[Communication]

Influence of Water on Adsorption Properties of Lithium Exchanged Low Silica X Zeolite *

Jiang Hua   Zhao Bi-Ying   Xie You-Chang

(*State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871*)

Abstract   This paper shows quantitatively the consequence of adsorbed water on N_2 or O_2 adsorbed on LiLSX lithium exchanged low silica X zeolite. In the range of 0 ~ 32 H_2O/u. c. (unit cell), water present in LiLSX sharply declined the capacity for N_2 or O_2 adsorption. The reason is that the adsorption mainly occurs on the Li^+ ions on the 32 SIII sites in LiLSX. When H_2O molecules residual after the desorption of hydrated LiLSX are adsorbed tightly on Li^+ at SIII site, they block the adsorption of nitrogen or oxygen. Water molecules introduced from outside into the dehydrated LiLSX influenc the adsorption of nitrogen less seriously than the residual water molecules do, because of the heterogeneity of adsorption sites and the diffusion behavior of water in LiLSX. When diffused into the inner part of a LiLSX particle, some water molecules may adsorb on weaker sites other than the strongest SIII sites.

Keywords: Water,   Adsorption,   Air separation,   Low silica X zeolite

Nitrogen and oxygen are widely used in industry. They are traditionally produced *via* air separation by cryogenic distillation. Since 1970s, PSA(pressure swing adsorption) or VPSA (vacuum pressure swing adsorption) has become new technologies to separate air, especially in middle and small scales production.

Synthetic zeolites 5A and faujasite X have been typically used as adsorbents for air separation. These adsorbents adsorb N_2 more strongly than O_2. The extraframework cations in the zeolites play a major role for the nitrogen adsorption selectivity. Because the quardruple moment of nitrogen is about 3 times that of oxygen, the interaction between the cations and nitrogen is much stronger. In 1989, Chao[1] reported that low silica X (LSX) having a Si/Al ratio of 1. 0 with lithium exchange level greater than 70% showed unexpected high capacity for nitrogen adsorption. Two reasons account for the excellent performance of lithium LSX(LiLSX) . First, Li^+ has the smallest radius, so its interaction with N_2 is strong. Second, LSX has the lowest Si/Al ratio, so that it can contain the uppermost amount of Li^+. Now LiLSX is the best adsorbent for O_2 manufacture by VPSA or PSA in industry.

It is well known that zeolites have a strong affinity for water, which greatly affects the adsorption of nonpolar molecules. This point is very important for the industrial use in air separation, for it was observed that a little water present in LiLSX sharply declined the capacity for N_2 adsorption. In this paper, we show quantitatively the consequence of adsorbed water on air separation.

Sodium, potassium LSX (NaKLSX) was synthesized following the procedure reported by Kuhl[2]. LiLSX was prepared by five static ion exchange of NaKLSX at 100 ℃ with a 5. 6-fold equivalent excess
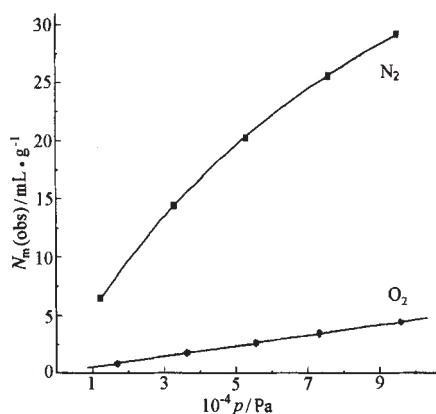
Fig. 1   **N_2 and O_2 adsorption isotherms at 25 ℃ on LiLSX**

Fig. 2   **Adsorption capacity *versus* residual water at 1.01×10^5 Pa, 298 K**

a)N_2,   b) O_2

of 2.0 mol· L^{-1} LiCl[3]. Previously, LiOH was added into the LiCl solution to adjust the pH to 8 ~ 10. After the ion exchange, the sample was stirred with deionized water and filtered. This procedure was repeated until no Cl^- was detected by 0.1 mol· L^{-1} AgNO$_3$. Finally, the obtained LiLSX was dried at 80 ℃. To analyze the composition of LiLSX, circa 0.2 ~ 0.3 g sample was decomposed using HCl, then filtered and washed with deionized water until no Cl^- residual on the filter cake. After being calcined at 800 ℃, the filter cake was turned into SiO_2 and weighed. Al^{3+} in the filtrate was determined by complexometric titration. Li^+, Na^+ and K^+ in the filtrate were analyzed by inductively coupled plasma-atomic emission spectroscopy(ICP-AES). Table 1 shows the results of element alanalysis for LiLSX.

