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Study on Channel Features and Mechanism of Clinoptilolite Modified by $LaCl_3$

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Abstract

Natural clinoptilolite was modified by $LaCl_3$ at different ion concentrations, particularly focusing on the effects of $LaCl_3$ on surface area, average pore width and pore volume distribution. And the structure was characterized by analyzing the X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, and Energy Dispersive Spectroscopy (EDS). The results showed that the surface area, total pore volume and micropore area decreased after modified by $LaCl_3$, while the average pore width increased, among which the micropore area most significantly changed. The result of IR indicated that $LaCl_3$ did not enter into silico-oxygen tetrahedron skeleton to participate in skeleton vibration. The result of XRD showed that the crystallinity of the modified clinoptilolite was slightly reduced, and the diffraction peak deviated to small angle, but the crystal structure kept invariant. The result of EDS, FT-IR and XRD demonstrated that $LaCl_3$ can be loaded on the surface and channels of clinoptilolite, which led to degradation in absorption performance of clinoptilolite to ammonia nitrogen while for phosphorus increases.

Keywords: clinoptilolite, surface area, average pore width, pore volume distribution, infrared spectrum, X-ray diffraction

1. Introduction

Clinoptilolite is a porous material with a regular structure and aperture less than 10 nm, composed of aluminosilicate framework, cavities, channels, cations, and water molecules (Krishnarao & Subrahmanyam, 2003). The specific surface area increases ten million times when the cube with side length of 10^{-2} m is divided into small cubes with side length of 10^{-9} m. Thus the nanometer-grade grain has an ultra-high specific surface area, with many unique surface effects (Dou et al., 2009). Pores in the framework and channels of the clinoptilolite have a large internal surface area, and thus leads to the potential of adsorption (Zhang & Shi, 2012; Chen, 2012). However, clinoptilolite has a poor adsorption performance to phosphate because its structure is negatively charged (Sun et al., 2010). Since rare earth metals have good affinity with phosphate ions, the application of rare earth metals in sewage treatment has become a new technical focusing point (Wu & Hu, 2011). Lanthanum is cheaper when compared with other rare earth elements and the effect of trace lanthanum on human health is not yet conclusive (Chen et al., 2010). Therefore lanthanum has been widely used to improve the performance of existing adsorbents and the phosphorus removal rate.

Currently, researchers often use lanthanum chloride and lanthanum nitrate for clinoptilolite modification, adjusting the pH by adding NaOH to make lanthanum hydroxide precipitate to the surface of clinoptilolite. Or roasting the clinoptilolite modified by lanthanum hydroxide in order to render lanthanum hydroxide decompose to lanthanum oxide (Zhang, Wan, & Chang, 2011; Zhang, Zhou, & Liu, 2012). Considering that the generation of lanthanum hydroxide needs to consume a lot of alkali, and if using lanthanum oxide to modify directly, the problems are that lanthanum oxide is insoluble in water and the pharmaceutical utilization is low. Furthermore, previous studies mostly concentrated on the performance of lanthanum-modified clinoptilolite to remove contaminants, but the pore characteristics of modified clinoptilolite particles and the action mechanism between lanthanum and clinoptilolite are little studied. Thus this article uses clinoptilolite as research subject, and uses $LaCl_3$ to modify clinoptilolite. Then through analyzing the surface area, average pore width and pore volume distribution changes of modified and unmodified clinoptilolite, the influence law of clinoptilolite pore characteristics caused by modification can be found. Using EDS, IR, XRD, and etc. to characterize its structure, and analyze the action mechanism of $LaCl_3$ and clinoptilolite particles.

2. Materials and Methods

2.1 Materials and Equipments

Sample materials: Natural clinoptilolite from Shenyang was chosen for sample materials. After grinding for a certain period of time and sieving, particle size of natural clinoptilolite between 0.12 to 0.16 mm was selected to be cleaned its surface impurities with deionized water, then it was oven-dried for preparation (Sun et al., 2012). The chemical concentrations of the sample were: SiO_2 (68.75%), Al_2O_3 (12.26%), Fe_2O_3 (1.21%), CaO (2.57%), K_2O (2.83%), Na_2O (1.08%), MgO (0.81%). XRD diffraction analysis showed that the clinoptilolite is calcium type clinoptilolite. During the test, the pharmacy used were of analytical pure, the water used was deionized water.

