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Gas Separation

PST-1: A Synthetic Small-Pore Zeolite that Selectively Adsorbs H_2[**]

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The ability of zeolites to discriminate between molecules of different sizes and shapes has long been recognized.[1] This ability legitimates their consideration as "molecular sieves" and has been the basis for many applications in catalysis and gas separation technologies.[2] Some separation processes may also be based on specific host–guest interactions, rather than relying just on size or shape recognition.[3] However, examples of selective adsorption of the smallest gases in zeolites are scarce. Herein, we report on a zeolite denoted PST-1 (POSTECH number 1), which can adsorb only the smallest gases (H_2, He, and H_2O with Lennard–Jones (L–J) sizes of 2.89, 2.60, and 2.65 Å, respectively[4]), thus allowing discrimination from slightly larger molecules (Ar and CO_2 with L–J sizes of 3.40 and 3.30 Å). Furthermore, PST-1 is selective for H_2 over He, despite the smaller size of the latter.

PST-1 is a synthetic small-pore zeolite with the natrolite (NAT) topology[5] and a potassium gallosilicate composition. It can be obtained within a narrow window of synthesis conditions and contains a concentration of Ga atoms in tetrahedral (T) positions ($Si/Ga = 1.28$) significantly exceeding that typically found in synthetic gallosilicate NAT materials ($Si/Ga \geq 1.5$).[6] Its orthorhombic crystal structure, space group *Fdd*2, is remarkable for a natrolite with such a high heteroatom content, where T ordering is hindered by the Loewenstein rule.[7] All known aluminosilicate NAT materials with $Si/Al < 1.50$ are tetragonal and essentially completely disordered. However, PST-1 does present a noticeable, although modest, degree of ordering (the average long-range ordering coefficient, as defined by Alberti, is $S = 0.10$, where 0 corresponds to complete disorder and 1 to complete order)[8] to which the observed symmetry lowering should be ascribed.

Dehydration of PST-1 occurs remarkably easily, even at 333 K under vacuum to a residual pressure of 5×10^{-3} Torr, or at 443 K at atmospheric pressure, and brings about a large shrinkage of the framework (ca. 16%). This deformation mainly occurs along the x and y directions, with the unit cell edge along z remaining almost constant (-8.27, -8.39, and -0.02% variation of the a, b, and c cell edges, respectively). The orthorhombic symmetry is lost in the dehydrated material (monoclinic $B112$), at variance with the orthorhombic ($I2_12_12_1$) to tetragonal ($I\bar{4}2d$) transition observed upon dehydration in a very highly disordered Ga-rich natrolite.[6,8]

Despite its large Ga content, PST-1 is thermally stable up to at least 1073 K (Supporting Information, Figure 1S), and it also withstands hydrothermal treatments up to at least 873 K in the presence of 10% water vapor. The ease of dehydration and the high thermal and hydrothermal stability of PST-1 sharply contrast with the behavior of its more siliceous sodium gallosilicate NAT counterparts with $Si/Ga \approx 1.6$, which require dehydration temperatures of 673 K or higher and become amorphous upon exposure to the laboratory humidity conditions.[6,8] The high stability of PST-1 is unexpected, because higher concentrations of trivalent lattice-substituting heteroatoms, which introduce a negative charge into the framework, generally correlate with lower thermal and hydrothermal stability in zeolites.[9] The breaking and reorganization of Ga-O-Si bonds may require the presence of water, together with some thermal energy, as these processes are mediated by the formation of Ga−OH and Si−OH groups. As described above, however, all water in PST-1 is lost at a very low temperature, probably owing to weaker interactions of K^+ ions with water molecules within the pores compared to smaller Na^+ ions. Hence, when the temperature becomes high enough to break bonds, PST-1 is completely dehydrated and its reorganization is no longer possible.

After dehydration and framework volume shrinkage, the pores of PST-1 become extremely elongated, which should effectively block them to any molecule, even without considering pore blockage by K^+ ions in the channels (Figure 1). The free diameter along the short axis of the nine-ring pores, for instance, is reduced to just 1.6 Å in the dehydrated material (compared to the hydrated one).