The adsorption isotherms of N_2 and O_2 were measured using constant volume method. Fig. 1 shows the adsorption isotherms of N_2 and O_2 on dehydrated LiLSX, obtained by *in situ* pretreatment at 350 ℃ under vacuum (~8 Pa) for 2 h. The adsorption properties (Table 1) can be deduced from the isotherms and characterized by the following three parameters[3]:
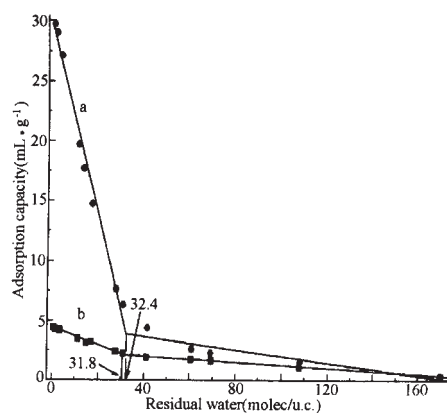
N_m(obs)   nitrogen adsorption capacity at 1.01×10^5 Pa, 25 ℃

N_m(delta)   nitrogen working capacity = N_2 adsorption capacity(1.01×10^5 Pa) − N_2 adsorption capacity ($0.2 \times 1.01 \times 10^5$ Pa), at 25 ℃

$S(N_2/O_2)$ N_2/O_2 selectivity = N_2 adsorption capacity ($0.25 \times 1.01 \times 10^5$ Pa)/O_2 adsorption capacity ($0.25 \times 1.01 \times 10^5$ Pa)

The samples with different water contents were prepared by heating at various temperatures from ambient temperature to 350 ℃ under vacuum. Then N_2 and O_2 adsorption isotherms were measured. Water contents were calculated from the weight loss supposing that the sample heated at 450 ℃ under 8 Pa contains no water, for the weight loss on this condition is in correspondence with that of the same sample calcined at 800 ℃. Fig. 2a shows the relationship between the N_2 capacity and the residual water in the zeolites. At first, as the water content goes up, the N_2 capacity drops sharply from 30 to 3.8 mL· g^{-1}, then it descends much more slowly. Fig. 2b, which is the O_2 capacity *versus* residual water, shows the same

Table 1   Nitrogen adsorption capacity and N_2/O_2 selectivity over LiLSX at 25 ℃

Sample	Si/Al	Li/Al*	Na/Al	K/Al	N_m(obs)/mL· g^{-1}	N_m(delta)/mL· g^{-1}	$S(N_2/O_2)$
LiLSX**	1.0	0.98	0	0	30.2	20.5	9.51

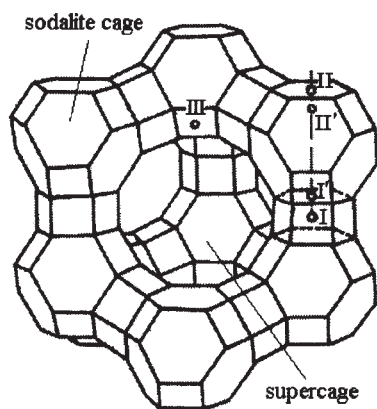*molar ratio;   **sample was activated at 450 ℃, 8 Pa

Fig. 3   Unit cell of faujasite zeolite and the distribution of cation sites

trend. Two figures reveal a common turn-point, *viz* about 32 H_2O molec./u. c. (molecules per unit cell).