Test and analysis equipment: Rigaku DMAX-RB 12KW X-ray diffractometer, Nicolet 5MX Fourier Transform Infrared Spectrometer, V-Sorb 4800 Specific surface area and pore size analyzer, S250MK3 Scanning electron microscopy.

2.2 The Preparation of Modified Clinoptilolite

4 grams of natural clinoptilolite were dissolved in a series of solution with different concentration of lanthanum chloride, add deionized water to 200 ml. Natural clinoptilolite was dispersed in solution by prolonged stirring (2 h, 300 $r{\cdot}min^{-1}$) with a magnetic stirrer. After filtering, the sample was oven-dried at 60 ^{o}C for 3 h, place the samples in the dryer for preparation.

2.3 Characterization of Modified Clinoptilolite

2.3.1 Characterization of Channel Characteristics Change

Using V-Sorb 4800 specific surface area analyzer and pore size distribution, with static volumetric method for measuring principle, according to the nitrogen adsorption isotherm, using the BET method to calculate the specific surface area of the natural clinoptilolite and the modified, using BJH method to calculate the pore width distribution of mesoporesand macropores, HK method for micropore, micropore volume is calculated using t-plot method.

2.3.2 Structural Characterization

EDS was used for testing the composition difference between natural and modified clinoptilolite, XRD was used for testing their crystal structure change, and IR spectroscopy was for testing their group change.

3. Results and Discussion

3.1 Pore Characteristics of $LaCl_3$-Modified Clinoptilolite before and after the Modification

Physical adsorption method-BET is now recognized as one of the best ways to determine specific surface area of solid. Pore size distribution is a characterization of the relationship between pore radius and pore volume of porous materials, and the BJH method is one of the most widely used methods to determine pore size distribution. But BJH ignores the enhancement of adsorption potential in micropores, only suitable for describing pore size distribution of mesopores. HK model considers the enhancement of microscopic potential, resulting in a good description of pore size distribution to some certain extent (Zhang et al., 2006).

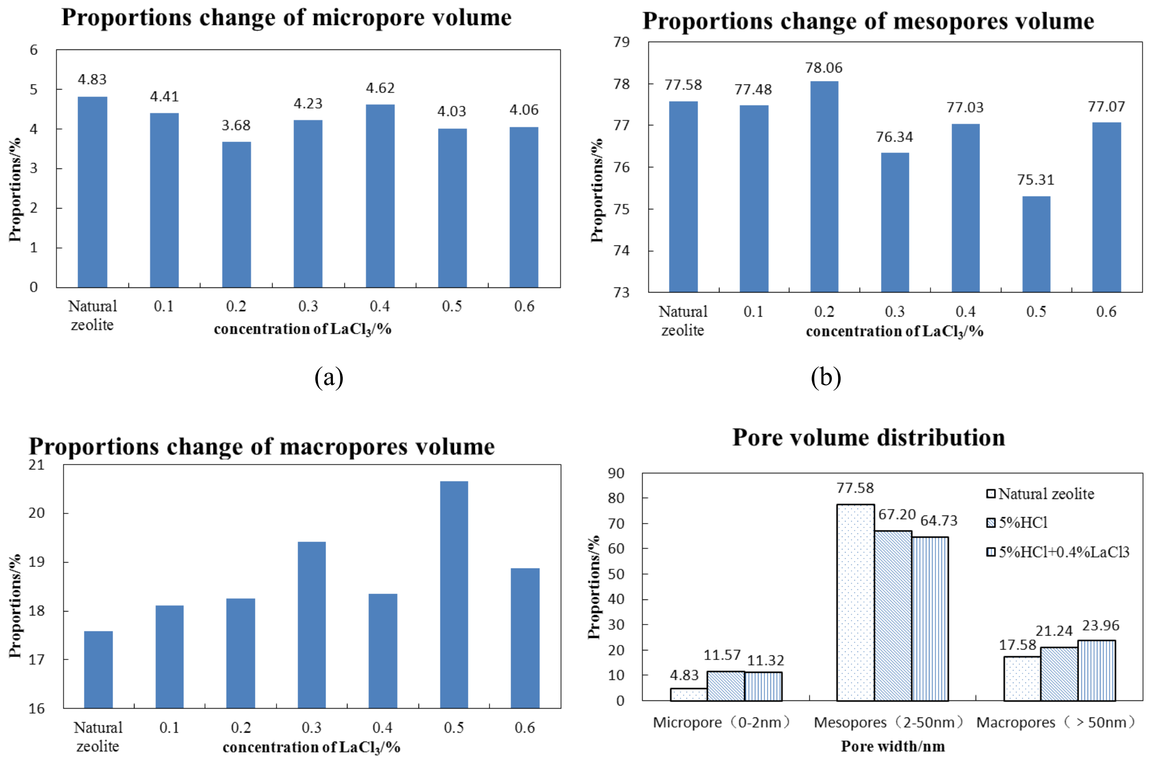
Table 1 shows the data of surface area and pore size distribution of unmodified and modified clinoptilolite. The BET specific surface area of unmodified clinoptilolite is 38.54 m^2/g, and the total pore volume is 0.058 cm^3/g. T-plot method shows that micropore area is 6.49 m^2/g. After modification of $LaCl_3$ with different concentrations, the surface area, total pore volume, micopore area decreased, but the average pore width increased.