However, adsorption occurs in dehydrated PST-1. The breakthrough curves at 303 K for different mixtures of gases show that relatively small molecules such as Ar or CO_2 are excluded from PST-1, while smaller molecules such as H_2 and He are adsorbed (Supporting Information, Figure 2S). The H_2 and He sorption isotherms at 77 K up to 760 Torr partial

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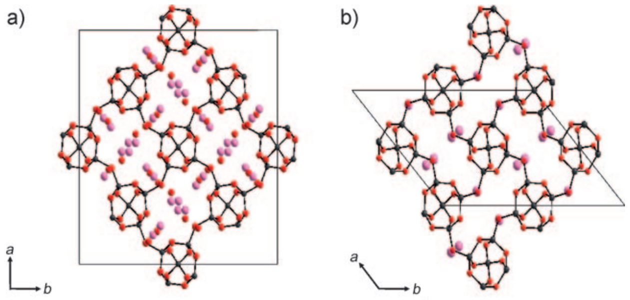

Figure 1. Refined structures of a) hydrated and b) dehydrated forms of PST-1. Si/Ga gray, O red, K pink.

pressure (Supporting Information, Figure 3S) suggest a moderate selectivity for H_2 at this temperature. In contrast, the isotherms at 303 K, in which PST-1 gives essentially zero Ar uptake, show similar uptakes (ca. 0.5 $cm^3 g^{-1}$) for both gases, and hence no selectivity was expected. However, in competitive dynamic experiments (breakthrough curves) at the same temperature, PST-1 selectively adsorbs H_2 over He in He-rich mixtures, with H_2 being able to displace previously adsorbed He (Figure 2). This apparent contradiction is likely due to the static and dynamic nature of the adsorption isotherm and breakthrough curve experiments, respectively, and to the competitive character of the latter. The selectivity for H_2 over the inert and more symmetrical He cannot be due to size discrimination (L–J sizes of 2.89 and 2.60, respectively[4]), but suggests a specific interaction of PST-1 with H_2 through polarization and quadrupolar interactions with its cationic centers.[10]

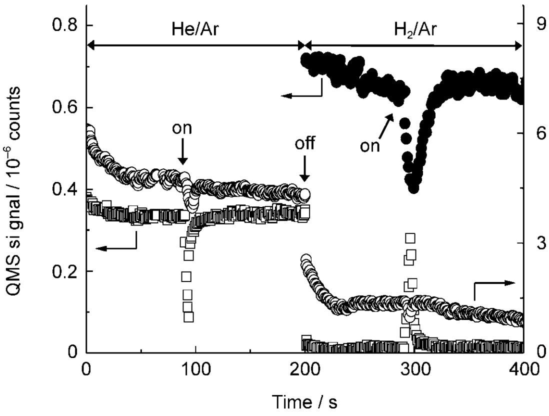

Figure 2. Breakthrough curves at 303 K. He (□), H_2 (●), and Ar (○) for PST-1 first using a He/Ar mixture (4:96 v/v) and then a H_2/Ar mixture (4:96 v/v). Mean value from triple parallel experiments (standard deviation $\sigma \leq 6\%$) was adopted for each data point. QMS = quadrupole mass spectrometer.

The adsorption properties of dehydrated PST-1 are remarkable for a material with such a small pore size that is also crowded with K^+ ions. Powder XRD experiments (Supporting Information, Figure 1S) reveal that completely dehydrated PST-1 restores its original state within 0.5 h when rehydrated in ambient air. The ease with which PST-1 expands and contracts reflects a very high degree of framework flexibility that is, in our view, central to its adsorption behavior. A similar but less pronounced behavior has also been observed in Sr-ETS-4, which showed a significant contraction on dehydration (14.5 % cell contraction at 573 K) and a temperature-dependent pore size variation providing this material with the ability to discriminate between very closely sized small molecules (for example, N_2 and CH_4).[11] Unlike PST-1, however, Sr-ETS-4 completely loses these properties when heated at temperatures above 600 K.

Given the fast kinetics of the adsorption observed in the breakthrough curves, PST-1 could be a potential candidate for H_2 or He separation processes based on pressure swing adsorption (PSA) or membrane technology. Because H_2-rich streams are currently purified by high-temperature processes based on Pd or Pd/Ag membranes (a dissociative process selectively diffusing monatomic H at temperatures above 573 K)[12] or by PSA processes (selectively removing gases different from H_2 on multicomponent adsorbents),[13] for example, PST-1 is attractive for low-temperature and low-cost membrane applications and for H_2 enrichment by PSA technology of H_2-poor mixtures. Of course, dehydrated PST-1 also adsorbs water, and in competitive experiments water is selectively adsorbed over H_2 (Supporting Information, Figure 2S), so applications would be restricted to dried streams.

