J|A|C|S
ARTICLES

Anion-Controlled Pore Size of Titanium Silicate Molecular Sieves

Christopher C. H. Lin,[†] James A. Sawada,[‡] Lan Wu,[†] Tony Haastrup,[†] and Steven M. Kuznicki*,[†]

Department of Chemical and Materials Engineering, University of Alberta, Edmonton, AB, Canada T6G 2V4, and QuestAir Technologies Inc., 6961 Russell Avenue, Burnaby, BC, Canada V5J 4R8

Received August 13, 2008; E-mail: steve.kuznicki@ualberta.ca

Abstract: Titanium silicate molecular sieves contain structural units that are fundamentally different from classical aluminosilicates. In addition to ordered octahedral titanium chains, members of the zorite family contain pentagonal titanium units which project into the main adsorption channels of the framework. We report that the effective pore size of these materials can be controlled by substituting halogens at the O7 sites that cap the pentagonal pyramids projecting into the channel. The quantity and type of halogen used determines the adsorptive properties of the molecular sieve. Barium exchange stabilizes these materials over a wide temperature range (nominally 200−400 °C). The barium-exchanged materials do not contract appreciably with calcination, as is observed in related Molecular Gate materials, and thus halogen content can control the pore size of the materials. This new approach to pore size control may have important implications for the purification of multiple classes of compounds, including light hydrocarbons and permanent gases.

1. Introduction

Zeolite molecular sieves are an important class of inorganic materials widely employed in the chemical processing industry for applications ranging from adsorption to catalysis and ion-exchange.[1−3] Molecular sieves are crystalline microporous metal oxides that derive their name, in part, from their ability to separate molecular species by size.[4] Precise separations are possible because the three-dimensional network of uniformly sized pores and channels within the molecular sieve can discriminate between molecules on the basis of the difference in their sizes. This unique structure has resulted in the utilization of molecular sieves in many commercial adsorptive separation processes, especially hydrocarbon purification.[5−9]

Classical aluminosilicate molecular sieves have pore openings which range from 2.5 to 10 Å. The pore aperture of each sieve is determined by the 6-, 8-, 10-, or 12-membered rings inherent to its specific zeolitic structure.[10] The pore size of these materials can be modified to some extent by cation substitution within the porous framework, but the control is incremental and restricted to certain structure types.[10] For example, potassium ion-exchange with zeolite NaA (pore size of ∼3.8 Å) reduces its effective pore size to ∼3.3 Å because potassium, being a larger monovalent cation than sodium, blocks the pore openings more effectively. This reduction does not occur gradually with increasing ion-exchange but changes suddenly at a threshold of ∼25% potassium exchange.[10] Similarly, the effective pore size of NaA increases abruptly to ∼4.3 Å after ∼30% calcium exchange. This approach to pore size control allows step-size changes in pore aperture but does not yield molecular sieves with a continuum of effective pore sizes. Since some important separations (such as CO/N_2 and O_2/Ar) require intermediate pore sizes that are currently unachievable with titanium silicate molecular sieves, a new approach to channel aperture control would expand the possible applications of this family of molecular adsorbents.

An evolution in pore size control for crystalline molecular sieves began when a unique property of Engelhard Titanosilicate-4 (ETS-4),[11,12] the first synthetic zorite[13,14] analogue, was reported.[15] In most cation forms, the crystal lattice of ETS-4 systematically contracts upon structural dehydration at elevated

---

[†] University of Alberta.

[‡] QuestAir Technologies Inc.

(1) Keller G. E., II; Anderson, R. A.; Yon, C. M. In *Handbook of Separation Process Technology*; Rousseau, R. W., Eds.; Wiley: Hoboken, NJ, 1987; pp 644−696.

(2) Weitkamp, J. *Solid State Ionics* **2000**, *131*, 175.

(3) Helfferich, F. *Ion Exchange*; Dover: New York, 1995.

(4) Cundy, C. S.; Cox, P. A. *Chem. Rev.* **2003**, *103*, 663.

(5) Butwell, K. F.; Dolan, W. B.; Kuznicki, S. M. U.S. Patent 6,197,092, March 6, 2001.

(6) Kuznicki, S. M.; Bell, V. A.; Petrovic, I.; Desai, B. T. U. S. Patent 6,068,682, May 30, 2000.

(7) Kuznicki, S. M.; Bell, V. A. U.S. Patent 6,517,611, February 11, 2003.

(8) Roeseler, C. M.; Kulprathipanja, S.; Rekoske, J. E. U.S. Patent 6,706,938, March 16, 2004.

(9) Choi, S.; Lee, S.-J.; Kang, S.-C.; Kim, S.-W.; Ku, M. S.; Choi, A.-S.; Chang, B.-M. U.S. Patent 6,870,073, March 22, 2005.

