A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
GDCh
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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201915232
Angew. Chem. 10.1002/ange.201915232

Link to VoR: http://dx.doi.org/10.1002/anie.201915232
http://dx.doi.org/10.1002/ange.201915232

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An extra-large-pore pure silica zeolite with 16 × 8 × 8-membered ring pore channels synthesized by using an aromatic organic directing agent

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Dedicated to the 100th anniversary of the School of Chemistry and Chemical Engineering, Nanjing University

Abstract: Extra-large-pore zeolites for processing large molecules have long been sought after by both the academic and industrial communities. However, the synthesis of these materials, particularly extra-large-pore pure silica zeolites, remains a big challenge. Herein we report the synthesis of a new extra-large-pore silica and aluminosilicate zeolite, designated NUD-6, by using an easily-synthesized aromatic organic cation as structure-directing agent. NUD-6 possesses an intersecting 16×8×8-membered ring pore channel system constructed by four-connected (Q^4) and unusual three-connected (Q^3) silicon species. The organic cations in NUD-6 can be removed in nitric acid to yield a porous material with high surface area and pore volume. The synthesis of NUD-6 presents a feasible means to prepare extra-large pore silica zeolites by using assembled aromatic organic cations as structure-directing agents.

The synthesis of zeolites with a new structure has drawn great attention owing to their potential industrial applications in adsorption, separation and catalysis. Particularly of interest are extra-large-pore zeolites possessing pores with more than 12-membered ring (12-MR) opening, as these materials may serve as ideal catalysts or catalyst supports for processing large molecules such as heavy oils and biomass.[1] However, the syntheses of these materials have not been easy, because they usually require the use of expensive and difficult-to-prepare bulky organic cations of appropriate rigidity and hydrophobicity as structure-directing agents (SDAs).[2] Nonetheless, by using the bulky organic cations, together with the use of heteroatoms (*i.e.* other than Al and Si) and fluoride, a number of extra-large-pore zeolites have been synthesized. Examples include UTD-1 (14-MR),[3] CIT-5 (14-MR),[4] SSZ-53 (14-MR),[5] ITQ-33 (18-MR),[6] ITQ-44 (18-MR),[7] NUD-1 (18-MR),[8] SYSU-3 (24-MR),[9] ITQ-37 (28-MR),[10] ITQ-43 (30-MR),[11] *etc*. Most of them are germanosilicates, which are mainly attributed to the formation of subunits of double-four-membered rings (D4Rs) promoted by Ge and F. However, these heteroatom-containing extra-large-pore zeolites are not stable in water or moist atmosphere after removal of SDAs because of the hydrolysis of Ge-O bonds.[12] In comparison, pure silica and aluminosilicate zeolites possessing stable frameworks are highly desirable and can be used as solid acid catalysts in industry. To the best of our knowledge, there are only four stable extra-large-pore silica or aluminosilicate zeolites reported so far, *i.e.* UTD-1 (14-MR),[3] CIT-5 (14-MR),[4] SSZ-61 (18-MR),[13] EMM-23 (21-MR).[14] UTD-1 and CIT-5 were prepared with expensive organic SDAs, while SSZ-61 and EMM-23 possess severely distorted pores that prevent large molecules passing through. As a result, the application of these zeolites has been hindered. Therefore, the synthesis of extra-large-pore silica zeolites remains a big challenge.

Recently, a class of aromatic organic cations has been found to be effective in the synthesis of large- and extra-large-pore zeolites.[15] These cations can form larger supramolecular assemblies through interactions between the aromatic rings during the synthesis, which then act as SDAs for the formation of large- and extra-large-pore zeolites. This method allows the use of small organic cations to direct the formation of extra-large-pore or -cage germanosilicate zeolites, such as ITQ-29,[15a] ITQ-37,[16] NUD-1,[8] NUD-2 (14-MR),[17] *etc*. Herein, we report the synthesis of an extra-large-pore pure silica zeolite, denoted as NUD-6, by using an easily-synthesized aromatic organic cation as SDA. NUD-6 possesses a one-dimensional (1-D) 16-MR pore channel, inside which the assembled organic SDAs reside. Unlike most silica zeolites, NUD-6 consists of both three-(Q^3) and four-connected (Q^4) Si atoms (Q^n represents $Si(OSi)_n(OH)_{4-n}$), which renders the framework thermally unstable at high temperature. However, the SDAs in NUD-6 could be removed in nitric acid to produce a microporous zeolite material with large specific surface area and pore volume.

