

Studies on Natural CXN Zeolite: Modification, Framework De-alumination and Ion-exchange

LONG, Ying-Cai^{*a}(龙英才) XIA, Xiao-Hui^b(夏晓慧) YANG, Bo^b(杨波)
 ZHANG, Ling-Mei^b(张玲妹) ZHOU, Wei-Zheng^a(周伟正)
 CAO, Zhi-Long^b(曹智龙) LI, Cai-Yun^b(李彩云)

^a Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200433, China.

^b Shanghai WU-JING Chemical Corporation Ltd., Shanghai 200241, China

A natural CXN zeolite (stilbite, type code-STI) discovered in China was modified with NH_4^+ exchange by using ammonium salt and calcinations (procedure I), or with NH_4^+ exchange followed by treatment with acid (procedure II). The coordination state of Si and Al atoms in the framework, the property of ion exchange, and the adsorption of the H-STI zeolite samples prepared by different modification procedure were investigated with XRD, EDX, ^{29}Si and ^{27}Al MAS NMR, Ag^+ ion exchange and N_2 adsorption. The results of the investigations indicate that different procedure of the modification made variety on the distribution of the framework Si atoms and Al atoms, the content of non-framework aluminum, and the blocking channels and the shielding effect to the positions of the exchangeable cations. The H-STI zeolite prepared by the procedure II possesses high ion exchange capacity, open and perfect pore system, and high thermal stability.

Keywords STI zeolite, modification, ^{29}Si and ^{27}Al MAS NMR, ion exchange, N_2 adsorption

Introduction

CXN natural zeolite (Stilbite, framework type STI) is a rich mineral in China. The raw zeolite was identified by the laboratory of Exxon company in New Jersey, U.S.A, and its excellent quality was confirmed with high crystallinity and absence of other impurity of minerals. The cell composition is $\text{Na}_{0.2}\text{Mg}_{0.1}\text{Ca}_{8.4}[\text{Al}_{17.2}\text{Si}_{54.8}\text{O}_{144}] \cdot 65\text{H}_2\text{O}$, belonging to calcium-rich type STI zeolite.¹ STI type natural zeolite is found in India, Europe and America as well. The exploring of the application for the mineral is a meaningful topic. Up to now the successful industrial application of STI zeolite in large scale has not been reported.

The earlier studies in our group² have found the poor thermal stability of the raw zeolite, the framework of which collapses in the dehydration process at elevated temperature to 350 °C. Therefore, the raw zeolite is greatly limited to be used as adsorbent and catalyst. Being ion-exchanged with NH_4Cl solution for removing Ca^{2+} , Mg^{2+} and Na^+ and followed calcination in nitrogen, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in framework of the formed $\text{NH}_4\text{-STI}$ increases from 6.4 of the raw zeolite to 12—16. The thermal stability of the modified zeolite increases to 700 °C, leading to its potential value to be used as adsorbent or as catalyst. The investigations of the adsorption behavior on H-STI and Na-STI also found the unusual selectivity to the organic molecules

with different length of the carbon chain, and good catalytic selectivity in the isomerization of *n*-butene to *iso*-butene.^{2,3} The modified zeolite is a good substrate, for assembling some other functional materials. For example, an assembly guest/host $\text{LiCl}/\text{H-STI}$ material is a solid electrolyte and possesses excellent humidity-sensitivity characters.⁴⁻⁶

The framework $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the raw STI zeolite is about 6.4, which is lower than that of 10 for mordenite zeolite (MOR type), and higher than that of 5.0 for zeolite Y (FAU type). In common, the ion-exchange capacity of STI zeolite should be the amount between those of mordenite and zeolite Y. As well known, zeolite Y is extremely unstable in acidic media, and mordenite possesses high resistance to acid.

It is generally believed that the collapse of STI zeolite structure during dehydration is due to the presence of exchangeable cations. When removing the water molecule ligands, the cations must coordinate directly to the oxygen in the framework. Because of their high charge density, the cations can distort the framework to achieve the best environment for possible coordination. The distortion in STI zeolite is so serious that some of the bonds connected to tetrahedral atoms (silicon or aluminum) are broken, rendering the zeolite almost useless as an industrial catalyst and dehydrating agent.⁷ For this reason, the essential factor for determining the stability of STI zeolite structure during heating process

* E-mail: yclong@fudan.edu.cn

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is the variety of the cations and the interaction between the framework and the cations. Usually, zeolites in the alkali or alkaline earth form are thermally more stable than those in the hydrogen form. However, in the case of STI, the hydrogen form is more stable. The thermal stability of the zeolite increases with increasing the degree of ammonium exchange. The collapse of the framework can be prevented by reduction of the cation/framework interaction.⁸⁻¹⁰ But, a serious dealumination must occur during calcination of $\text{NH}_4\text{-STI}$, leading to a great lower of the ion-exchange capacity and the adsorption property. The investigation upon the influence of de-alumination on the ion-exchange and the adsorption has not been reported yet. In this paper, we present an obvious variation of the ion-exchange and the adsorption properties caused by the framework de-alumination during different modification procedure. Our results will be important to exploit the nature resource in the application as an material with high ion-exchange capacity and with resistance to acid, and as an adsorbent.