(10) Breck, D. W. *Zeolite Molecular Sieves: Structure, Chemistry and Use*; Wiley: New York, 1974.

(11) Yilmaz, B.; Miraglia, P. Q.; Warzywoda, J.; Sacco, A., Jr *Microporous Mesoporous Mater.* **2004**, *71*, 167.

(12) Kuznicki, S. M. U.S. Patent 4,938,939, July 3, 1990.

(13) Sandomirskii, P. A.; Belov, N. V. *Sov. Phys. Crystallogr.* **1979**, *24*, 686.

(14) Mer‘kov, A. N.; Bussen, I. V.; Goiko, E. A.; Kul’chitskaya, E. A.; Men’shikov, Y. P.; Nedorozova, A. P. *Zap. Vses. Mineral. Obshchest.* **1973**, *102*, 54.

(15) Kuznicki, S. M.; Bell, V. A.; Nair, S.; Hillhouse, H. W.; Jacubinas, R. M.; Braunbarth, C. M.; Toby, B. H.; Tsapatsis, M. *Nature* **2001**, *412*, 720.

10.1021/ja806114z CCC: $40.75

temperatures and, through this mechanism, the lattice dimensions and, consequently, the channel apertures of ETS-4 can be controlled to “tune” the effective size of the pores. This phenomenon, known as the Molecular Gate effect, has achieved commercial success in natural gas purification.[5,6] Contracted Sr-ETS-4 (CTS) adsorbents, for example, have been applied to difficult size-based separations including N_2/CH_4 (3.64 vs 3.76 Å, respectively[16]) on an industrial scale. However, the contraction process inevitably damages the ETS-4 framework and introduces crystal lattice defects, eliminating some pore volume and reducing the capacity of the adsorbent.[17,18] Therefore, only certain cation-exchanged forms of ETS-4-based adsorbents are stable under thermal activation, limiting the practical usage of Molecular Gate technology.

2. Experimental Methods

Synthesis. Synthesis of halogen-free zorite (HFZ-1) and three members of a new class of titanosilicate materials, the halogen-containing zorites (ETS-4, RPZ-1, and RPZ-2), was performed hydrothermally in 125 mL Teflon-lined autoclaves (PARR Instruments) using the compositions, synthesis temperatures, and reaction times outlined below. All mixtures were stirred in a Waring blender for 1 h prior to charging the autoclaves. The typical procedure for HFZ-1 synthesis (molar ratio of $SiO_2/TiO_2/Na_2O/K_2O/H_2O/F/Cl/I = 6.82:1:4.46:0.76:205.25:0:0:0$) involved mixing 1.32 g of potassium hydroxide (85+% KOH, Fisher) with 3.00 g of sodium hydroxide (97+% NaOH, Fisher) in 15.00 g of deionized water (resistivity >18 MΩcm). This mixture was then added to 22.00 g of sodium silicate (28.80% SiO_2, 9.14% Na_2O, Fisher), followed by the addition of 32.22 g of titanium oxysulfate solution (4.27% Ti, Aldrich). Unlike monovalent anions, divalent anions (such as SO_4) cannot be linked to the chain-bridging titanium units, thus will not be incorporated into the HFZ-1 framework. The reaction mixture for HFZ-1 was autoclaved at 215 °C for 48 h. ETS-4 (molar ratio of $SiO_2/TiO_2/Na_2O/K_2O/H_2O/F/Cl/I = 5.75:1:4.45:1.55:40.97:3.10:4.27:0$) was synthesized at 150 °C for 168 h in a mixed F/Cl system as described in the patent literature.[12] RPZ-1 synthesis (molar ratio of $SiO_2/TiO_2/Na_2O/K_2O/H_2O/F/Cl/I = 5.75:1:4.45:0.95:40.97:0:6.18:0$) involved mixing 25.10 g of sodium silicate, 4.60 g of sodium hydroxide, 3.00 g of potassium chloride (99% KCl, Fisher), and 16.30 g of titanium trichloride (20% $TiCl_3$, 6% HCl, Fisher), and autoclaved at 200 °C for 40 h. RPZ-2 (molar ratio of $SiO_2/TiO_2/Na_2O/K_2O/H_2O/F/Cl/I = 5.75:1:4.45:1.55:61.92:0:4.27:3.10$) was synthesized by mixing 25.10 g of sodium silicate, 4.60 g of sodium hydroxide, 10.88 g of potassium iodide (99% KI, Fisher), and 16.30 g of titanium trichloride. The reaction mixture for RPZ-2 was autoclaved at 215 °C for 16 h. All materials were thoroughly washed and filtered prior to cation-exchange. Ion-exchange for Ba^{2+} was carried out by refluxing at 100 °C in 0.82 M of aqueous barium chloride for 2−24 h. The Ba-exchanged materials were pelletized by mixing 6.00 g of the molecular sieves (equilibrated at 100 °C) with 2.50 g of Ludox HS-40 colloidal silica (Aldrich). The mixture was homogenized using a mortar and pestle and compressed in a pellet press to 10 000 psi. The resulting cakes were crushed and sieved to obtain 16−50 mesh particles and utilized for gas chromatography analysis.