NUD-6 was prepared by using N,N-dimethyl-(2-methyl)benzimidazolium as a structure-directing agent. The crystalline and pure samples of NUD-6 were hydrothermally made from the gel with molar ratios of 1 SiO_2: 0.5 SDA(OH): 0.5 HF: (5-10) H_2O at 160°C for 15 d (Table S1). Powder X-ray diffraction (PXRD) patterns of the as-synthesized samples are in good agreement with the simulated patterns derived from the single-crystal structure data, suggesting the as-synthesized samples are pure (Figure 1). Scanning electron microscopy (SEM) images showed that the as-synthesized samples consist of long stick-shaped crystals, free of impurities (Inset in Figure 1).

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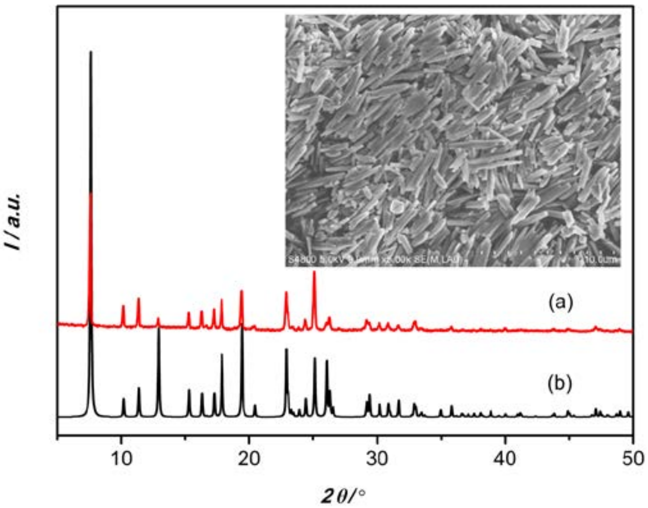

Figure 1. PXRD pattern of the as-synthesized NUD-6 (a), compared with the calculated NUD-6 (b) derived from the single-crystal structure data. Insert shows the SEM image of NUD-6.

Single-crystal X-ray diffraction analyses reveal that NUD-6 crystallizes in the orthorhombic space group *Imma*, with a = 7.4356(14) Å, b = 15.528(3) Å, c = 17.361(3) Å, and V = 2004.5 Å^3 (see Tables S2-S4 in the Supporting information for details). As depicted in Figure 2, NUD-6 is built from a composite building unit (CBU) called *bea*, *i.e.* a [$4^3 5^2 6^1$] cage, which consists of three 4-MRs, two 5-MRs and one 6-MR. The *bea* CBU is found in several zeolites, notably Beta and SSZ-26.[18] Each *bea* CBU in NUD-6 shares two of its three 4-MRs in an alternate manner to form infinite 1D chains running along the (100) direction. Each *bea* chain then connects to four neighboring chains *via* sharing common oxygen vertexes on 5-MRs to form a porous 3D framework with straight 16-MR pore channels in the (100) direction and 8-MR pore channels in the (111) directions.

From another point of view, NUD-6 can be constructed from a CBU double crankshaft chain (*dcc*) (Figure 2c) and a pair of SiO_4 tetrahedra. The *dcc* CBU is an edge-sharing 4-MR chain, which has been found in zeolite AlPO-21, UTD-1, *etc*.[18] The *dcc* chains in NUD-6 are aligned parallel to the *a*-axis direction, and linked to four neighboring *dcc* chains by dimers Si_2O_7 to form an open framework. The two Si atoms in every dimer Si_2O_7 are three-connected Si (Q^3), each having an uncoordinated terminal O atom. The Q^3:Q^4 ratio in NUD-6 is 1:2. The presence of unusually large percentage of Q^3 Si species in NUD-6 is confirmed by the distinct resonance peak at -101 ppm in ^{29}Si MAS and ^{1}H-^{29}Si cross-polarization MAS NMR spectra (Figure S1). It is noted that extra-large-pore silica zeolites SSZ-61 [13] and EMM-23 [14] also consist of well-defined Q^3 or Q^2 species.

