Adsorption Properties of the SAPO-5 Molecular Sieve

Enping Hu,[†] Zhiping Lai,[‡] and Kean Wang*[,†]

School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459, and Division of Chemical and Life Sciences and Engineering, 4700 King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia

The adsorption properties of an aluminophosphate molecular sieve, SAPO-5, were measured for a number of gases and vapors, including N_2, water, isopropanol, and xylenes. The data showed that SAPO-5 is quite hydrophobic and has a strong selectivity of *o*-xylene over its isomers *m*- and *p*-xylene.

Introduction

Zeolite molecular sieves (ZMS) have well-defined pore structures that can separate different species on the molecular level based on adsorption or diffusion selectivity. They also possess high thermal, chemical, and mechanical stabilities because of their inorganic crystalline nature. Hence, ZMS have been widely used in gas/vapor separations, membrane reactors, chemical sensors, and optoelectronic devices.[1,2] A notable example is the AFI (one of the zeolite framework type codes) type of aluminophosphate molecular sieves AlPO-5 and its derivative SAPO-5, which contains one-dimensional hexagonally arrayed straight channels parallel to the crystallographic *c*-axis with a pore opening of 0.73 nm.[3] AlPO-5 consists of alternatively linked aluminum tetrahedra and phosphorus tetrahedra which form a neutral framework, whereas in SAPO-5, a portion of aluminum or phosphorus is replaced by silicon, resulting in a charge unbalanced framework. Acidity or ions can thus be introduced into the structure of SAPO-5 for specific applications such as catalysts, ion-exchangers, and adsorbents.[4−7]

Although the adsorption properties of AlPO-5 have been reported in a number of studies,[8−12] few reports have studied SAPO-5 crystals, especially the plate-like crystals. Compared with rod-like SAPO-5 particles, plate-like ones, which possess a larger surface area,[13] are more popular in membrane fabrication[14] and adsorption applications. In addition, plate-like SAPO-5 crystals can be conveniently synthesized with microwave heating, which compares favorably with the use of conventional heating techniques in preparing AlPO-5.[13,15,16]

This article will report the adsorption properties of gases and vapors on SAPO-5 crystals. It is well-known that AlPO-5 can selectively adsorb xylenes;[10] hence the isotherms of xylene isomers were also reported.

Experimental Section

Isopropanol (anhydrous) was purchased from BDH Prolab. *p*- and *m*-Xylene (0.99, Reagentplus), *o*-xylene (0.97, Reagentplus), and triethylamine (TEA, 0.995, Sigma-Aldrich) were supplied by Sigma-Aldrich.

Plate-like SAPO-5 seeds were synthesized by microwave heating from a precursor solution with a molar composition of 1 Al_2O_3:0.8 P_2O_5:1 SiO_2:3.5 TEA:50 H_2O. The detailed procedure was described in Hu et al.[14] The obtained SAPO-5 crystals were calcined at 540 °C for 8 h to remove the organic template.

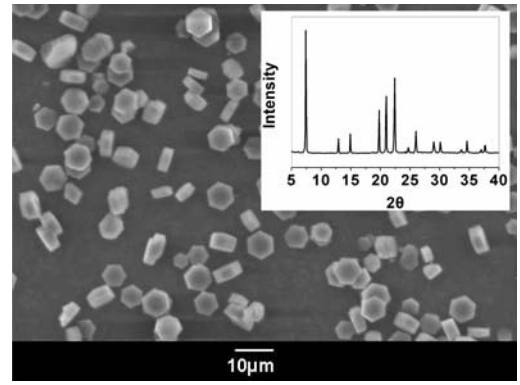

Figure 1. SEM image of SAPO-5 crystals with the XRD pattern in the inset.

The X-ray diffraction (XRD) pattern was taken from a Bruker D8 advanced X-ray diffractometer with Cu Kα radiation. The scanning electron microscopy (SEM) image was taken from a field-emission scanning electron microscope (JEOL JSM-6700F). Prior to the sorption measurement, all of the samples were degassed at 200 °C for 24 h under high vacuum (< 0.01 Pa). A pore and surface analyzer (PSA, Quantachrome, Autosorb-1) was used to measure the N_2 isotherm at 77 K. The bulk density of the sample was measured on an Ultrapycnometer 1000 (Quantachrome corporation). Water and isopropanol isotherms were measured on the PSA using its vapor sorption function. The isotherms of xylene isomers were also measured on a volumetric rig. A fixed-bed breakthrough experiment[17] was conducted at 100 °C, in which the binary mixture of *p*- and *o*-xylene (50:50 volume fraction) was directed through the column (L = 100 mm, d_i = 4.25 mm) packed with 0.98 g of SAPO-5. The concentration of the gas at the outlet was monitored by a GC with flame-ionization detector (FID).