Characterization. HFZ-1, ETS-4, RPZ-1, and RPZ-2 were characterized by instrumental neutron activation analysis (INAA), wavelength dispersive X-ray spectroscopy (WDX), powder X-ray diffraction (XRD), inverse-phase gas chromatography (IGC), and equilibrium adsorption isotherm analysis. INAA was conducted using the SLOWPOKE Nuclear Reactor Facility located at the University of Alberta. WDX data were collected using a JEOL JZA-8900R WD/ED Combined Microanalyzer. Signals were obtained from secondary electrons at an accelerating voltage of 15 kV. Phase identification of the as-synthesized materials was conducted through XRD using a Rigaku Geigerflex 2173 with a vertical goniometer equipped with a graphite monochromator for filtration of K-β wavelengths. IGC analysis was performed on a Varian 3800 GC equipped with a thermal conductivity detector (TCD). Test adsorbents were packed into 10-in. long copper columns with an OD of 0.25 in. The columns were filled with ~4 g of pelletized adsorbents (16−50 mesh), which were activated at 250 °C for 10 h under a helium flow of 30 cm^3/min. Characterization gas (single-phase or mixture) was introduced by a 1 mL pulse injection into the column. Equilibrium adsorption isotherms were measured volumetrically at 25 °C up to 100 kPa using an AUTOSORB-1-MP from Quantachrome Instruments (Boynton Beach, FL) on crystalline powders (no binders or diluents were added to the samples). All samples were activated at 250 °C for 10 h under vacuum (<0.0005 Torr).

Structure Modeling. Unit cell representations of anion-controlled zorite analogues, viewed along the [0 1 0] direction (*b*-axis), were generated and modified using the CCDC software Mercury[19] with crystallographic data obtained from the literature.[20] The model portrays the statistical occupancies of Si and Ti in the unit cell. Titanium and silicon atoms are depicted as black and gray, respectively. Other species include O (red), F (green), Cl (blue), and I (violet). Van der Waals radii were used to depict the size of all framework elements.[21] Extra-framework cations and water molecules were omitted for clarity.

3. Results and Discussion

We have developed a novel mechanism to precisely control the effective pore size of synthetic titanium silicate zorite analogues. The new control mechanism does not rely on cation substitution or structural contraction; instead, the channel dimensions are manipulated by controlling the size and concentration of framework anions projecting into the channels. ETS-4 and zorite analogues contain chains of octahedrally coordinated Ti propagating in the [0 1 0] direction that are connected by silicate tetrahedra in the [0 0 1] crystal plane.[22,23] Relative to these six-coordinated titanium atoms (Ti1) of occupancy factor 1, the unit cell also contains chain-bridging units consisting of five-coordinated titanium atoms (Ti2) having a fractional occupancy of ~0.25.[20,24,25] This model is statistically portrayed by the Rietveld-refined crystal structure of zorite analogues presented in Figure 1. On the basis of this proposed structure, an atom at the terminal position of the five-coordinated square-pyramid, designated as the O7 crystallographic site (Figure 1a), will project into the [0 1 0] channel system (*b*-axis) and act as a physical barrier restricting the effective pore size of the molecular sieve. It has been proposed that the O7 sites are occupied by hydroxyl groups[23] or related species such

---

(16) Sircar, S.; Myers, A. L. In *Handbook of Zeolite Science and Technology*; Auerbach, S. M., Carrado, K. A., Dutta, P. K., Eds.; Marcel Dekker Inc.: New York, 2003; pp 1063−1104.

(17) Marathe, R. P.; Farooq, S.; Srinivasan, M. P. *Langmuir* **2005**, *21*, 4532.

(18) Marathe, R. P.; Mantri, K.; Srinivasan, M. P.; Farooq, S. *Ind. Eng. Chem. Res.* **2004**, *43*, 5281.

(19) Cambridge Crystallographic Data Center. Mercury 1.4.2−Structure Modeling Software. http://www.ccdc.cam.ac.uk/products/mercury/ (accessed June 15, 2008).

(20) Nair, S.; Jeong, H.-K.; Chandrasekaran, A.; Braunbarth, C. M.; Tsapatsis, M.; Kuznicki, S. M. *Chem. Mater.* **2001**, *13*, 4247.

(21) Pauling, L. *The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry*; Cornell University Press: New York, 1960.

(22) Philippou, A.; Anderson, M. W. *Zeolites* **1996**, *16*, 98.

(23) Cruciani, G.; De Luca, P.; Nastro, A.; Pattison, P. *Microporous Mesoporous Mater.* **1998**, *21*, 143.