NUD-6 possesses a very open structure with a framework density of 12.0 T/1000 Å^3, which is one of the lowest among the known zeolites.[18] The straight extra-large 16-MR pore channels run along the (100) direction, which are intersected by two 8-MR pore channels running along the (111) and (11-1) directions (Figures 2 and 3), respectively, to form a three-dimensional pore system. The 16-MR pore channels are elliptical, and the longest interatomic distances between the axial O atoms across the pore channel are 11.3 Å × 9.0 Å (taking account of an oxygen radius of 1.35 Å). However, four terminal O atoms protrude into the 16-MR pore channel, shrinking the pore opening to 9.0 Å × 6.4 Å. The 8-MR pore channels are also elliptical, with the longest interatomic distances between the O atoms across the pore channel of 4.7 Å × 3.8 Å.

Further single-crystal X-ray diffraction analyses revealed disordered SDA cations were located inside the 16-MR pore channels. As shown in Figure 4, the benzimidazolium planar rings of SDAs are nearly perpendicular to the 16-MR pore channel axis, only slightly tilted *ca*. ±3.5°. The two neighboring benzimidazolium cations form an inverted, eclipsed face-to-face dimer, which then stack over each other to form a 1D array along the 16-MR pore channels (Figure S2). The benzimidazolium planes parallel with each other, with interplanar distances of *ca*. 3.4 Å and 4.0 Å, respectively, indicating the presence of π interactions between the neighboring SDA cations. This observation implied that the benzimidazolium cations possibly formed supramolecular assemblies through aromatic interactions during the synthesis, and the assemblies might act as SDA to direct the formation of extra-large-pore zeolite NUD-6. The hypothesis is supported by photoluminescence studies (Figure S3). The photoluminescent spectra of the dilute solution of SDAI (1.0 × 10^{-3} M) showed a broad emission band at *ca*. 375 nm, attributed to the intra-molecular transitions. However, the concentrated solution of the SDAI salt (0.3 M, *c.f.* the SDA concentration of the zeolite synthesis gel was in the range of 1.7 – 14 M) showed the main emission peak at *ca*. 450 nm owing to

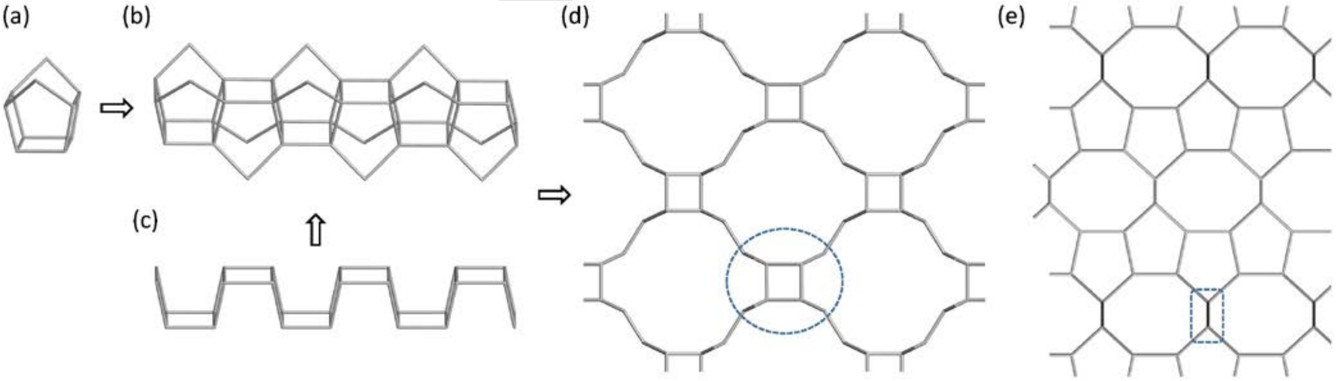

Figure 2. Stick views of the structure of NUD-6. (a) the *bea* SBU. (b) the *bea* chain. (c) the *dcc* SBU. (d) 3D structure of NUD-6 along the (100) direction, showing the 16-MR pore channels. (e) 3D structure of NUD-6 along the (111)-direction, showing the 8-MR pore channels. The O atoms and SDAs have been omitted for clarity. The dashed circle and retangle show the *bea* and Si_2O_7 units, respectively.

