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Low Si/Al Ratio Zeolites

Open-Framework Materials Synthesized in the TMA^+/TEA^+ Mixed-Template System: The New Low Si/Al Ratio Zeolites UZM-4 and UZM-5**

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For over half a century, zeolites have played a major role in the development of modern processes in the chemical and petroleum industries.[1] Their unique combination of physical and chemical properties are ideal for catalysis and separations for a broad range of molecules. Recent advances in zeolite synthesis have centered on high silica zeolite systems or have employed exotic templates.[2] However, low Si/Al ratio zeolites are particularly attractive because they can offer high acid site density for catalytic applications and greater ion-exchange capacity and compositional diversity for separation processes. We report here our discovery of two new zeolite materials, UZM-4 and UZM-5, synthesized at low Si/Al ratios ($Si/Al < 10$) by using combinations of two of the most common organic templating agents, the tetramethylammonium (TMA^+) and tetraethylammonium (TEA^+) ions.[3] UZM-4 is a large pore 12-ring zeolite with the BPH framework type[4,5] and a sufficiently high Si/Al ratio (1.5–2.5) to enable thermal stability. UZM-5 has an unprecedented framework type that contains an 8-ring pore system similar

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[**] TMA^+ = tetramethylammonium ion, TEA^+ = tetraethylammonium ion.

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to that of zeolite A in two dimensions, and a catalytically active surface that contains 16-ring cups.

UZM-4 is a thermally stable zeolite synthesized with the BPH framework type, which exhibits appropriate stability (600 °C) for use in catalytic and adsorbent applications.

The BPH framework type, first described for the beryllophosphate $K_7Na_7Be_{14}P_{14}O_{56}$,[6] has hexagonal symmetry and consists of one-dimensional 12-ring pores linked by intersecting 8-ring pores. Zeolite Q,[7] the first zeolite discovered with this framework type, was unstable and not shown to be a large-pore zeolite until 30 years later by Andries et al.[8] Whereas zeolite Q is crystallized in the K^+-Al-Si-O system with an Si/Al ratio of 1, UZM-4 has been prepared with an Si/Al ratio of 1.5:1–2.5:1 in the Li^+, TMA^+, TEA^+ template system. A typical reaction mixture formulation is $4.0\,TEAOH:2.5\,SiO_2:Al(OH)_3:1\,TMACl:0.5\,LiCl:100\,H_2O$, which yields a product of unit cell formulation $Li_{6.1}TMA_{3.3}TEA_{0.1}Al_{10}Si_{18}O_{56}$.

The higher Si/Al ratio is evident in the X-ray diffraction pattern and IR spectrum of UZM-4, in which diffraction lines were shifted to higher 2Θ values and asymmetric T-O-T stretches to higher frequencies, respectively.[9] The resultant shrinkage of the unit cell from $a = 13.50$ and $c = 13.40$ Å for zeolite Q (Si/Al = 1) to $a = 13.3069(6)$ and $c = 13.2510(8)$ Å for UZM-4 (Si/Al = 1.78) is consistent with the substitution of the smaller Si^{4+} ion for the Al^{3+} ion. As is well known for many zeolites, the higher Si/Al ratio in UZM-4 increases its thermal stability. Variable-temperature X-ray diffraction studies show as-synthesized UZM-4 is stable to 600 °C under dry conditions.[10] By comparison, the structure of zeolite Q collapses at 200 °C.[11]

An unusual aspect of UZM-4 is that most or all (typically > 95 %) of the organic template can be removed from the pores directly by ion exchange. This is facilitated by the 12-ring pore with a free diameter of 7 Å that periodically opens up to a cavity with a diameter of 12.5 Å. These exchange properties may be enhanced by the fact that UZM-4 crystallizes as hexagonal plates 10–40 nm thick, and the 12-ring pores run perpendicular to the plate surface. The ability to remove the organic template from the pores without calcining circumvents the need to deal with potentially unstable acidic forms that would result from template decomposition. Thus, ion-exchanged UZM-4 compositions are directly accessible for adsorbent applications. In addition, the higher Si/Al ratio of UZM-4 affords enough stability to withstand the modifications necessary to develop acidic catalysts.[12] Therefore, UZM-4 is a novel, large-pore zeolite with sufficient stability for both adsorbent and catalytic applications.