(24) Braunbarth, C.; Hillhouse, H. W.; Nair, S.; Tsapatsis, M.; Burton, A.; Lobo, R. F. *Chem. Mater.* **2000**, *12*, 1857.

(25) Nair, S.; Tsapatsis, M.; Toby, B. H.; Kuznicki, S. M. *J. Am. Chem. Soc.* **2001**, *123*, 12781.

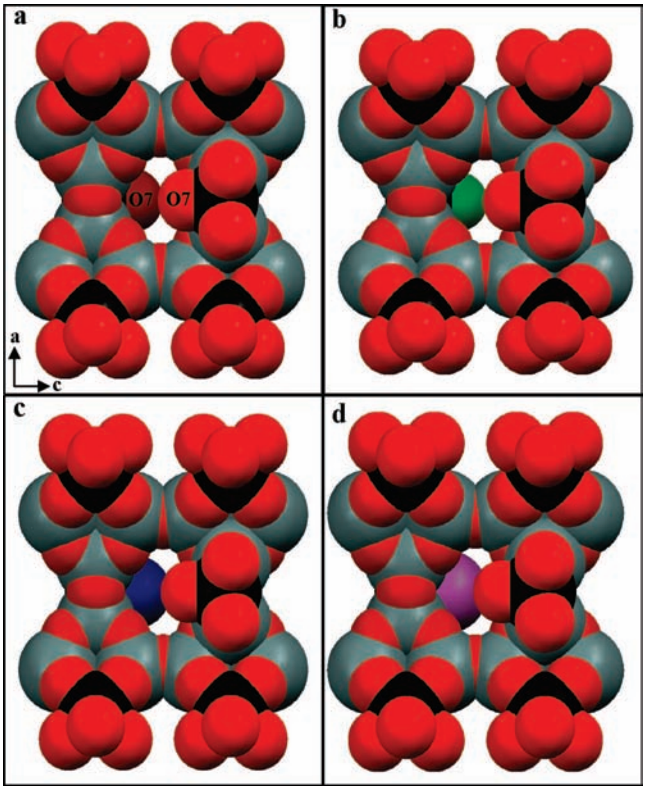

Figure 1. Unit cell representations of anion-controlled zorite analogues. (a) The zorite framework with OH occupying the O7 sites, viewed along the [0 1 0] direction (*b*-axis). Halogen-free zorite has the largest effective pore size and channel accessibility of the series. Titanium, silicon, and oxygen atoms are depicted as black, gray, and red, respectively. (b) Fractional substitution of F (green) for O (red) at an O7 site. This substitution does not substantially change the effective pore size since F (1.35 Å) and O (1.40 Å) are nearly identical in size.[21] (c) Halogen-containing zorite with Cl (blue) substitution at an O7 site. Pore size reduction, through a steric effect, is evident when (c) is compared to (a) and (b). (d) Iodine (violet) substitution at an O7 site. This zorite analogue has the smallest effective pore size of the series.

as structural water,[26] and we propose that these groups can be substituted through synthesis with monovalent anions, particularly halogens. Halogen substitution is not uncommon in nature, especially in rock-forming silicates such as topaz[27] and tremolite.[28] Our model suggests that large halogens such as Cl or I (panels c and d of Figure 1, respectively), when positioned at the O7 sites, create a steric effect that reduces the effective pore size of titanium silicate zorite analogues.

Certain cations, such as barium, stabilize the pore size of zorite analogues against contraction over a large temperature regime.[29] In our current approach, the pore size of the Ba-stabilized materials is then controlled by manipulating the type and quantity of anions along the channel walls. This new approach may allow greater precision and flexibility than other methods of pore size control reported to date, and has potential applications in multiple areas of size-based separation, including light hydrocarbon purification and permanent gas separation.

Table 1. Quantitative Bulk Elemental Analyses of Anion-Controlled Zorite Analogues[a]

sample	Si	Ti	Ba	F[b]	Cl	I
			INAA (Mass Percent) Composition Data			
Ba-HFZ-1	18.7	11.8	27.9	–	<0.02	ND
Ba-ETS-4	18.3	11.4	28.7	–	0.15	ND
Ba-RPZ-1	18.5	12.0	29.5	–	0.22	ND
Ba-RPZ-2	18.1	11.1	28.9	–	0.28	0.20
			WDX (Mass Percent) Composition Data			
Ba-HFZ-1	18.6	11.8	27.7	ND	<0.01	ND
Ba-ETS-4	18.3	11.8	27.8	0.20	0.14	ND
Ba-RPZ-1	18.0	11.7	28.9	ND	0.23	ND
Ba-RPZ-2	18.1	11.9	28.8	ND	0.24	0.19

[a] ND = not detectable (below detection limit). [b] Fluorine cannot be quantified by INAA.