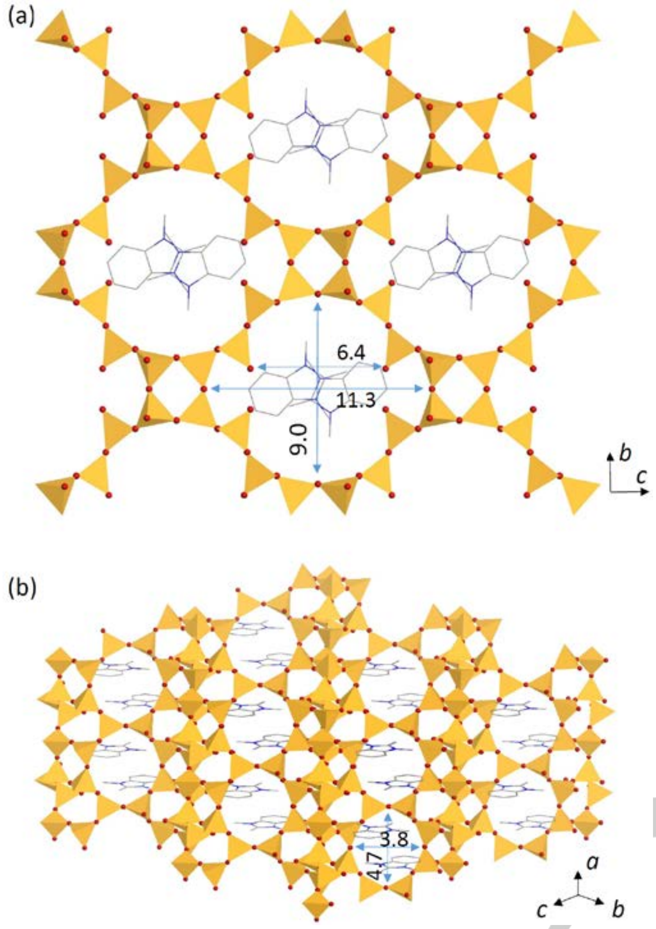

Figure 3. Polyhedral presentations of NUD-6 (a) along the *a*-axis, showing the SDAs in 16-MR pore channels, (b) along the (111)-direction, showing the 8-MR pore channels. Only one possible set of SDAs are shown. The H and F atoms have been omitted for clarity.

the inter-molecular transitions, suggesting the formation of excimers, *i.e*. aggregates of the SDA cations. The spectra of the as-synthesized NUD-6 and the solid SDAI salt are very similar to that of the concentrated SDAI solution. These results implied that the aggregates of the SDA cations possibly played a role during the crystallization of NUD-6.

The presence of the SDA benzimidazolium cations in NUD-6 was confirmed by elemental analyses and solid state ^{13}C MAS NMR studies. Elemental analyses revealed the C/N molar ratio of 4.9 in the as-synthesized NUD-6, close to the theoretical value (5.0) of SDA. The ^{13}C NMR peaks of the benzimidazolium cations in as-synthesized NUD-6 matched well with those dissolved in the solvent (Figure S4), indicating the SDA cations in NUD-6 were intact. Thermogravimetric (TG) analyses showed that NUD-6 lost 34.7% of its weight from 30°C to 1000°C (Figure S5), attributed to the loss of SDA (theoretical 32.3%) and hydroxyl groups (theoretical 3.2%). These results suggest there are four SDA cations in a unit cell of NUD-6, consistent with the single crystal X-ray diffraction results. Based on the above results, the formula of the as-synthesized NUD-6 can be deduced as $Si_6O_{11}(OH)_2 \cdot (C_{10}H_{13}N_2F)$.

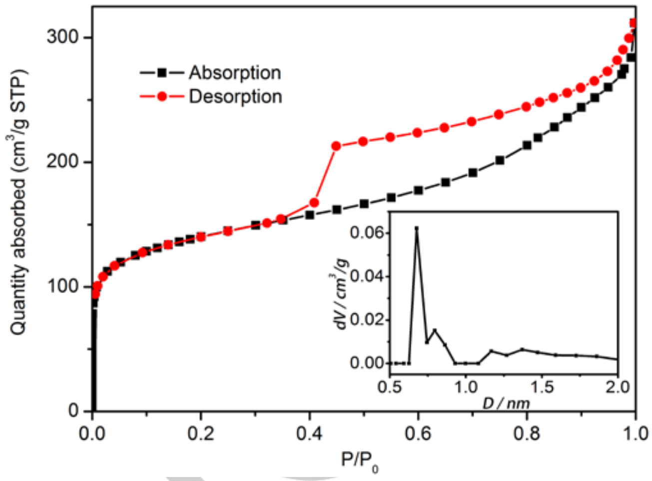

Figure 4. Ar adsorption and desorption isotherms of the acid-treated NUD-6. Insert shows the DFT pore size distribution curves.