Table 1. Change of surface area and distribution of pore width about clinoptilolite modified by $LaCl_3$

Concentration of $LaCl_3$ (%)	Surface area (m^2/g)	Average pore width (nm)	Total pore volume (cm^3/g)	T-plot micropore area (m^2/g)
0	38.54	6.27	0.058	6.49
0.1	30.41	6.70	0.050	5.14
0.2	32.10	6.68	0.052	4.62
0.3	31.92	6.88	0.045	5.67
0.4	32.70	6.51	0.051	5.79
0.5	30.86	7.01	0.052	4.91
0.6	31.71	6.65	0.051	4.88

Table 2. Change of surface area and distribution of pore width about clinoptilolite modified by HCl

Sample	Surface area (m^2/g)	Average pore width (nm)	Total pore volume (cm^3/g)	T-Plot micropore area (m^2/g)
Natural Clinoptilolite	38.54	6.27	0.058	6.49
5% HCl	52.15	5.78	0.075	19.27
5% HCl + 0.4% $LaCl_3$	41.54	6.16	0.064	15.29



(a) (b)

(c) (d)

Figure 1. (a) Micropore volume proportions of clinoptilolite modified by $LaCl_3$ at different ion concentrations; (b) Proportions change of mesopores volume; (c) Proportions change of macropores volume; (d) Pore volume distribution change of clinoptilolite modified by 5%HCl, 5%HCl with 0.4%$LaCl_3$

Figures 1(a-c) showed pore volume distributions of micropore, mesopore and macropore of clinptilolite modificated by $LaCl_3$ with different concentrations, respectively. The results showed that different concentrations of $LaCl_3$ had different effects on clinoptilolite modification, and pore volume distributions of micropore, mesopore and macropore were also different. This data of pore volume distribution was obtained by combining BJH adsorption method and HK model. The overall tests showed that $LaCl_3$-modification caused decrease in pore volume ratio of micropore and mesopore, but increase in pore volume ratio of macropore, compared with the unmodified clinoptilolite. This is mainly due to that the adsorption sites of La presented in the surface and pores of clinoptilolite, thus a proportion of $LaCl_3$ was loaded within channels in the clinoptilolite, and this part of La mainly existed in micropores and mesopores.