The results of quantitative bulk elemental analyses of synthetic halogen-free zorite (HFZ-1) and three members of a new class of titanosilicate materials, the halogen-containing zorites (ETS-4[12] and the reduced-pore zorites[30] RPZ-1 and RPZ-2), by instrumental neutron activation analysis (INAA) and wavelength dispersive X-ray spectroscopy (WDX) are shown in Table 1. The analyses confirm that the halogen content of the four materials reflects the molar composition of the synthesis mixtures from which the materials were prepared. These results indicate that halogens can be incorporated directly into the framework of titanium silicate zorite analogues through the synthesis process. Partial, rather than total, replacement with halogens at the O7 sites was observed in all cases (except HFZ-1). The highest level of halogen incorporation at the O7 sites was observed in ETS-4, with almost 30% replacement by halogen species, predominantly fluorine. In other mixed halogen systems, substitution was always dominated by the smaller of the halogen species. The data suggest that these titanosilicate frameworks prefer hydroxyl groups and appear to be selective toward halogens with smaller atomic radii, preferentially incorporating halogens in the sequence of F > Cl > I (Van der Waals radii: 1.35, 1.80, and 2.15 Å, respectively[21]). Additional experimentation is underway to determine whether this selectivity series is driven by thermodynamic or kinetic factors.

Phase identification for the four zorite analogues was conducted through powder X-ray diffraction analysis (XRD). The XRD patterns (Figure 2) indicate that the as-synthesized materials are highly crystalline with unit cell parameters closely resembling those of mineral zorite.[13,14] The data also demonstrate that the unit cell size does not change with the type or quantity of halogen incorporated. Within the framework, only an isomorphic substitution at the O7 position can account for this observation, as substitutions at any other position would create either a distortion or a change in the lattice parameters. The inversion in the relative intensities of the two dominant peaks observed at 2θ angles of 8.8° and 14.7° (for HFZ-1 and ETS-4 compared to RPZ-1 and RPZ-2) is likely an effect of preferred orientation or coarse grain effects, and not indicative of a change in the overall lattice structure.

According to our model, the effective pore size of halogen-containing zorites should decrease as the number of framework halogens increases, since the halogen atoms will act as physical barriers and reduce channel accessibility for adsorbate molecules. Figure 1 indicates that the effective pore size should be influenced not only by the type (size) of halogens occupying the O7 positions but also by the quantity of halogen atoms that line the channel walls. A large population of halogens in the

---

(26) Usseglio, S.; Calza, P.; Damin, A.; Minero, C.; Bordiga, S.; Lamberti, C.; Pelizzetti, E.; Zecchina, A. *Chem. Mater.* **2006**, *18*, 3412.

(27) Alberico, A.; Ferrando, S.; Ivaldi, G.; Ferraris, G. *Eur. J. Mineral.* **2003**, *15*, 875.

(28) Cameron, M.; Gibbs, G. V. *Am. Mineral.* **1973**, *58*, 879.

(29) Kuznicki, S. M.; Bell, V. A.; Petrovic, I.; Blosser, P. W. U.S. Patent 5,989,316, November 23, 1999.

(30) Kuznicki, S. M.; Sawada, J. A.; Rode, E. J.; Lin, C. C. H. World Patent No. WO/2008/002463, March 1, 2008.

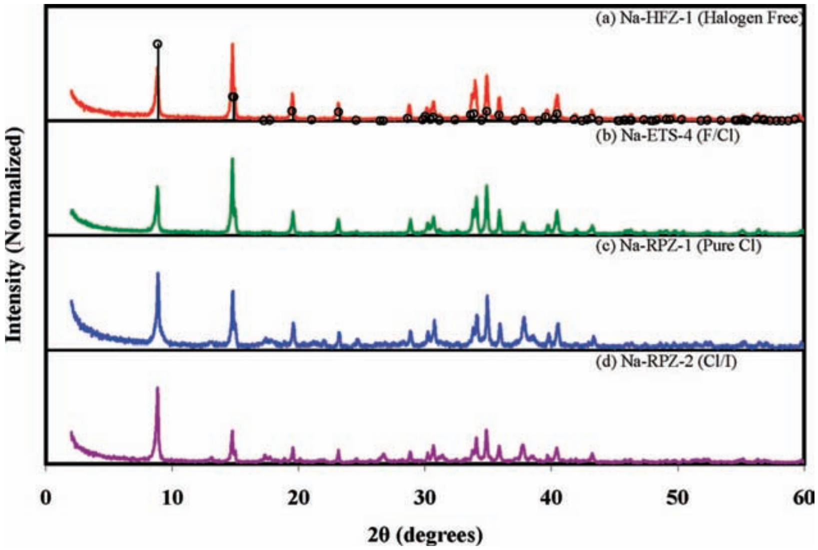

Figure 2. Powder X-ray diffraction of as-synthesized anion-controlled zorite analogues. (a) XRD pattern for HFZ-1. All of the zorite analogues have unit cell parameters that closely resemble those of mineral zorite.[13,14] The JCPDS reference for zorite (PDF no. 01-084-0144) is superimposed on the HFZ-1 XRD pattern for comparison (black circles). (b) XRD pattern for ETS-4. Fractional substitution of F and Cl for O has no discernible effect on the unit cell parameters. (c) XRD pattern for RPZ-1. Inversion in the relative intensities at 2θ angles of 8.8° and 14.7°, as compared to HFZ-1 and ETS-4, is likely due to coarse grain effects in HFZ-1 and ETS-4, and not structural differences between the zorite analogues. (d) XRD pattern for RPZ-2. Mixed Cl/I incorporation increases the observed peak inversion.