Results and Discussion

The SEM image of the SAPO-5 crystals is shown in Figure 1, which reveals that the crystals possess a well-defined hexagonal disk shape with a short dimension along the *c*-axis. They are quite uniform, 5 μm in width and 1.5 μm in thickness, with a bulk density of 2.31 g·mL^{-1}. The XRD pattern is shown

* Corresponding author. E-mail: mkwang@ntu.edu.sg.
[†] Nanyang Technological University.
[‡] King Abdullah University of Science and Technology.

10.1021/je100093u
Published on Web 04/13/2010

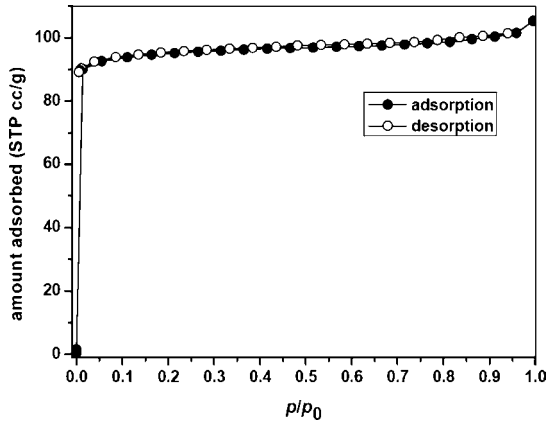

Figure 2. N_2 isotherm at 77 K on SAPO-5 crystals (p_0 = 100 kPa).

as the inset of Figure 1, which matches well with the standard pattern. The Si/Al ratio of these plate-like crystals was found to be 0.05:1.[15]

Figure 2 shows the N_2 isotherm measured at 77 K on the SAPO-5 crystals. The S_{BET} derived from multi-point analysis is 342.3 $m^2 \cdot g^{-1}$. The sharp rise of the isotherm at low pressure, the flat plateaus, and the absence of a desorption hysteresis loop suggest that the sample is predominantly microporous.

The isotherms of water and isopropanol were measured at (283 and 293) K, respectively, and are shown in Figure 3 parts a and b, respectively. From the isotherms of water in Figure 3a, we can see that the surface of SAPO-5 is quite hydrophobic, without showing any hysteresis in the desorption isotherms. The adsorption isotherms of water on SAPO-5 are concave at both (283 and 293) K in the low pressure region where $p/p_0 < 0.2$. The adsorption almost stops at $p/p_0 \sim 0.4$, which may correspond to the filing of the micropores/channels. The adsorption isotherm of isopropanol (Figure 3b) is largely type I at low pressure. However, its adsorption capacity is only ~1/10 that of the water molecules, because of its large molecular dimensions. There is no obvious hysteresis found in the desorption of isopropanol.

The adsorption isotherms of xylenes at 303 K are shown in Figure 4. We see that the adsorption equilibrium was reached at low pressure ($p/p_0 \leq 0.1$), corresponding to the filling of the micropores. The persistent uptake at high pressure is caused by adsorption in interparticle space.

The adsorption data of xylenes were fitted to the Langmuir equation

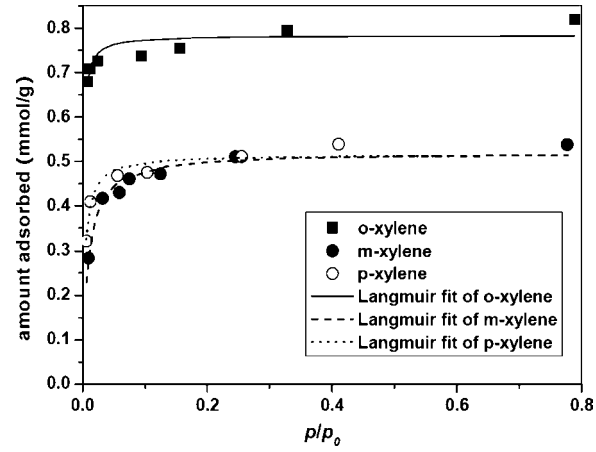

Figure 4. Isotherms of xylene isomers on SAPO-5 crystals at 303 K. Langmuir isotherm with $C_{\mu s}$ = 0.782 mmol·g^{-1}, b = 636.453 kPa^{-1} for *o*-xylene; $C_{\mu s}$ = 0.520 mmol·g^{-1}, b = 78.635 kPa^{-1} for *m*-xylene; and $C_{\mu s}$ = 0.516 mmol·g^{-1}, b = 170.7804 kPa^{-1} for *p*-xylene.

