.

3.1.3 SEM analysis

We used the SEM technique to characterize the morphology before and after modification (**Figure 3**). Compared to the unmodified LiX zeolite molecular sieve, the powder surface after modification is coarser and shows signs of corrosion. Nevertheless, both have a small spherical powder structure with a uniform particle size distribution and a diameter of about 4 μm. The powder particle of the CeLiX zeolite molecular sieve has an octahedral structure, and its lattice structure does not collapse.

3.2 Specific Surface Area and Pore Diameter Analysis

3.2.1 Specific surface area of molecular sieve

The BET technique was used to measure the N_2 adsorption data at –196 °C for CeLiX zeolite molecular sieves that were treated for different exchange times. The specific surface area can be calculated using the BET equation (**Table 2**). The CeLiX zeolite molecular sieve has a slightly smaller specific surface area than that of the LiX zeolite molecular sieve perhaps because of the smaller radius of Li$^+$ (0.068 nm) relative to Ce^{3+} (0.103 nm). The charge density of Li$^+$ is also lower than Ce^{3+}. This makes it difficult for Ce^{3+} to find a stable location in the pores of the zeolite molecular sieve. Therefore, the content of Ce^{3+} in the CeLiX zeolite molecular sieve is not high. The change in the specific surface area of the CeLiX zeolite molecular sieve is small. In addition, the XRF analysis shows that the Ce^{3+} exchange percentage increases with exchange times. After three rounds of exchange, the exchange percentage of cerium ion reaches 61.2 %.

Table 2: Ce^{3+} exchange percentage and specific surface area of CeLiX zeolite molecular sieves

Molecular Sieve	Specific surface area /(m^2 g^{-1})	Ce^{3+} exchange percentage/%
LiX	56.31	0
CeLiX1	50.74	26.4
CeLiX2	51.02	46.5
CeLiX3	48.67	61.2

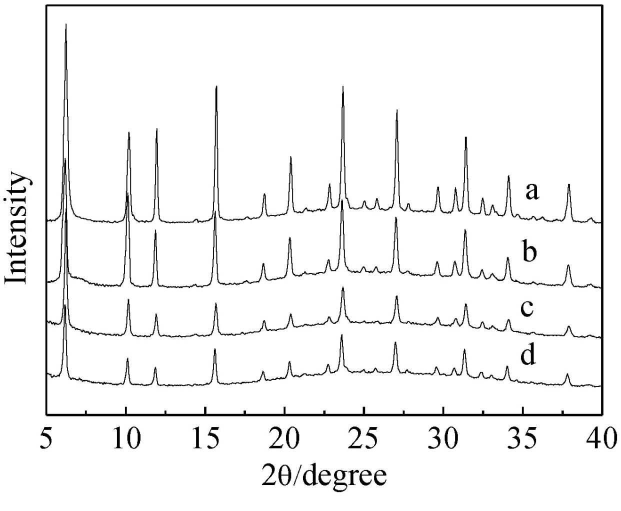

Figure 2: XRD spectra of zeolite molecular sieve: a) for LiX, b) for CeLiX1, c) for CeLiX2, d) for CeLiX3)

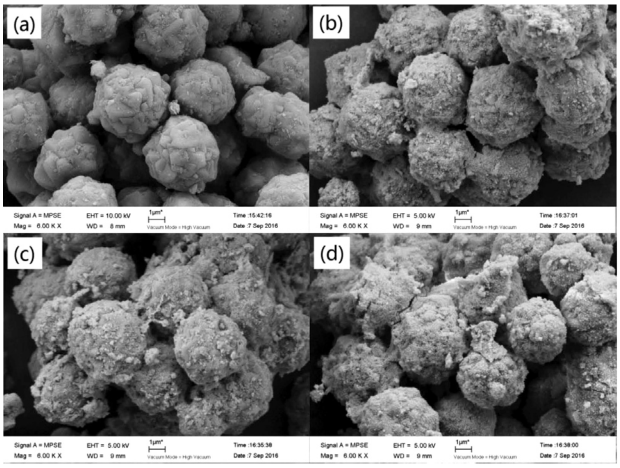

Figure 3: SEM image of zeolite molecular sieve: a) for LiX, b) for CeLiX1, c) for CeLiX2, d) for CeLiX3, 6 K magnification)

3.2.2 Pore size of zeolite molecular sieve

Figure 4 shows the adsorption-desorption curves of the LiX and CeLiX zeolite molecular sieves measured at the temperature of liquid nitrogen. The shape of the curve is related to the pore structure. The IUPAC classification shows four types (I, II, IV, VI) of curves that fit the porous materials. The adsorption-desorption curves of LiX and CeLiX in **Figure 4** match type IV. Furthermore, the zeolite molecular sieve showed a single-layer adsorption with more obvious capillary condensation. This shows a significant increase in the large pores after modification.