channel should result in pores that appear smaller to the diffusing gas species and restrict the rate of mass transfer. Conversely, if halogens are absent from the channels, as in the structure of HFZ-1, channel accessibility should be maximized, creating the largest possible effective pore diameter.

Both gas chromatography and equilibrium adsorption isotherm analysis (Figure 3 and Figure 4, respectively) support this model. The data illustrate that, despite their limited crystallographic differences, the adsorption properties and effective pore size of Ba-exchanged HFZ-1, ETS-4, RPZ-1, and RPZ-2 differ significantly, and that those differences correlate to composition. HFZ-1 contains no halogens, while ETS-4, RPZ-1 and RPZ-2 have been substituted (relative to HFZ-1) with F/Cl, Cl, and Cl/I, respectively (Van der Waals radii: F = 1.35 Å, Cl = 1.80 Å, and I = 2.15 Å[21]). The adsorptive characteristics of Ba-exchanged HFZ-1, ETS-4, RPZ-1, and RPZ-2 were examined by chromatographic separation of O_2/Ar. The O_2/Ar (3.47 and 3.54 Å, respectively[16]) pair was chosen because subtle changes in the pore size (<0.1 Å resolution) of the adsorbents should significantly affect the separation of these probe molecules. Separation of oxygen and argon was not observed on either Ba-HFZ-1 or Ba-ETS-4 (Figure 3a). Comparison with the pure gas chromatograms of oxygen and argon (data not shown) indicates that both oxygen and argon molecules are free to enter the channels of Ba-HFZ-1 and Ba-ETS-4. Since the isosteric heats of adsorption for oxygen and argon are similar,[31] thermodynamic selectivity is not expected if both species are fully adsorbed. However, when the pore size is systematically restricted by increasing the halogen content, as in Ba-RPZ-1 and Ba-RPZ-2, the marginally larger Ar molecules are excluded based on size. Water adsorption capacities of the samples (~10% at saturation) are nearly identical in all cases, indicating that the intracrystalline void spaces are comparable. The degree of halogen substitution is apparently too small to substantially change the internal pore volume.

It appears that synthetically incorporated halogens can be replaced by hydroxyl groups during prolonged reflux in an aqueous solution. Inverse-phase gas chromatography (IGC) analysis of O_2/Ar separation in Figure 3b indicates that the effective pore size of Ba-RPZ-1 systematically increases as a function of ion-exchange time during reflux in a barium chloride solution. At short exchange times (2 h), high quantities of framework Cl in Ba-RPZ-1 restrict the diffusion of both oxygen and argon. As the exchange time is extended (up to 24 h), an increasing number of framework Cl atoms are selectively replaced with OH. Reducing the framework Cl in Ba-RPZ-1 increases the effective pore size and channel accessibility, allowing oxygen to diffuse into the molecular sieve and facilitating the kinetic separation of oxygen from argon. The data suggest that materials with a continuum of pore sizes can be derived from a parent material (such as Na-RPZ-1) simply by controlling the ion-exchange times and conditions. It is important to note that, while the effective pore size of halogen-containing zorite materials can be systematically manipulated to allow size-based separation of O_2 and Ar, this system is not currently optimized for commercial separations of these probe molecules.

This new, finely controlled mechanism allows for the design of adsorbents with highly specific pore sizes and adsorptive characteristics. The data presented in Figure 4 illustrate the adsorption or exclusion of three selected gas molecules, ethane (4.44 Å), methane (3.76 Å), and nitrogen (3.64 Å),[16] based on kinetic diameter. Ba-HFZ-1, which is synthesized in the absence of halogens, has the largest channel accessibility and is the only material of the series that can adsorb ethane. Methane, having a smaller diameter than ethane, can enter the pores of both Ba-HFZ-1 and Ba-ETS-4, but is excluded from the Ba-RPZ materials. The exclusion of methane is the result of halogens in both the Ba-RPZ-1 and Ba-RPZ-2 frameworks restricting pore size and channel accessibility. In the case of nitrogen (the smallest molecule of the three examined), all of the materials except

---

(31) Peter, S. A.; Sebastian, J.; Jasra, R. V. *Ind. Eng. Chem. Res.* **2005**, *44*, 6856.