In summary, we have demonstrated that a synthetic potassium gallosilicate natrolite with a high Ga content (Si/Ga = 1.28), denoted PST-1, can selectively adsorb the smallest gases, especially H_2, and hence discriminate them from slightly larger molecules such as Ar or CO_2. Because of the remarkable ease of its dehydration and great thermal and hydrothermal stability, PST-1 could be a potential candidate for fast, selective H_2 or He separation processes based on PSA or membrane technology.

Experimental Section

In a typical synthesis of PST-1, gallium oxide (3.75 g, 99.99+ %, Aldrich) and KOH (19.95 g, 45 % aqueous solution, Aldrich) were first mixed in H_2O (5.59 g). Then the mixture was heated overnight at 373 K. After cooling to room temperature, colloidal silica (15.00 g, Ludox AS-40, DuPont) was added to this translucent solution. The gel composition of the resulting mixture was $8.0\,K_2O \cdot 2.0\,Ga_2O_3 \cdot 10.0\,SiO_2 \cdot 150\,H_2O$. The final synthesis mixture was stirred at room temperature for one day, transferred to a Teflon-lined 45 mL autoclave, and heated at 423 K under rotation (60 rpm) for 1.5 days. The solid product was recovered by filtration, washed repeatedly with water, and then dried overnight at room temperature (yield: 6.33 g, 14.3 % based on the total weight of the synthesis mixture).

Synchrotron diffraction data for PST-1 in the as-made, hydrated form and after dehydration at 373 K were collected on the 8C2 beamline equipped with a ceramic furnace of the Pohang Acceleration Laboratory (Pohang, Korea) using monochromated X-rays (λ = 1.54220 Å). The detector arm of the vertical scan diffractometer consists of seven sets of soller slits, flat Ge(111) crystal analyzers, antiscatter baffles, and scintillation detectors, with each set separated by 20°. The synchrotron diffraction data were obtained on the sample in flat plate mode, with a step size of 0.01° and overlaps of 2° to the next detector bank over the 2θ range 10–120°. Further details of the crystal structure analysis can be found in the Supporting Information.

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The gas separation properties of PST-1 were tested by breakthrough experiments at 303 K and atmospheric pressure using H_2/Ar, He/Ar, H_2/He (4:96 v/v), H_2/CO_2/He (4:4:92 v/v/v), and H_2/H_2O/Ar (2:2:96 v/v/v) gas mixtures. In a typical breakthrough experiment, hydrated PST-1 (160.8 mg) was packed in a vertically placed fixed-bed microreactor (0.64 cm inner diameter), giving a sample height of 0.7 cm, and then dehydrated in flowing He or Ar (50 $cm^3 min^{-1}$) at 723 K for 1 h. After cooling to 303 K, a gas mixture was passed through the dehydrated PST-1 (150.0 mg) at the same temperature. The total gas flow at the quartz reactor inlet was fixed to 100 $cm^3 min^{-1}$ to maintain a gas hourly space velocity of 26500 h^{-1}. H_2/Ar (4:96 v/v) tests with gas flow rates of 50 and 150 $cm^3 min^{-1}$ were also performed; these experiments showed an increased area of the H_2 depletion peak as the flow rate diminished, as expected. The intensities of each gas passing through the PST-1-packed reactor were monitored on a Hiden Analytical HPR20 gas analysis system detecting ion peaks at $m/z^+ = 2$ (H_2), 4 (He), 18 (H_2O), 40 (Ar), and 44 (CO_2). Prior to passing a gas mixture through PST-1, the mass spectrometer was stabilized for 90 s with the gas mixture, while only the carrier gas passed through PST-1. After this time (tagged “on” in the breakthrough curves), the gas mixture was passed through PST-1. Similarly, in consecutive experiments such as those in Figure 2, switching off the first gas mixture (tagged “off”) is followed by 90 s of stabilization of the mass spectrometer with the new gas mixture (while only the new carrier passed through PST-1), and then the new gas mixture was allowed to pass through PST-1 (tagged “on”). The H_2, He, and Ar sorption isotherms of PST-1 at 77 and 303 K were measured using a Mirae SI nanoPorosity-XG analyzer.

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