Experimental

Preparation of samples

The parent sample of CXN, a pure mineral zeolite of stilbite with crystallite size of 5—10 μm collected in the Beijing region of China, was treated with the following procedure:

Procedure I: The parent STI zeolite was ion-exchanged four times in 1.0 $\text{mol}\cdot\text{dm}^{-3}$ NH_4Cl solution at 95—100 $^\circ\text{C}$ for 2 h with a solid/solution ratio of 1 : 10 under stirring. After being washed with distilled water, filtered and dried at 80 $^\circ\text{C}$ for several hours, the $\text{NH}_4\text{-STI}$ sample was calcined at 500 $^\circ\text{C}$ for 2 h in air, and then ion-exchanged with 1.0 $\text{mol}\cdot\text{dm}^{-3}$ acetic acid solution with the same solid/solution ratio to get a sample of H-STI-I by followed washing, filtering and drying at 80 $^\circ\text{C}$.

Procedure II: The parent STI was ion-exchanged four times in 1.0 $\text{mol}\cdot\text{dm}^{-3}$ NH_4NO_3 solution at 95—100 $^\circ\text{C}$ for 2 h with a solid/solution ratio of 1 : 10 under stirring. Then the sample was treated twice with 0.5 $\text{mol}\cdot\text{dm}^{-3}$ acetic acid solution at 95—100 $^\circ\text{C}$ for 2 h. After being washed with distilled water, filtered and dried at 80 $^\circ\text{C}$ for several hours, a sample of H-STI-II was obtained.

Both H-STI-I and H-STI-II samples are H-form zeolite absent of detectable Ca^{2+} , Mg^{2+} and Na^+ cations.

Determination of ion-exchange proportion

The investigated samples were exchanged respectively for once, twice and three times in 0.5 $\text{mol}\cdot\text{dm}^{-3}$ AgNO_3 solution at 90 $^\circ\text{C}$ for 2 h per time. After washing with distilled water, filtering and drying at 80 $^\circ\text{C}$, the content of Si, Al, Ag and O in the Ag^+ exchanged sample was determined. The ion-exchange proportion was calculated and expressed with the atomic ratio of Ag/Al for the samples.

Characterization

X-ray diffraction (XRD) identification of the samples was carried out with a Rigaku D-MAX/IIA X-ray diffractometer in a scanning range of 5°—35° (2θ) at a rate of 4 ($^\circ$)/min with Cu $\text{K}\alpha$ radiation. Relative crystallinity (D_I), which is defined by the ratio of the net diffraction intensity/sum diffraction intensity, can be calculated and printed automatically by the software in the X-ray diffractometer from the integral area data of the diffraction pattern for the investigated sample.

^{29}Si and ^{27}Al magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Bruker MSL-300 spectrometer. The ^{29}Si resonance frequency used was 59.592 MHz, the width of the spectrum was δ 335, and the rotor was spun at 4.0 kHz. Q_8M_8 (trimethylsilyl ester of cubic octameric silicate) was used as second reference of the ^{29}Si chemical shift. The ^{27}Al resonance frequency was 78.205 MHz, the width of the spectrum was δ 200, and the rotor was spun at 3.0 kHz. $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$ was used as a reference for the ^{27}Al chemical shift.

The chemical composition of the samples was determined with an energy dispersion X-ray analysis (EDX) accompanied in Philip SEM-515 scanning electron microscopy.

The surface area and the pore volume of the samples were measured from the adsorption and desorption isotherms of N_2 at -196 $^\circ\text{C}$ using a Micromeritic ASAP 2000 instrument. The sample tested was dehydrated at 550 $^\circ\text{C}$ for 4 h before determination.