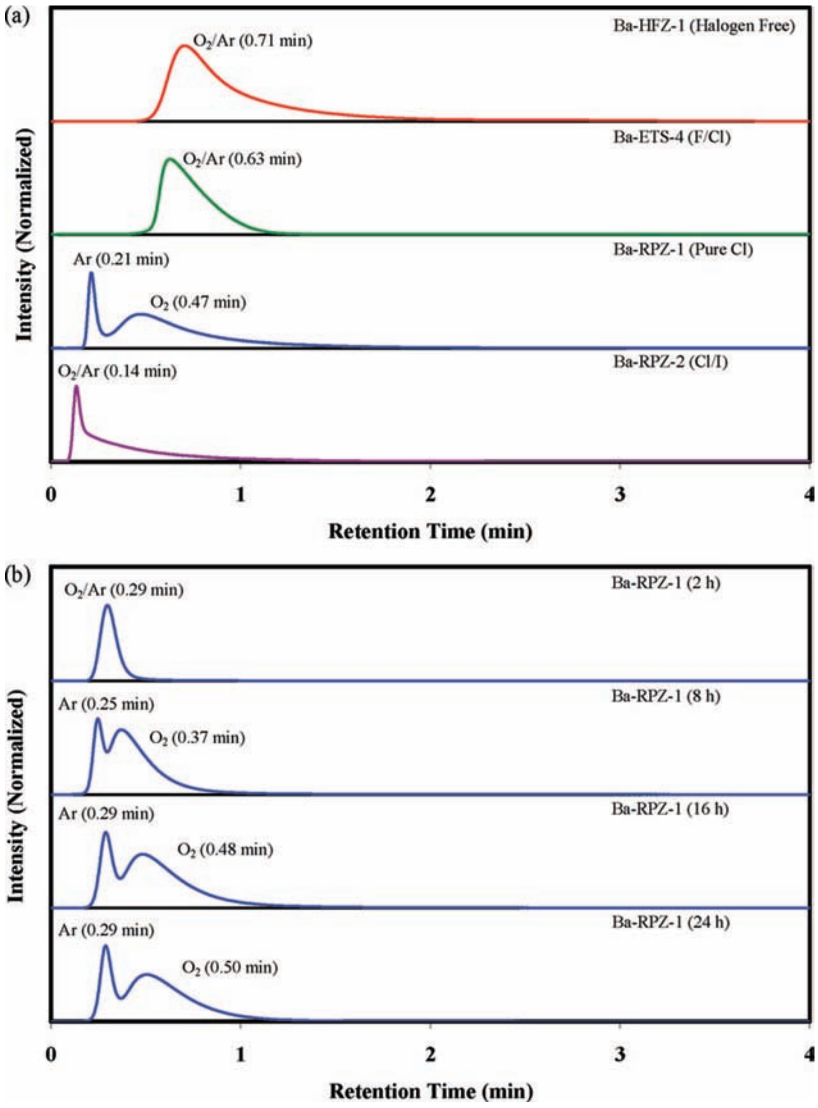

Figure 3. Chromatographic separation of O$_2$/Ar on anion-controlled zorite analogues. (a) Chromatographic separation of O$_2$/Ar (3.47 and 3.54 Å, respectively[16]) on Ba-HFZ-1, Ba-ETS-4, Ba-RPZ-1, and Ba-RPZ-2. As framework halogen incorporation increases in the synthetic zorite series, Ar is selectively size-excluded, facilitating the kinetic separation of oxygen from argon, as seen in Ba-RPZ-1. At the highest level of halogen incorporation, Ba-RPZ-2 excludes both oxygen and argon at a zero-time (minimum time for gas molecules to diffuse through the void space of the column) of 0.14 min. (b) Chromatographic separation of O$_2$/Ar (3.47 and 3.54 Å, respectively[16]) on four samples of Ba-RPZ-1 that have been ion-exchanged for increasing time periods. As the exchange time increases, the Cl atoms within the Ba-RPZ-1 framework are replaced by smaller hydroxyl groups (OH), increasing the effective pore size of the zorite analogue. Systematic enlargement of effective pore size facilitates the kinetic separation of oxygen from argon.

Ba-RPZ-2 show substantial adsorption, confirming that Ba-RPZ-2, which contains the highest level of framework halogens, has the smallest effective pore size of the series. The small capacities for C_2H_6 and CH_4 on Ba-RPZ-2 can be attributed to the adsorption of C_2H_6 and CH_4 on the external surfaces of the adsorbent. Surface adsorption of N_2 is not observed, as it is a less polar species. The correlation between framework anion concentration and functional pore size validates the model that the pore size of these titanium silicate molecular sieves can be controlled by manipulating the anions in the framework structure. The quantity and type of O7 substituted halogens directly controls the effective pore size of these titanium silicate zorite analogues.