If the desorption and adsorption processes are not completely reversible, then the discrepancy between the adsorption and desorption curves can be observed. This is called hysteresis, and the adsorption and desorption curves form a hysteresis loop. IUPAC classifies hysteresis loops into four types (H1, H2, H3, and H4). In **Figure 4**, the hysteresis loops are formed by the adsorption-desorption curve for LiX and CeLiX zeolite molecular sieves. These are H3 and H1 types, respectively. The H3 type is mostly attributed to the narrow slit pore channel, and the H1 type is mostly attributed to the pore channel with a uniform size and regular shape. The common pore structures result in a H1-type hysteresis loop. These are individual and cylindrically narrow pores and long channels with a uniform pore size. The packing of uniform spherical particles forms the cavity. This result agrees with the SEM image, indicating that the prepared CeLiX zeolite molecular sieves are spherical particles with uniform size.

The pore size distribution is shown in **Figure 5**. After exchange with Ce^{3+}, the 7 nm medium-size pore was created in the LiX zeolite molecular sieve. This shows that the ion-exchange method cannot only decorate the surface property of zeolite molecular sieve, but can also adjust the structure of the medium-size pores. The number of pores with diameters between 2 nm and 6 nm greatly decreased after the ion-exchange. This indicates that ion exchange can impact the original pore channel. The result matches the adsorption isotherm and shows the increased pore diameter.

3.3 N$_2$ and O$_2$ Adsorption Performance of Zeolite Molecular Sieve

The adsorption isotherm curve of CeLiX zeolite molecular sieves with N$_2$ and O$_2$ is shown in **Figure 6** at 25 °C and 5–110 kPa. The N$_2$ adsorption of LiX zeolite molecular sieve decreases while O$_2$ adsorption increases after cerium exchange. After three rounds of exchange, the O$_2$ adsorption quantity of the CeLiX3 zeolite molecular sieve is larger than the N$_2$ adsorption quantity. This is related to the existing f-orbital in the Ce^{3+} as seen in reference.[22] The Ce^{3+} has a 4f^1 electron structure, and the Ce-O bond has both ionic and valence components. This makes Ce^{3+} easier to oxidize to stable CeO$_2$ and increases the O$_2$ adsorption quantity.

The N$_2$ and O$_2$ adsorbing capacity and the N$_2$/O$_2$ adsorptive selectivity of LiX and CeLiX zeolite