Results and discussion

XRD patterns

The XRD patterns show (Figure 1) that the diffraction peaks for both H-STI-I and H-STI-II are almost the same and closed to the pattern of the raw STI zeolite,^{1,3} which are consistent with the reference.¹¹ It indicates that the framework of both samples prepared with different modification procedure remain intact. The value of D_I is 0.832 and 0.864 for H-STI-I and H-STI-II, respectively, implying higher crystallinity of the latter. Our earlier investigation has proved the good thermal stability of the STI sample prepared with the procedure

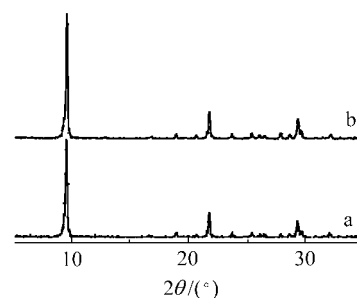


Figure 1 XRD patterns of modified CXN zeolite samples (a) H-STI-I and (b) H-STI-II.

I.^{1,3} Here we present the investigation on the thermal stability of H-STI-II. Figure 2 exhibits the XRD patterns of H-STI-II after calcination at various temperatures for 4 h. From the patterns, the calculated data of D_1 are 300 °C/0.805, 400 °C/0.788 and 500 °C/0.760, respectively, indicating that the framework of H-STI-II still remains intact at 500 °C.

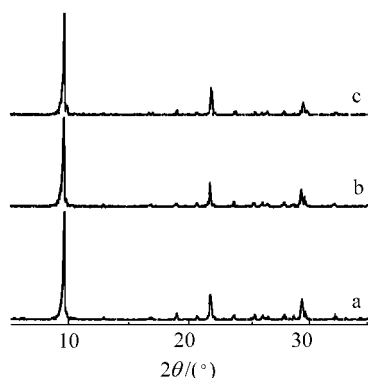


Figure 2 XRD patterns of H-STI-II calcined at the temperature of (a) 300, (b) 400 and (c) 500 °C.

Chemical composition

The chemical compositions of the investigated samples measured with EDX are listed in Table 1. The ratio of Si/Al for H-STI-I is 3.72, close to 3.75 for H-STI-II. After ion-exchange of once, twice and three times with AgNO_3 solution, the data of Ag/Al ratio and Ag loading determined for the samples show that the Ag loading for H-STI-I is 67%, 61% and 62% of that for H-STI-II, respectively. As well known, Ag^+ is at the first position in the ion-exchange order of zeolites. Therefore, a method with Ag^+ -exchange can be used to accurately characterize the ion-exchange properties of investigated zeolites. Theoretically, the Ag/Al ratio should be 1.0 for an STI zeolite sample with the degree of 100% ion-exchange. Actually, the highest degree of ion-exchange with Ag^+ is 46% for the sample of H-STI-I, even after three times of Ag^+ ion-exchange. In comparison, the degree of ion-exchange of Ag^+ is 92% for H-STI-II sample treated with three times of ion-exchange. The facts imply that the obvious difference in the degree of ion-exchange may be caused by different content of framework aluminium (FAL) in the

zeolite, the existing of various position of ion-exchange, and by blocking the channels with a species of non-framework aluminum (NFAL).

²⁹Si MAS NMR spectra

Figure 3 presents the ²⁹Si MAS NMR spectra of H-STI-I and H-STI-II. It can be seen that the broad overlap peak at δ -90—115 is composed of several resonance peaks. Computer simulation with Gaussian fits of the NMR spectra shows seven resonance peaks, which can be assigned as follows: the peaks at δ -107 and at δ -111 belonging to Si(0Al) at different structural position of the zeolite; both peaks at δ -101 and at δ -104 belonging to Si(1Al) at different structural position and the peak at δ -104 which may include SiOH; the peaks at δ -95 and -97 which are the resonance of Si(2Al), and the peak at δ 91 which is for the resonance of Si(3Al).¹³⁻¹⁶ The relative contents of each coordinative silicon atom in the framework, calculated from the integral surface of the resonance peak, are listed in Table 2.

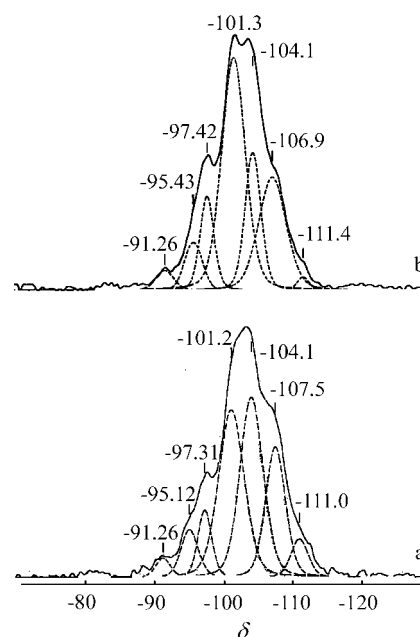


Figure 3 ²⁹Si MAS NMR spectra of CXN zeolite samples (a) H-STI-I and (b) H-STI-II with Gaussian fits by computer.