Through variations of specific surface area, average pore width, total pore volume, micropore surface area and pore volume distribution after modification by $LaCl_3$ with different concentrations, it can be inferred that the decrease in pore volume ratio of micropore and mesopore will inevitably result in a large increase in the pore volume ratio of macropore, which was not enough to prove that modification can widen the channels, but it can prove that $LaCl_3$ existed in the micropores and surface of the clinoptilolite, thereby causing reduction in the specific surface area and micropore area of modified clinoptilolite. As an adsorbent material, its structure feature has a great impact on its adsorption performance; so materials with large surface area and total pore volume have good adsorption performance. But the study found that phosphorus removal performance of the clinoptilolite is greatly improved after $LaCl_3$ modification (Lin et al., 2009), therefore the adsorption performance of clinoptilolite itself has not been improved after modification, while the phosphorus removal performance improvement is due to load of $LaCl_3$, but the rich pores and large specific surface area of the clinoptilolite itself played a catalytic role in $LaCl_3$ modification. It also can be found that the ammonia nitrogen adsorption performance of the clinoptilolite decreased after $LaCl_3$ modification, it is due to ammonia adsorption effect are mainly ion exchange and physical adsorption (Hrenovic et al., 2008; Zhang et al., 2010; Widiastuti et al., 2011). Thus, $LaCl_3$ does exist in the surface and pores of the clinoptilolite, plugging channels of the clinoptilolite, and resulting in degradation in ammonia adsorption performance (Li et al., 2012).

Since inorganic acid can dissolve some impurities plugging in the channels of the clinoptilolite, so that dredging the cavities and channels, and increasing pore volume and surface area of the clinoptilolite (Wender et al., 2011). To further prove that $LaCl_3$ has been loaded to the surface and channels of the clinoptilolite after $LaCl_3$ modification, the article first modified clinoptilolite with HCl (5%), and then further modified the clinoptilolite with $LaCl_3$. Results are shown in Table 2 and Figure 1 (d), it can be found that the specific surface area of the clinoptilolite greatly increased after modified by HCl, from 38.54 m^2/g to 52.15 m^2/g. Total pore volume also increased from 0.058 m^2/g to 0.075 m^2/g. Average pore width reduced to 5.78 nm after acid modification, which is due to a large number of micropores appeared after modification and micropore area increased from 6.49 m^2/g to 19.27 m^2/g. Pore volume ratio of micropore increased dramatically, pore volume ratio of mesopore decreased, and pore volume ratio of macropore slightly increased, thereby resulting in an decrease in average pore width.

After treated by $LaCl_3$, the pore characteristics of HCl-modified clinoptilolite also varied intensively. The specific surface area decreased from 52.15 m^2/g to 41.54 m^2/g, the total pore volume decreased from 0.075 m^2/g to 0.064 m^2/g, the micropore area decreased from 19.27 m^2/g to 15.29 m^2/g, and the average pore width increased to 6.16 nm. Pore volume ratio of micropore changed little, pore volume ratio of mesopore decreased from 67.20% to 64.73%. Thus proved the modification effect of $LaCl_3$ on clinoptilolite, and $LaCl_3$ could load to the surface and pores of the clinoptilolite.

3.2 Energy Dispersive Spectroscopy Analysis

According to different X-ray photon characteristic energy of different elements, energy spectrometer was used to analyze the composition of the material. Element distribution of substances can be characterized by EDS analysis. Although the contents and distributions of the elements or oxides within the whole sample can’t be quantitatively analyzed by EDS, the type of the each element contained in the sample and the trend of variation of the element content can be qualitatively analyzed. Table 3 showed the energy spectrum of the natural and modified clinoptilolite. The results showed that La did not exist in the natural clinoptilolite, and the composition of the clinoptilolite changed after $LaCl_3$-modification, La accounted for 0.26% in the atomic ratio, the atomic ratios of other elements except Si all decreased. Proved that $LaCl_3$ had loaded to the clinoptilolite, thereby improved phosphorus removal performance of the clinoptilolite.

Table 3. EDS patterns of natural clinoptilolite and modified clinoptilolite (Atomic%)

Element	O	Si	Al	Ca	K	Na	Mg	La	Cl
Natural clinoptilolite	67.12	23.5	5.78	0.83	1.39	0.86	0.52	0	0
Modified clinoptilolite	66.88	25.27	4.64	0.73	1.36	0.52	0.27	0.26	0.07

3.3 Infrared Spectrum Analysis

Infrared spectrum is a useful method in the study of the structure of clinoptilolite (Li et al., 2009). Infrared spectrum is based on the measurement of bond vibration or rotational frequency of the molecules, including stretching vibration of the bond and flexural vibration of the bond. Therefore, it has already been applied to determine the overall skeleton structure of clinoptilolite. Generally, the wave-number of absorption spectrum of clay minerals ranges from 400 to 4000 cm^{-1} and belongs to the middle infrared region (Shi et al., 2013).