It should be noted that the coordination state of the chain-bridging titanium atom (Ti2) in zorite analogues remains a subject of active debate in the literature.[20,23−26] Some studies have concluded that the O7 site is a titanyl group, with a Ti=O linkage to the apical oxygen,[20] while the results of other work indicate that the site is occupied by a titanol group (Ti−OH)[23] or a linkage to structural water.[26] In this work, location of the halogens was assigned to the O7 position because this is the position that is most strongly supported by the structural and functional data. On the basis of these data, the only location for the halogens that could have such a profound impact on the effective pore size and the observed adsorptive properties is the O7 position, as indicated in Figure 1. Further research will be required to definitively determine the coordination state of the chain-bridging titanium atom (Ti2) in titanium silicate molecular sieves and its implication for this proposed model of a novel mechanism for rational pore size control in a molecular sieve. This model best explains current observations, but we recognize that other explanations are possible. Irrespective, we report a new method to control the effective pore size of titanium silicate molecular sieves with extraordinary precision.

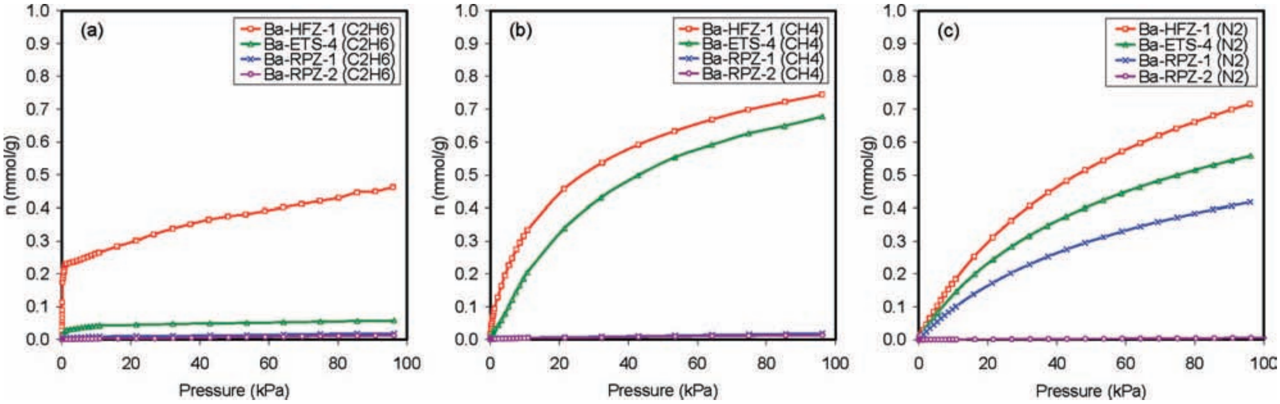

Figure 4. Equilibrium adsorption isotherms of anion-controlled zorite analogues. (a) Ethane (C_2H_6) isotherms for the series Ba-HFZ-1, Ba-ETS-4, Ba-RPZ-1, and Ba-RPZ-2. Ba-HFZ-1, which contains no framework halogens, is the only material that adsorbs ethane (4.44 Å[16]). Ethane is excluded from all three halogen-containing zorites. (b) Methane (CH_4) isotherms for the series Ba-HFZ-1, Ba-ETS-4, Ba-RPZ-1, and Ba-RPZ-2. Ba-RPZ-1 and Ba-RPZ-2, which have high concentrations of framework halogens, completely exclude methane (3.76 Å[16]). Both Ba-HFZ-1 and Ba-ETS-4 adsorb methane, indicating a larger effective pore size than the Ba-RPZ materials. (c) Nitrogen (N_2) isotherms for the series Ba-HFZ-1, Ba-ETS-4, Ba-RPZ-1, and Ba-RPZ-2 indicate that Ba-RPZ-2, which contains the highest level of framework halogens and is the only zorite analogue to exclude nitrogen (3.64 Å[16]), has the smallest effective pore size of the series.

4. Conclusions

We have established a novel mechanism to systematically control the pore size of titanium silicate molecular sieves through halogen substitution of terminal hydroxyl groups. These halogen-containing zorites represent a new class of size-selective adsorbents with readily tailored and highly specific pore sizes. Anion-controlled titanium silicate molecular sieves have promise in multiple areas of size-based separation, particularly light hydrocarbon purification and permanent gas separation.

Acknowledgement. The authors thank Tong Qiu for general contributions and Dr. Amy Dambrowitz for assistance with manuscript development. J.A.S. thanks Dr. Mati Raudsepp for his assistance and insights. Support from the Canada Research Chair in Molecular Sieve Nanomaterials (S.M.K.), and the Natural Sciences and Engineering Research Council Industrial Research Chair in Molecular Sieve Separations Technology (S.M.K.) is gratefully acknowledged.

JA806114Z