This result is in good agreement with that of Yang and co-workers reported[4]. Why the adsorption capacity of N_2 and O_2 drops sharply before the number of water in the LiLSX increases to 32 molec./u. c. ? As we know, the unit cell of thoroughly exchanged LiLSX is $Li_{96}(AlO_2)_{96}(SiO_2)_{96}$. Five cation sites exist as SI, SI′, SII, SII′ and SIII. The location of these sites are shown in Fig. 3. Feuerstein[5] employed ^7Li MAS NMR to investigate the site population of Li^+. Their results showed that Li^+ occupied SI′, SII and SIII by 32 each kind of site. SI′ sites are located in β cages which are sterically inaccessible to N_2 or O_2. SII sites are on the wall of a supercage. The small Li^+ at this site sits in the center of a six-membered oxygen ring. This allows the electric field generated by Li^+ to be nearly completely shielded. Besides, the six oxygen atoms in the ring prevent N_2 and O_2 from contacting the Li ions closely, so that Li ions at these sites can not adsorb N_2 and O_2. SIII sites are located near the four rings inside the supercage, which are in a high-energy state, low coordination environment. So only the 32 Li^+ at SIII sites may interact with N_2 or O_2, that means each Li^+ at SIII site adsorbs about 0.5 N_2 molecule. It′s obvious that the Li^+ at SIII sites also prefer to attract H_2O molecules. Because of the very strong interaction between H_2O and Li^+,

when H_2O molecules are adsorbed on the 32 Li^+ at SIII sites, they will block the adsorption of other molecules. This explains why it takes only 32 H_2O molecules to significantly diminish the N_2 adsorption capacity.

Hereinbefore, we used hydrated LiLSX as starting material and removed water bit by bit to study the water effect on nitrogen adsorption. However, in the industrial application, dehydrated zeolites are the starting material, loaded in the bed. As time elapses, water in the air is adsorbed gradually and decreases the performance of VPSA or PSA. To simulate this case, we quantitatively introduced water into thoroughly dried LiLSX at ambient temperature. It can be seen from Fig. 4, when water amount was below about 7 molecules/u. c., the nitrogen capacity was almost the same in both cases. Yet above that amount, the nitrogen capacity was always higher in the latter case. After heating the samples in the latter case at temperatures much lower than their desorption temperatures of water, the nitrogen capacity dropped again to almost the same amount as that of the former case.

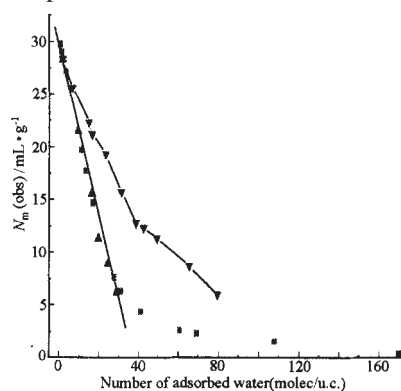The phenomena can be explained by the heterogeneity of adsorption sites and the diffusion behavior

Fig. 4   Nitrogen adsorption capacity on various conditions of water adsorption at 1.01×10^5 Pa, 298 K

■ water remained after heating hydrated LiLSX

▼ water introduced from outside at ambient temperature

▲ water introduced from outside then heated at temperature lower than desorption temperature

of water in LiLSX. TPD results obtained by Hunger[6] showed four desorption peaks for water adsorbed on lithium LSX, the desorption energies of which were 50, 58, 69 and 85 kJ· mol^{-1}, respectively. The number of water corresponding to the maximum desorption energy （85 kJ· mol^{-1}） peak was about 29 molecules／u. c., quite near 32 molecules／u. c. Though thase authors didn't make designation to this peak, according to our results, we tentatively attribute it to water adsorbed on Li$^+$ at SIII site inside the supercages. When water molecules were introduced from outside, they were firstly adsorbed on the strongest sites, namely Li$^+$ at SIII sites, thus caused the sharp decrease of nitrogen capacity. Part of the subsequent water molecules were most likely adsorbed on other weaker sites before they could diffuse into the inner part of a LiLSX particle. Therefore, some Li$^+$ at SIII sites located in the inner part of LiLSX remained intact, leading to the higher nitrogen capacity.

Heating the samples caused the migration of water molecules from the weaker sites to Li$^+$ at SIII sites so that the nitrogen capacity decreased again. That the water introduced from outside influences nitrogen adsorption less seriously provides for us a round understanding of the water effect and supplies some basic data for the industrial application.

References

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——   LiLSX

.   LiLSX   0 ~ 32   ／

N$_2$ O$_2$.   N$_2$ O$_2$ SIII   32   .

SIII   Li$^+$ N$_2$ O$_2$.

.   LiLSX

SIII   .

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