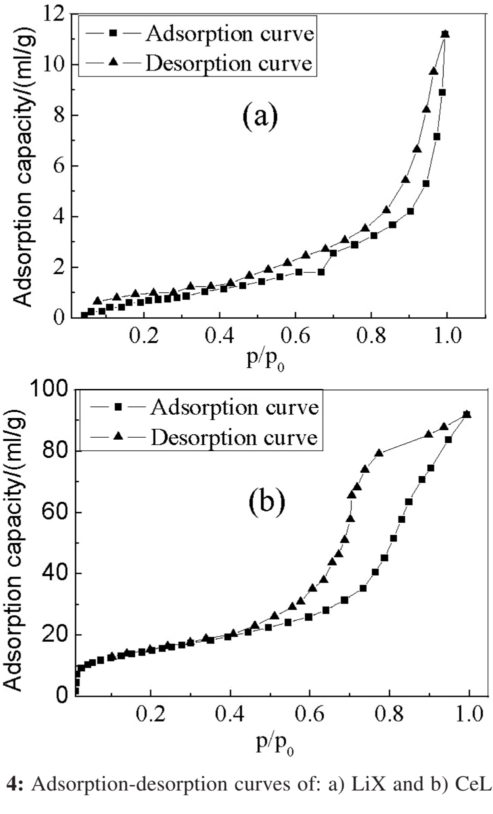

Figure 4: Adsorption-desorption curves of: a) LiX and b) CeLiX

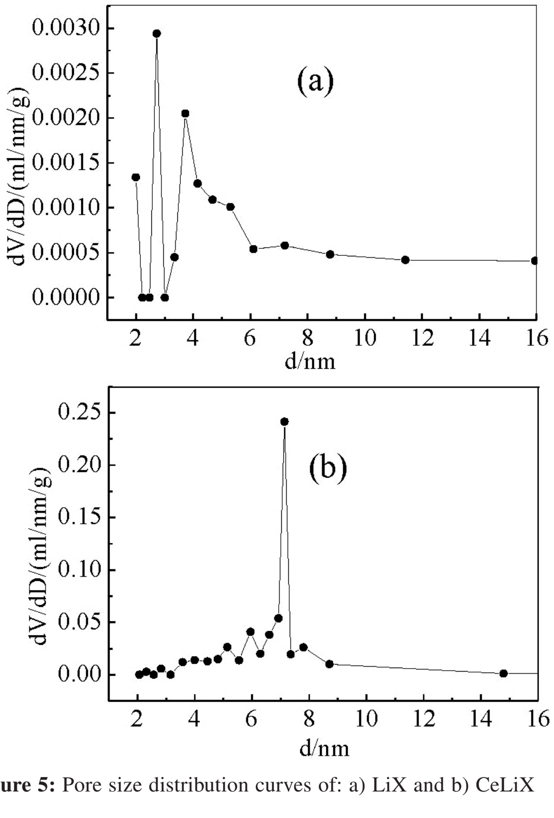

Figure 5: Pore size distribution curves of: a) LiX and b) CeLiX

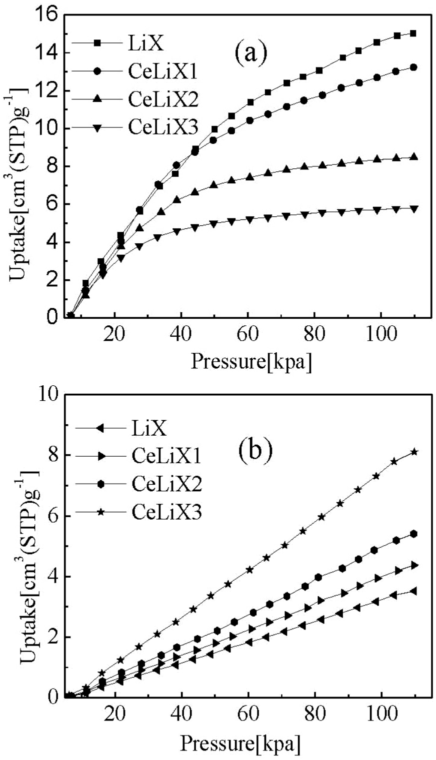

Figure 6: N_2 (a) and O_2 (b) adsorption isotherms of LiX and CeLiX zeolite molecular sieves (25 °C)

molecular sieve at 25 °C and 110 kPa are listed in **Table 3**. The N_2 adsorbing capacity of the CeLiX zeolite molecular sieve gradually decreased to 5.8 cm^3/g with increasing exchange times. This is because the major force between Ce^{3+} and N_2 is Π complexation. This is weaker than the polarization between Li$^+$ and N_2. The O_2 adsorption capacity initially increases, which indicates that introducing Ce^{3+} increases the adsorption of LiX on the zeolite molecular sieve. This is possibly because Ce^{3+} increases the active sites for O_2 adsorption on LiX zeolite molecular sieves. This is related to the pH of the salt solution used for the exchange.

Table 3: Nitrogen and oxygen adsorption properties of LiX and CeLiX molecular sieve (25 °C)

Molecular sieve	Adsorbing capacity /(cm^3·g^{-1})		N_2/O_2	O_2/N_2
	N_2	O_2		
LiX	15.0	3.5	4.3	0.2
CeLiX1	13.2	4.4	3.0	0.3
CeLiX2	8.5	5.4	1.6	0.6
CeLiX3	5.8	8.1	0.7	1.4

4 CONCLUSIONS

The cation-exchange method from an aqueous solution can successfully introduce Ce^{3+} into the LiX zeolite molecular sieve. The introduction of Ce^{3+} reduced the crystallinity of the LiX zeolite molecular sieve while maintaining the same crystal structure as X-type zeolite molecular sieves. The powders had a small spherical structure before and after the modification. The particle diameter was around 4 μm. Corrosion was seen on the particle surface after modification. Modification with Ce^{3+} increased the pore diameter of the zeolite molecular sieve and made the pore size distribution more uniform. These results show that the modification of LiX zeolite molecular sieves by Ce^{3+} is feasible. Adding Ce^{3+} can enhance the adsorption capability of zeolite molecular sieves for O_2 and suppress N_2 adsorption. This reverses its adsorptive selectivity to N_2/O_2 and makes it an oxygen superior adsorptive agent.

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