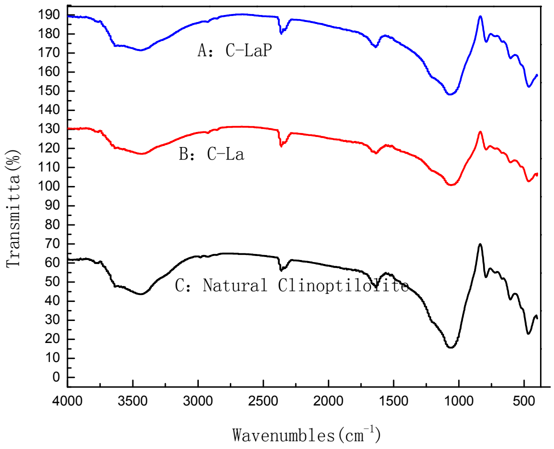


Figure 2. The FT-IR spectra of natural clinoptilolite, clinoptilolite modified by $LaCl_3$(C-La), modified clinoptilolite after phosphate adsorption(C-LaP)

Clinoptilolite belongs to the typical tectosilicate and the strongest adsorption band lies between 950 and 1200 cm^{-1} and the main bond vibrations include Si (Ai)-O, which includes the stretching vibration of Si (Ai)-O and flexural vibration of O-Si (Ai)-O and Si-O-Si (Ai), and the tetrahedron skeleton vibration of Si (Ai)-O (Yang et al., 2006). The asymmetric stretching vibration of Si (Ai)-O is 1150~930 cm^{-1}, the symmetric stretching vibration of Si-O-Si (Ai) is 800~760 cm^{-1}, the bicyclo-vibration of O-Si (Ai)-O and flexural vibration of Si-O are near 600~440 cm^{-1}, the flexural vibration of O-H is 1640~1620 cm^{-1} and stretching vibration of O-H is 3700~3200 cm^{-1} (Kawashita et al., 2010).

From Figure 2, it is revealed that there is no change in the FT-IR between the modified and natural clinoptilolite. The bond peak and strength of Si-O, Si-O-Si (Ai) and Si-O-Si (Ai) are within the allowed error range. No new key band is observed in the clinoptilolites modified by $LaCl_3$. If La enters the tetrahedron skeleton and joins the skeleton vibration, the flexural vibration of Si-O loaded with La will be stronger because the covalent radius of La is larger. Meanwhile, the flexural vibration of Si-O-Si (Ai) becomes more difficult after the modification and wave number decreases. Therefore, La is loaded only to the surface of clinoptilolites and does not enter its tetrahedron skeleton structure and joins the skeleton vibration. Figure 2 also shows that FT-IR of the modified clinoptilolites after phosphorus adsorption corresponds with that before phosphorus adsorption and no new key band is observed, which indicates that during the phosphorus adsorption process, phosphorus only reacts with La loaded on the surface and pore canal of clinoptilolites and does not enter its tetrahedron skeleton structure, neither react chemically with clinoptilolites, which may arise the new key band of P-O.

In conclusion, La is only loaded to the surface and pore canal of clinoptilolites and does not enter its tetrahedron skeleton structure and joins the skeleton vibration. Besides, the La loaded to the surface and pore canal of clinoptilolites constitutes the adsorption site for phosphorus, which enhances the adsorption ability of clinoptilolite for phosphorus.

3.4 XRD Analysis

XRD, which makes use of the diffraction phenomena of X-ray in the crystal, is used to analyze the crystal structure, parameters and defect of the materials. It is the most effective way to analyze the space structure of clinoptilolite (Castaldia et al., 2008).