The second zeolite presented here, UZM-5, is a completely new framework type. It can be synthesized from the TMA^+/TEA^+ mixed-template system and has a Si/Al ratio of 5:1–12:1 and a framework density of 14.8 T atoms per 1000 Å^3. A typical synthesis composition (molar ratios) of $8\,TEAOH:8\,SiO_2:Al(OH)_3:1\,TMACl:240\,H_2O$ is crystallized by digestion at 150 °C for 96 h to yield a material with an approximate unit cell composition $TMA_4TEA_4Al_8Si_{56}O_{128}$.

UZM-5 typically crystallizes as thin plates (2–20 nm) in the TMA^+/TEA^+ system but forms rosette-shaped platelike aggregates in the $Na^+/TMA^+/TEA^+$ system. The UZM-5 materials are characterized by two peaks in the X-ray diffraction pattern at $d \sim 8.7$ and 3.9 Å, which were indexed as the (110) and (310) peaks, respectively. These peaks are apparent after 12 h and remain major features of the diffraction pattern until the final stages of crystallization. The lack of a c-axis component in these peaks indicates that the initial crystal growth is primarily in the a and b axis directions. As a consequence of the very small crystallite size and anisotropic morphology, X-ray diffraction patterns for UZM-5 samples were not of sufficient quality to solve the structure by ab initio methods, although indexing the patterns did provide the crystal system (tetragonal) and approximate lattice parameters ($a = 12.3$ Å, $c = 28.5$ Å). The structure of UZM-5 was solved by model building, incorporating information from a broad range of analytical techniques. Adsorption measurements showed a diminished uptake of i-C_4H_{10} versus n-C_4H_{10}, suggesting an 8-ring or small 10-ring channel system.[13] Also, peaks in the IR absorption spectrum at 1216 and 545 cm^{-1} implied the presence of 5-rings, while a band at 569 cm^{-1} suggested the possibility of double 4- or double 6-rings in the structure.[14] Electron diffraction was used to confirm the unit cell from X-ray diffraction data and to narrow the range of possible space groups to five body-centered groups. The information from high-resolution transmission electron microscopy (HRTEM; Figure 1 a) was key to the model building, as it pinpointed the locations of the channels and double 4-rings. The light areas in Figure 1 indicate positions of low atomic density (e.g., the main pore system), and dark areas indicate positions of high projected atomic density (e.g., the double 4-rings). A trial model of the structure consistent with the TEM images and the analytical data mentioned above was built in the space group $I4/mmm$. The atomic coordinates were optimized by distance least-squares (DLS) refinement.[15] The constraints used, the atomic coordinates, and the residuals are given in Table 1. The DLS refinement technique is commonly used particularly

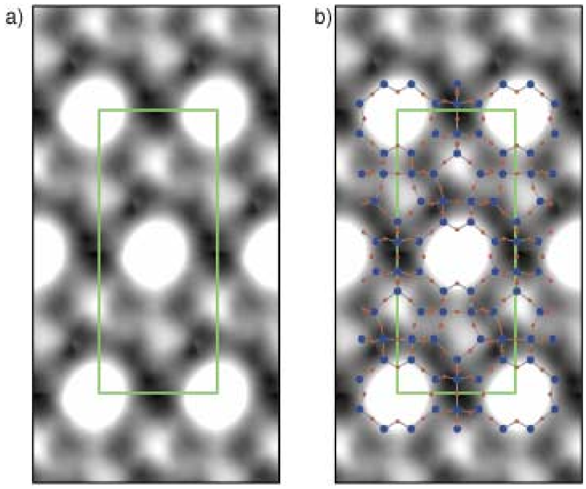

Figure 1. a) HRTEM image along [100], after averaging the contrast from several adjacent unit cells. Unit cell outline is shown. b) As (a), but with structure model overlain. The image clearly shows the body-centered arrangement of 8-ring pores, as well as the arrangement of the smaller 5-ring channels.