$$C_\mu = C_{\mu s}\frac{bP}{1 + bP}$$

where C_μ is the adsorbed phase concentration; $C_{\mu s}$ is the adsorption capacity; b is the affinity; and P is the bulk phase pressure. The fitted parameters are listed in the caption of Figure 4, while the adsorption data of water, isopropanol, and xylene are listed in Table 1. Table 2 compares the xylene adsorption capacities on a few ortho-selective materials. It is seen that $AlPO_4$-11 presents the lowest capacity, while the microporous metal−organic framework (MOF 1) gives the highest capacities but the lowest selectivity. The adsorption capacities of SAPO-5 is slightly lower that of AlPO-5,[10] but with an improved selectivity. This may be due to the introduced silicon. The silicon substitution brings in unbalanced charge and Lewis centers which affect the interaction between the xylenes and the SAPO-5 framework.

The preferential adsorption of *o*-xylene in the SAPO-5 crystals was explored in separation applications. Figure 5 demonstrates the fixed-bed separation of xylene isomers (*o*-:*p*-xylene = 1:1 by volume). The breakthrough curves were plotted as the normalized concentration against time. We see that *p*-xylene penetrates the column much faster than *o*-xylene, while *o*-xylene, which is slowly moving but more strongly adsorbed, can displace *p*-xylene from the ZMS channels/pores. The difference in breakthrough time and the strong overshoot

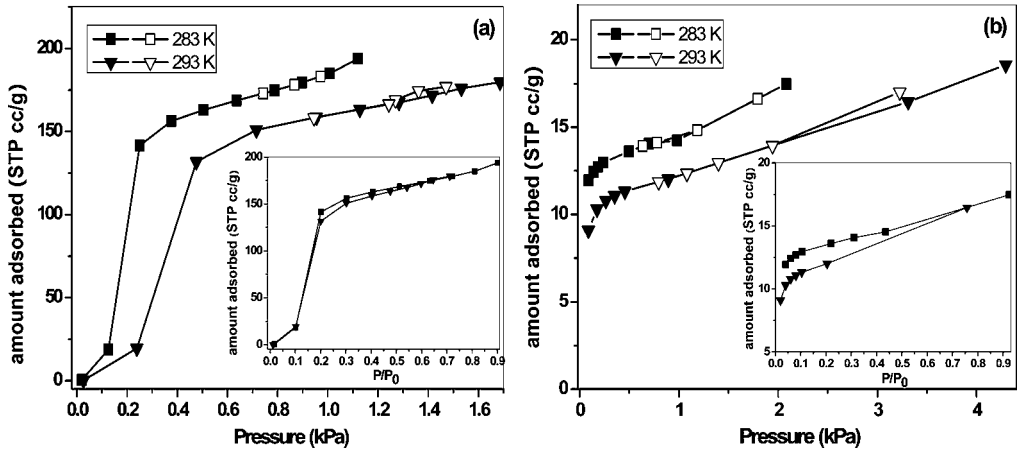

Figure 3. Isotherms of water (a) and isopropanol (b) at (283 and 293) K. Solid symbols (■, ▼) are the adsorption data, while open symbols (□, ▽) show the desorption data. The inset plots show the adsorption isotherm in terms of relative pressure.