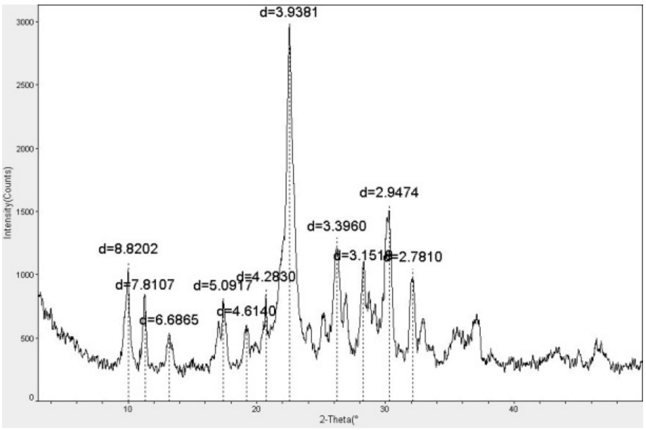


Figure 3. XRD of the natural clinoptilolite

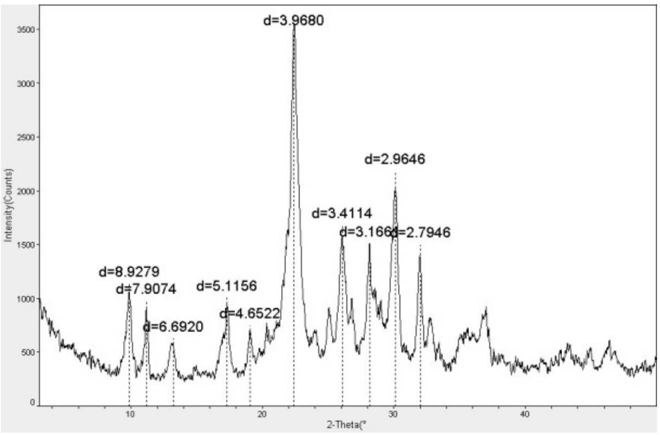


Figure 4. XRD of clinoptilolite modified by $LaCl_3$

Comparing Figure 3 and Figure 4 with the standard maps, the diffraction peaks of this natural clinoptilolite are mainly composed of clinoptilolite (about 22.5°, 25° and 30°), SiO_2 (about 22° and 44.5°) and other silicon and aluminium oxides (about 39°, 58° and 68°) (Karapınar, 2009). Clinoptilolites before and after modification both show obvious crystal structure, with nearly same spectral lines and few changes in the number of diffraction peaks. This indicates that the overall skeleton structure and structural holes are not changed by the modification process. Comparing Figure 3 with Figure 4, there is a slight decrease in the intensity of the main diffraction peak, which means that the degree of crystallinity of the clinoptilolites modified by $LaCl_3$ decease slightly. There is not obvious change in the interplanar spacing between the main diffraction peaks. However, there is a trend that the diffraction peaks of modified clinoptilolite shift to small angles, which indicates that the aperture of modified clinoptilolite has the trend to increase. This is corresponded with the specific surface area and pore size analysis. The diffraction peak of La is not observed from the modified clinoptilolite, which indicates that La is only loaded to the surface of clinoptilolite and does not change its structure.

4. Conclusions

(1) After modified by $LaCl_3$ of different concentrations, the surface area, total pore volume and micropore area of clinoptilolites decreased equally and the average pore width increases. The pore distribution test shows that the volume proportion of micropore and mesopore decreases while the volume proportion of macropore increases. Combined with the EDS test, it showed that $LaCl_3$ is loaded on the surface and pore canal of clinoptilolites, so its adsorption for ammonia nitrogen decreases while for phosphorus increases as a result of the presence of La.

(2) After modified by hydrochloric acid, the surface area, total pore volume of clinoptilolites increase greatly, and the volume proportion of micropore increases greatly while the volume proportion of mesopore decreases and the volume proportion of macropore increases slightly. After modified by $LaCl_3$, the surface area, total pore volume and micropore area of the hydrochloric acid-modified clinoptilolites change greatly. This verifies that $LaCl_3$ can be loaded on the surface and pore canal of clinoptilolites.

(3) The infrared spectrum shows that La is only loaded to the surface and pore canal of clinoptilolites and does not enter its tetrahedron skeleton structure and the skeleton shake. From another aspect, the loaded La forms the adsorption site for phosphorus which enhances the adsorption ability of clinoptilolite for phosphorus.

(4) XRD spectrums of modified and unmodified clinoptilolites show that the crystallinity of the clinoptilolites modified by $LaCl_3$ decease slightly, there is not obvious change in the interplanar spacing, and there is a trend that the diffraction peaks of modified clinoptilolite shift to small angles. However, the crystal structure is not changed. La is only loaded to the surface of clinoptilolite and does not change its overall skeleton structure and structural holes.

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