Table 1: Distance least-squares optimized atomic coordinates for UZM-5.[a]

Atom label	Wyckoff notation	*x*	*y*	*z*
Si1	16n	0.1776	0.0000	0.0556
Si2	32o	0.3784	0.1909	0.2013
Si3	16n	0.3727	0.0000	0.1281
O1	16n	0.2941	0.0000	0.0827
O2	8i	0.1993	0.0000	0.0000
O3	16m	0.1085	0.1085	0.0698
O4	16k	0.3757	0.1243	0.2500
O5	32o	0.3483	0.1085	0.1590
O6	16n	0.5000	0.2410	0.1931
O7	16m	0.2899	0.2899	0.2030
O8	8g	0.5000	0.0000	0.1119

[a] Space group *I4/mmm*; optimized cell constants $a = 12.332$, $c = 29.096$ Å. Reference constants: ⟨T–O⟩ 1.639, ⟨O–O⟩ 2.676, ⟨T–T⟩ 3.126 Å (assuming Si:Al 7.0; Si–O 1.623, Al–O 1.748 Å; ⟨O-T-O⟩ 109.5, ⟨T-O-T⟩ 145°). Final convergence gave $R_{DLS} = 0.0017$, $\sigma = 0.008$, $R_{DLS} = (\Sigma(w(D_o - D))^2/\Sigma(wD_o)^2)^{1/2}$, $\sigma_{DLS} = (\Sigma(w(D_o - D))^2/(M - NV))^{1/2}$.

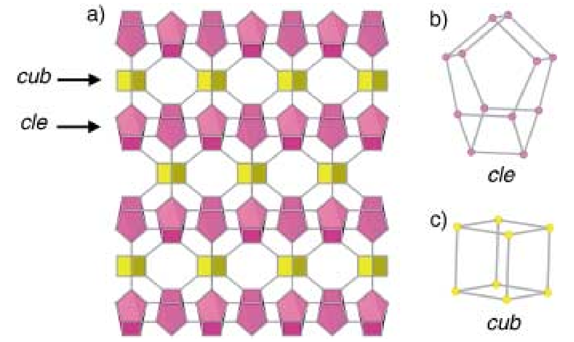

Figure 3. a) (100) projection of the UZM-5 structure showing *cle* (pink) and *cub* (yellow) polyhedra. b) *cle* polyhedron c) *cub* polyhedron (double 4-ring).

in the zeolite community for the evaluation and preliminary refinement of hypothetical structures. The calculated diffraction pattern based on the DLS coordinates agrees well with the experimental diffraction pattern as shown in Figure 2. The UZM-5 framework is confirmed by agreement between the model and HRTEM images along several crystallographic directions (see for example Figure 1b). Rietveld refinement of the X-ray powder data also confirms the structure, but because of peak broadening and asymmetry the resulting atomic coordinates are considered preliminary.[16]

The structure of the fully connected three-dimensional end member of the UZM-5 family consists of alternating layers along the *c* axis of two different composite building units or polyhedra, designated *cub* and *cle* (Figure 3).[17] Alternatively, the structure can be visualized as being built from two larger composite building units, designated *grc* and *wbc* (Figure 4a). The *grc* polyhedron, found in several other zeolites such as LTA, has usually been called an alpha cage but according to recent IUPAC recommendations is more properly called an alpha cavity.[18] The *wbc* polyhedron has not previously been found in any zeolite to our knowledge. Both of these cavities are accessible for adsorption of molecules larger than water through 8-ring windows. In UZM-5, the alpha cavities are fused through 8-rings along the *a* and *b* axis directions to form a two-dimensional 8-ring channel system. In the *c* direction *wbc* cavities are fused with the 8-rings above and below each alpha cavity (Figure 4a). The three-dimensional structure is formed by linking the bicapped alpha cavities in the *c* direction, which creates a *cub* cage at the apices. The UZM-5 framework is projected on a HRTEM image along the ⟨100⟩ direction in Figure 1b. The body-centered 8-ring pore system and the 5-ring channels in the model fit the features of the high-resolution image.