NUD-6 with occluded SDAs was stable when heated at 450°C in vacuum or 350°C in air atmosphere (Figure S6). However, after calcination at 550°C in air to remove organic SDAs, the framework of NUD-6 collapsed into a non-porous amorphous material, as confirmed by PXRD and N_2 adsorption measurements (Figures S7 and S8). This could be attributed to condensation of large amount of Q^3 silanol groups in NUD-6 at high temperature. Consistently, ^{29}Si MAS NMR spectra of the calcined sample showed the Q^3 Si peak almost disappeared compared with that of the as-synthesized sample (Figure S9).

A porous material was obtained after the as-synthesized NUD-6 was immersed in concentrated nitric acid at 120°C for 22 h to remove the SDAs. TG and elemental analyses suggested that most SDA cations have been removed after acid treatment (Figure S10). The morphology of the acid-treated NUD-6 remained intact (Figure S11). PXRD studies showed that the acid-treated NUD-6 retained its framework with only partial loss of its crystallinity owing to the acid leaching (Figure S12). The removal of SDAs resulted in the framework distortion, which led to partial changes in the PXRD pattern. As shown in Figure 4, the acid-treated NUD-6 after activation at 300°C displayed a steep Ar gas uptake at very low p/p_0 pressures, suggesting the presence of micropores. At higher relative pressures, the adsorption curve displayed a type II isotherm with an H4 desorption hysteresis loop, implying the presence of micro-mesoporous network.[19] The Brunauer–Emmett–Teller (BET) surface area and pore volume were calculated to be 434 m^2/g and 0.346 cm^3/g, respectively (Table S5). The *t*-plot analyses showed the acid-treated NUD-6 had a large external surface area of 214 m^2/g, which likely resulted from the damage to the zeolite crystals by acid. The pore size distribution analyses based on density functional theory (DFT) revealed that the acid-treated NUD-6 possessed narrowly-distributed micropores at 6.8 Å and 8.0 Å, which could be related to the elliptical 16-MR pore channels (9.0 Å × 6.4 Å, Figure 3). The presence of narrow micropores implies the pore structure in NUD-6 was retained after acid treatment and subsequent activation at 300°C. In addition, there exist widely-distributed mesopores with pore diameters ranging between 2 and 20 nm in the acid-treated NUD-6 (Figure S13). The formation of these mesopores could be attributed to partial dissolution of the framework atoms during acid treatment of NUD-6. The mesopores are beneficial and could facilitate mass transport during catalysis. These results suggest that NUD-6 could be potentially used as adsorbents or catalyst supports.

In summary, a new extra-large-pore silica zeolite NUD-6 was synthesized by using N,N-dimethyl-(2-methyl)benzimidazolium as a structure-directing agent. NUD-6 possesses an open framework with intersecting 16×8×8-MR pore channels. Inside the 16-MR pore channels, the stacked planar organic aromatic cations are located, which form supramolecular assemblies. There exists high proportion of Q^3 versus Q^4 Si atoms in NUD-6, making NUD-6 thermally unstable during calcination at high temperature. The organic cations in NUD-6 can be removed in nitric acid to yield a porous zeolitic material with high surface area and pore volume, making it a promising candidate for adsorption and for shape-selective catalysis. This work further demonstrates that it is feasible to prepare extra-large-pore silica zeolites by using small, easily-synthesized aromatic organic cations as structure-directing agents.

Acknowledgements

The authors are grateful for financial support from the National Natural Science Foundation of China (grant numbers 21673115 and 21601004). They also thank the staffs from BL17B beamline of National Facility for Protein Science in Shanghai (NFPS) at Shanghai Synchrotron Radiation Facility, for assistance during data collection.

Keywords: extra-large pores • organic structure directing agents • structure elucidation • zeolites • synthesis design

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Layout 1:

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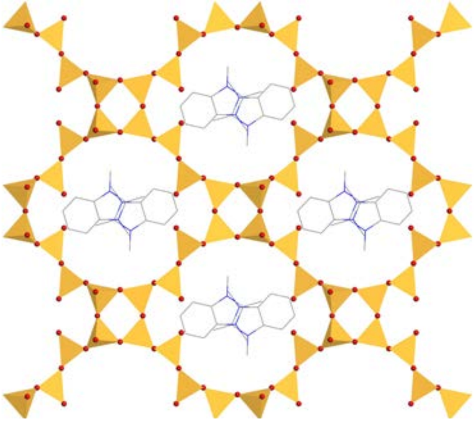

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