Table 1. Isotherm Data of Water, Isopropanol, and Xylenes on SAPO-5

pressure	adsorbed	pressure	adsorbed	pressure	adsorbed	pressure	adsorbed
kPa	mmol·g^{-1}	kPa	mmol·g^{-1}	kPa	mmol·g^{-1}	kPa	mmol·g^{-1}
			H_2O (283 K)				
0.019	0.019	0.505	7.272	1.008	8.253	0.742	7.714
0.126	0.832	0.637	7.527	1.120	8.649		
0.250	6.316	0.788	7.796	0.971	8.171		
0.377	6.975	0.898	8.008	0.867	7.947		
			H_2O (293 K)				
0.026	0.007	0.954	7.075	1.532	7.850	1.269	7.542
0.239	0.871	1.127	7.286	1.686	8.019	1.243	7.435
0.476	5.883	1.283	7.470	1.471	7.900	0.945	7.060
0.715	6.731	1.416	7.666	1.362	7.786		
			Isopropanol (283 K)				
0.091	0.534	0.497	0.607	2.253	1.322	0.634	0.621
0.138	0.555	0.699	0.628	1.794	0.742		
0.183	0.568	0.982	0.635	1.182	0.662		
0.239	0.578	2.082	0.780	0.779	0.630		
			Isopropanol (293 K)				
0.089	0.406	0.455	0.506	4.369	1.053	1.082	0.552
0.176	0.460	0.894	0.536	3.227	0.759	0.796	0.530
0.264	0.482	3.310	0.735	1.943	0.622		
0.353	0.494	4.294	0.829	1.399	0.578		
			o-Xylene (303 K)				
0.010	0.680	0.028	0.725	0.184	0.755	0.932	0.821
0.014	0.708	0.112	0.737	0.387	0.794		
			m-Xylene (303 K)				
0.014	0.284	0.088	0.430	0.186	0.472	1.157	0.538
0.048	0.412	0.112	0.461	0.365	0.511		
			p-Xylene (303 K)				
0.01	0.3216	0.088	0.469	0.399	0.511		
0.019	0.410	0.162	0.475	0.643	0.539		

Table 2. Comparison of Xylene Adsorption Capacities among Different Ortho-Selective Materials

	SAPO-5	AlPO-5[10,a]	$AlPO_4$-11[18,b]	MOF 1[17,c]
	(% g·g^{-1})	(% g·g^{-1})	(% g·g^{-1})	(% g·g^{-1})
o-xylene	8.302	10.828	4.250	29.5
m-xylene	5.520	8.068		28.6
p-xylene	5.478	7.644	3.791	29.0
difference between *o*- and *p*-xylene	2.824	3.184	0.459	0.5
difference between *o*- and *m*-xylene	2.782	2.76		0.9

[a] Data measured at 303 K. [b] Data measured at 333 K. [c] Data obtained from the breakthrough curves at 423 K.

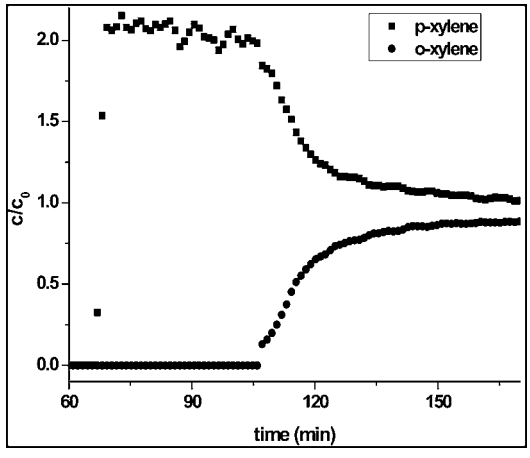

Figure 5. Breakthrough curves of *o*- and *p*-xylene mixture (1:1 in volume) on SAPO-5 at 100 °C.

of *p*-xylene is a good indication of the adsorption as well as the kinetic selectivity of the ZMS SAPO-5 toward the xylene isotherms.

Conclusion

The adsorption isotherms of N_2, water, isopropanol, and xylene isomers were measured on plate-like SAPO-5 crystals. It is shown that the ZMS present a hydrophobic surface and strong adsorption selectivity toward xylene isomers. The separation of *o*- and *p*-xylene is feasible on a fixed-bed rig.