The layers of fused alpha cavities in UZM-5 are similar to those found in zeolites of framework type LTA; both structures have the same 12.3 Å lattice repeat distance along *a* and *b*. In LTA-type zeolites successive layers of alpha cavities are connected through 8-ring windows, which allows three-dimensional diffusion. However, in UZM-5 successive alpha cavity layers are separated by intervening

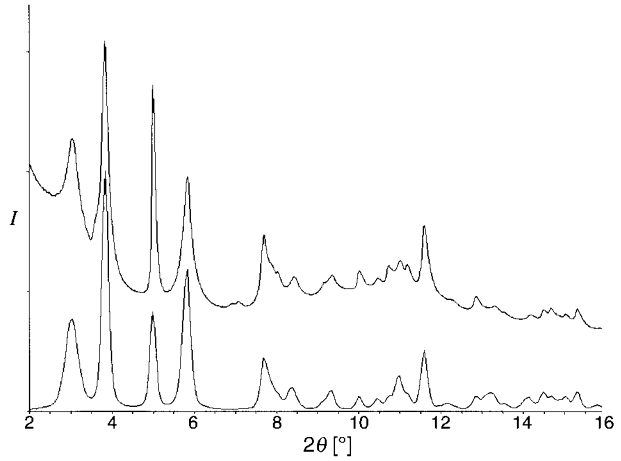

Figure 2. Comparison of the experimental diffraction pattern for a calcined never rehydrated UZM-5 (top) with a simulation using DLS coordinates (bottom). For the observed pattern, synchrotron wavelength = 0.7527 Å, space group *I4/mmm*, $a = 12.193(3)$ Å, $c = 28.403(17)$ Å. The simulation was done using Accelrys Materials Studio Version 2.1.5 and pseudo-voigt profiles with anisotropic crystallite size broadening (coherence lengths: $L_a = L_b = 125$ Å, $L_c = 50$ Å).

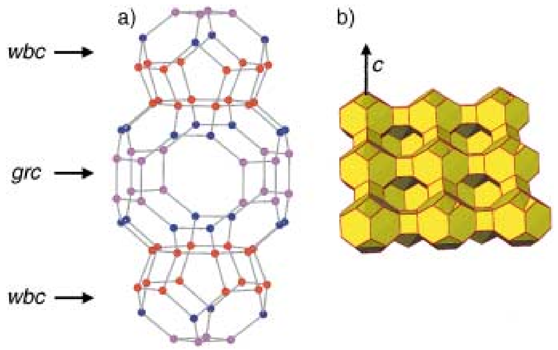

Figure 4. a) View of the alpha *(grc)* cavity bicapped in the *c*-axis direction by *wbc* cavities that form pockets accessible though 8-rings on opposite sides of each alpha cavity. The three unique T-atoms in the structure are color-coded. b) The predominant (001) surface contains 16-ring cups with an 8-ring bottom. These cups are essentially the bottom halves of alpha cavities sitting over *wbc* cavities.

layers of *wbc* cavities which block diffusion along the *c*-axis direction. The resulting 8-ring pore system is consistent with the observed adsorption of *n*-C_4H_{10} and the relative exclusion of *i*-C_4H_{10}.[13] In addition, the greatly favored crystal growth of UZM-5 in the *a* and *b* directions provides many sites on the (001) surface. This surface formed by the layer of the *wbc* cavities consists of 16-ring cups that are essentially the bottom halves of alpha cavities (Figure 4b). These cups are likely the sites where important catalytic reactions such as xylene isomerization and benzene alkylation occur, both of which involve molecules too large to fit in the 8-ring pores.[19] The presence of these surface cups is reminiscent of the MWW structure.[20]