Table 1 Composition of Ag^+ exchanged CXN zeolite samples

Exchange times	H-STI-I					H-STI-II				
	Si/Al ^a	Si/FAL ^b	Ag/Al ^a	Ag/FAL ^b	Ag loading/%	Si/Al	Si/FAL	Ag/Al	Ag/FAL	Ag loading/%
0	3.72	4.59	—	—	—	3.75	4.12	—	—	—
1	3.84	4.74	0.34	0.42	12	3.36	3.69	0.53	0.58	18
2	4.19	5.17	—	0.56	14	3.97	4.36	0.82	0.90	23
3	4.02	4.96	0.49	0.60	16	3.87	4.25	0.92	1.00	26

^a Based on chemical composition determined with EDX; ^b Based on framework composition calibrated with NFAL data measured by ²⁷Al MAS NMR.

Table 2 Contents of Si with various coordination and framework Si/Al ratio in the CXN samples prepared by different procedure

	Si atoms with various coordination/%				Si/Al ratio in framework
	Si(0Al)	Si(1Al)	Si(2Al)	Si(3Al)	
H-STI-I	23.4	62.0	12.5	2.04	4.29
H-STI-II	24.1	57.5	15.8	2.59	4.13

In comparison, the content of Si atom at $\delta -104$ position for H-STI-I is obviously higher than that of H-STI-II. It may be due to H-STI-I sample suffered calcinations in the modification procedure, leading to producing more Si(1Al) or SiOH defects. On the other hand, the area of the peak at $\delta -101.3$ for H-STI-II is visibly larger than that for H-STI-I, indicating that the content of FAL in the neighbor position of Si(1Al) for H-STI-II is much higher than that of the latter. There is a serious difference in the distribution of the Si(0Al) resonance peaks at $\delta -106.9$ and at $\delta -111.0$ for both samples as well. The data listed in Table 2 also show that the contents of Si(2Al) and Si(3Al) in H-STI-II are much higher than those in H-STI-I. All the facts above prove that the modified procedure influences not only on the content of FAL, but also on the distribution of Al and Si atoms with various coordination in the zeolite, and on the ion exchange behavior. Because of the difficulty for calculating the content of Si(1Al) and SiOH at $\delta -104$ independently, the resonance is usually to be used to calculate the content of Si(1Al) in the case of low silica zeolites.¹³⁻¹⁶ Therefore, we are able to assign the resonance at $\delta -104$ to Si(1Al) only for calculating the Si/Al ratio in the framework of the investigated sample. As a result, the calculated Si/Al framework ratio is 4.29 for H-STI-I and 4.13 for H-STI-II, respectively. These data show the same tendency with that from EDX.

²⁷Al MAS NMR spectra

The ²⁷Al MAS NMR spectra (Figure 4) show that the signal of NFAL (at $\delta 0$) for H-STI-I is relatively

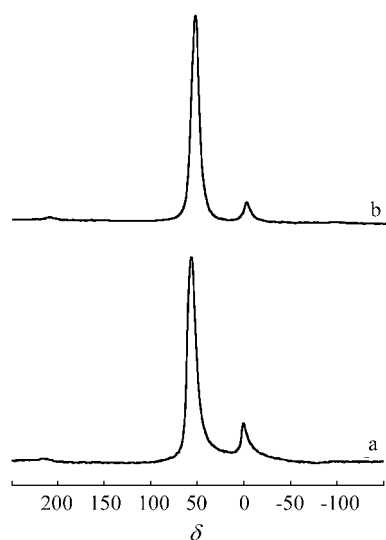


Figure 4 ²⁷Al MAS NMR spectra of CXN zeolite samples (a) H-STI-I and (b) H-STI-II.

stronger than that for H-STI-II. Actually, the calculated content of NFAL is 19% for H-STI-I, and 9% for H-STI-II, respectively. The fact indicates that the de-alumination of H-STI-I is so serious when suffering calcination that the formed NFAL can not be removed by the treatment with acid.