Literature Cited

(1) Caro, J.; Noack, M. Zeolite Membranes - Recent Developments and Progress. *Microporous Mesoporous Mater.* **2008**, *115*, 215–233.
(2) Tsapatsis, M.; Xomeritakis, G.; Hillhouse, H. W.; Nair, S.; Nikolakis, V.; Bonilla, G.; Lai, Z. P. Zeolite Membranes. *CATTECH* **2000**, *3*, 148–163.
(3) Baerlocher, C.; Meier, W. M.; Olson, D. H. *Atlas of Zeolite Framework Types*. Elsevier: Amsterdam, 2001.
(4) Raj, K. J. A.; Malar, E. J. P.; Vijayaraghavan, V. R. Shape-selective Reactions with AEL and AFI Type Molecular Sieves Alkylation of Benzene, Toluene, and Ethylbenzene with Ethanol, 2-Propanol, Methanol and t-Butanol. *J. Mol. Catal. A: Chem.* **2006**, *243*, 99–105.
(5) Dumitriu, E.; Guimon, C.; Hulea, V. Transalkylation of Toluene with Trimethylbenzenes Catalyzed by Various AFI Catalysts. *Appl. Catal., A* **2002**, *237*, 211–221.
(6) Hochtl, M.; Jentys, A.; Vinek, H. Isomerization of 1-Pentene over SAPO, CoAPO (AEL, AFI) Molecular Sieves and HZSM-5. *Appl. Catal., A* **2001**, *207*, 397–405.
(7) Arias, D.; Colmenares, A.; Cubeiro, M. L. The Transformation of Ethanol over $AlPO_4$ and SAPO Molecular Sieves with AEL and AFI Topology. Kinetic and Thermodynamic Approach. *Catal. Lett.* **1997**, *45*, 51–58.
(8) Martin, C.; Tosi-Pellenq, N.; Patarin, J.; Coulomb, J. P. Sorption Properties of A1PO_4-5 and SAPO-5 Zeolite-like Materials. *Langmuir* **1998**, *14*, 1774–1778.
(9) Rozwadowski, M.; Kornatowski, J.; Golembiewski, R.; Erdmann, K. Sorption of Benzene on $AlPO_4$-5 Containing Various Heteroatoms and Analytical Description of the System. *Langmuir* **1999**, *15*, 5857–5862.
(10) Chiang, A. S. T.; Lee, C. K.; Chang, Z. H. Adsorption and Diffusion of Aromatics in $AlPO_4$-5. *Zeolites* **1991**, *11*, 380–386.
(11) Izmailova, S. G.; Vasiljeva, E. A.; Karetina, I. V.; Feoktistova, N. N.; Khvoshchev, S. S. Adsorption of Methanol, Ammonia and Water on

the Zeolite-like Aluminophosphates $AlPO_4$-5, $AlPO_4$-17, and $AlPO_4$-18. *J. Colloid Interface Sci.* **1996**, *179*, 374–379.

(12) Newalkar, B. L.; Jasra, R. V.; Kamath, V.; Bhat, S. G. T. Sorption of *n*-pentane, 2-methylbutane and Cyclopentane in Microporous $AlPO_4$-5. *Microporous Mesoporous Mater.* **1997**, *11*, 195–205.

(13) Jhung, S. H.; Chang, J. S.; Hwang, Y. K.; Park, S. E. Crystal Morphology Control of AFI Type Molecular Sieves With Microwave Irradiation. *J. Mater. Chem.* **2004**, *14*, 280–285.

(14) Hu, E. P.; Huang, Y. L. W.; Yan, Q.; Liu, D. P.; Lai, Z. P. Synthesis of Highly *c*-oriented AFI Membranes by Epitaxial Growth. *Microporous Mesoporous Mater.* **2009**, *126*, 81–86.

(15) Jhung, S. H.; Chang, J. S.; Kim, D. S.; Park, S. E. Effects of Silica on the Synthesis of AFI Molecular Sieve in Acid and Base Conditions Under Microwave Irradiation. *Microporous Mesoporous Mater.* **2004**, *71*, 135–142.

(16) Jhung, S. H.; Hwang, Y. K.; Chang, J. S.; Park, S. E. Effect of Acidity and Anions on Syntesis of AFI Molecular Sieves in Wide pH range of 3−10. *Microporous Mesoporous Mater.* **2004**, *67*, 151–157.

(17) Nicolau, M. P. M.; Barcia, P. S.; Gallegos, J. M.; Silva, J. A. C.; Rodrigues, A. E.; Chen, B. Single- and Multicomponent Vapor-Phase Adsorption of Xylene Isomers and Ethylbenzene in a Microporous Metal-organic Framework. *J. Phys. Chem. C* **2009**, *113*, 13173–13179.

(18) Cavalcante, C. L., Jr.; Azevedo, D. C. S.; Souza, I. G.; Silva, A. C. M.; Alsina, O. L. S.; Lima, V. E.; Araujo, A. S. Sorption and Diffusion of p-xylene and o-xylene in Aluminophosphate Molecular Sieve $AlPO_4$-11. *Adsorption* **2000**, *6*, 53–59.

Received for review January 27, 2010. Accepted April 3, 2010.

JE100093U