The isolation of the new zeolite materials UZM-4 and UZM-5 by using combinations of simple well-studied organic templates such as TMA^+ and TEA^+ suggests the applicability of the mixed-template approach. In fact, we have discovered a number of other novel zeolites using this synthesis strategy that will be published at a future date. Moreover, these types of templates have the advantage of low cost and availability, which facilitates scale-up and applications testing. In addition, the mixed-template approach is compatible with modern exploratory screening capabilities such as combinatorial chemistry, which should accelerate invention in this field.

Experimental Section

UZM-4 synthesis: Aluminum hydroxide (27.2% Al, 75.6 g) was dissolved in TEAOH (35%; 1305.62 g) with vigorous stirring. To this mixture, de-ionized water (331.22 g) and then colloidal silica (287.56 g; Ludox AS-40, 40% SiO_2) were added. After homogenization, followed by aging for 24 h at 95 °C, the resulting reaction mixture contained 2.65% Si. To a 1600 g portion of this aluminosilicate mixture, a solution containing TMACl (97%; 67.95 g) and LiCl (13.30 g) dissolved in de-ionized water (80 g) was added slowly with vigorous stirring. After homogenization for 2 h, the reaction mixture was placed in a static 2-liter Parr autoclave and digested for 72 h at 125 °C. The solid products were isolated by centrifugation, washed with de-ionized water, and dried at room temperature. Analysis: Si/Al = 1.78:1, Li/Al = 0.61:1, N/Al = 0.34:1, C/N = 4.1:1. The experimental X-ray diffraction patterns for UZM-4 and zeolite Q, along with the calculated diffraction pattern from a DLS simulation of UZM-4 are included in the Supporting Information.

UZM-5 synthesis: Aluminum *sec*-butoxide (95 + %; 58.75 g), was added to TEAOH (35%; 836.34 g) with vigorous stirring. To this mixture, colloidal silica (294.73 g; Ludox AS-40, 40% SiO_2) and then distilled water (10.18 g) were added. After homogenization for 1 h, followed by aging for 18 h at 95 °C, the resulting reaction mixture contained 4.67% Si. To a 500 g portion of this aluminosilicate reaction mixture, a solution containing TMACl (97%; 11.77 g) dissolved in deionized water (23.0 g) was added with vigorous mixing. After homogenization for 30 min, the reaction mixture was distributed among eight teflon-lined autoclaves and digested at 150 °C for four days. The solid products were recovered by centrifugation, washed, and dried at 95 °C. Analysis: Si/Al = 6.88, N/Al = 0.83, C/N = 6.05.

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[3] Structure code: UZM = *U*OP *Z*eolitic *M*aterial.

[4] The uppercase three-letter codes in this article refer to zeolite framework types. Lowercase three-letter codes refer to composite building units or polyhedra (see reference [17]).

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[9] The asymmetric T-O-T stretch shifts from 961 cm^{-1} in zeolite Q to 1007 cm^{-1} in UZM-4.

[10] Hot-stage X-ray diffraction patterns were collected on samples bathed in a stream of dry air; measurements were taken at room temperature and then at multiples of 100 °C to 600 °C.

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[13] A McBain–Bakr gravimetric apparatus was used to determine adsorption capacities. At room temperature and $P/P_0 = 0.3$, UZM-5 adsorbed 0.22 mL *n*-C_4H_{10} per gram and 0.050 mL *i*-C_4H_{10} per gram. The kinetic diameters of *n*-C_4H_{10} and *i*-C_4H_{10} are 4.3 Å and 5.0 Å, respectively.

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