We can calibrate the data of Si/Al ratio measured from EDX by the NFAL data determined from ²⁷Al MAS NMR spectra to get a calibrated Si/FAL ratio for the investigated samples. Thus, the calibrated ratios of Si/FAL are 4.59 for H-STI-I and 4.12 for H-STI-II, respectively. Compared with the data of 4.29 for H-STI-I and 4.13 for H-STI-II respectively measured by ²⁹Si MAS NMR, the latter is very close with each other. But an obvious difference can be seen between the data of framework Si/Al ratio measured with ²⁹Si MAS NMR and the calibrated framework Si/FAL ratio for H-STI-I. This is probably due to more SiOH groups existing in H-STI-I, leading to lowering the value calculated from the ²⁹Si MAS NMR spectrum.

Calibrating the data of Ag/Al ratio measured from EDX with the FAL content from ²⁷Al MAS NMR spectra, the calculated data of Ag/FAL ratio in the investigated samples are listed in Table 1 as well. It can be seen that the ratio of Ag/FAL is 0.42, 0.56 and 0.60 for the H-STI-I sample ion-exchanged with Ag⁺ for once, twice and three times, respectively. On the other hand, the Ag/FAL ratio reaches to 0.58, 0.90 and 1.00, respectively, indicating the complete ion exchange for each FAL position has been achieved after three times of Ag⁺ exchange for H-STI-II.

The facts above evidence that 19% of NFAL in H-STI-I not only decreases the content of the essential exchangeable cations, but also blocks the zeolite channels, resulting in the shielding effect on the position of the exchangeable cations, and causing un-complete ion-exchange. However, the 9% NFAL in H-STI-II does not block the zeolite channels and does not shield obviously the position of the exchangeable cations due to that the FAL position in the structure of the sample is different from that in H-STI-I. Therefore, high degree ion exchange can be achieved for H-STI-II.

Nitrogen adsorption

The structure of STI zeolite possesses two channel systems: the channels with ten oxygen ring window (0.49 nm × 0.61 nm) are parallel to [100] direction, and the channels with eight oxygen ring window (0.27 nm × 0.56 nm) are parallel to [101] direction.¹² Obviously, the nitrogen molecules with size of 0.41 nm × 0.30 nm (Pauling value) can be adsorbed into these channels.

Figure 5 presents typical I type adsorption isotherms of N₂ at 77 K for the samples of H-STI-I and H-STI-II, respectively, after de-hydration at 550 °C. The Langmuir surface area and the microporous volume calculated are 288 m²/g and 0.117 cm³/g for H-STI-I, and 545 m²/g and 0.217 cm³/g for H-STI-II, respectively. Obviously, NFAL in H-STI-I blocks seriously the zeolite channels, resulting in that the data of the surface area and the microporous volume are half of those for H-STI-II. The result confirms the deduction on the investigation of ion exchange behavior above.

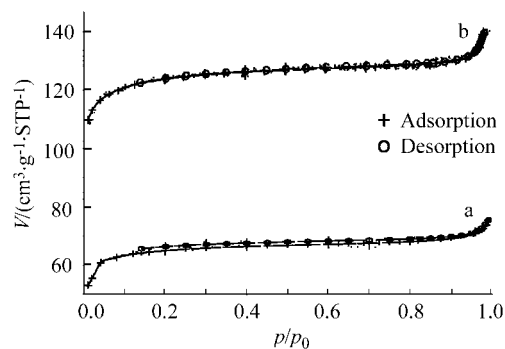


Figure 5 Nitrogen adsorption and desorption isotherms on modified CXN zeolite samples (a) H-STI-I and (b) H-STI-II.

On the other hand, the adsorption and desorption isotherms almost overlap with each-other for H-STI-II, and present an obvious hysteresis for H-STI-I. The facts prove the open, perfect and uniform channel system in H-STI-II, leading to achieving the more complete ion-exchange. The hysteresis from the adsorption and desorption isotherms for H-STI-II indicates the actual un-uniform channels in H-STI-II either, providing another evidence for the blocking effect of NFAL in the sample.

All results above suggest that a novel adsorbent and a material with high ion-exchange capacity and with resistance to acid can be developed with the natural STI type zeolite modified by using a procedure similar to that of procedure II.¹⁷

Conclusion

The calcination in the modification process of CXN zeolite makes a serious de-alumination and produces more NFAL, which blocks the channel, shields the posi-

tion of ion-exchange and intensively decreases the capacity of ion-exchange and adsorption of the zeolite. The H-STI zeolite, prepared by the modification process with NH₄⁺ exchange followed with H⁺ exchange without calcination, exhibits high thermal stability, intact framework, less produced NFAL, open and perfect and uniform channel system, resulting in an excellent properties of ion-exchange and adsorption.

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