Facile Synthesis and Catalysis of Pure-Silica and Heteroatom LTA

Ben W. Boal, Joel E. Schmidt, Mark A. Deimund, Michael W. Deem, Lawrence M. Henling, Stephen K. Brand, Stacey I. Zones, and Mark E. Davis

ABSTRACT: Zeolite A (LTA) has many large-scale uses in separations and ion exchange applications. Because of the high aluminum content and lack of high-temperature stability, applications in catalysis, while highly desired, have been extremely limited. Herein, we report a robust method to prepare pure-silica, aluminosilicate (product Si/Al = 12–42), and titanosilicate LTA in fluoride media using a simple, imidazolium-based organic structure-directing agent. The aluminosilicate material is an active catalyst for the methanol-to-olefins reaction with higher product selectivities to butenes as well as C₅ and C₆ products than the commercialized silicoaluminophosphate or zeolite analogue that both have the chabazite framework (SAPO-34 and SSZ-13, respectively). The crystal structures of the as-made and calcined pure-silica materials were solved using single-crystal X-ray diffraction, providing information about the occluded organics and fluoride as well as structural information.

1. INTRODUCTION

Microporous materials are crystalline solids formed from three-dimensional networks of oxide tetrahedra that contain pores (less than 2 nm) and cages that allow for shape-selective ion exchange, separations, and catalysis. These materials often exhibit robust hydrothermal stability that allows their application under demanding process conditions such as fluidized catalytic cracking, exhaust gas emissions, and treatment of toxic waste. Over 200 different microporous material frameworks have been identified, but of these, less than 20 have been commercialized, and the market is dominated by only a few frameworks. Despite this seeming barrier to market entry, the demand to innovate in these materials remains high, as there is often only a single framework and composition that deliver optimal performance in a given application. In recent years, microporous materials with pore diameters limited by 8-membered rings (8MRs) have received increased attention, as they demonstrate good activity and hydrothermal stability for high-demand applications such as the methanol-to-olefins (MTO) reaction (SAPO-34) and the reduction of NOₓ in emissions (SSZ-13).

Zeolite A (Linde Type A, framework code LTA) is one of the most used zeolites in separations, adsorption, and ion exchange. This structure contains large spherical cages (diameter ~11.4 Å) that are connected in three dimensions by small 8MR windows with a diameter of 4.1 Å. LTA is normally synthesized in hydroxide media in the presence of sodium with Si/Al ~ 1. By changing the cation, the limiting diameter of the 8MR windows can be tuned, creating the highly used series of adsorbents 3A (potassium form, 2.9 Å diameter), 4A (sodium form, 3.8 Å diameter), and SA (calcium form, 4.4 Å diameter) that are used to selectively remove species such as water, NH₄⁺, SO₂⁻, CO₃⁻, H₂S, C₂H₄, C₃H₆, C₄H₁₀, and other n-paraffins from gases and liquids. While LTA is used in vast quantities for the aforementioned applications, the low framework Si/Al ratio and subsequent poor hydrothermal stability limit its use under more demanding process conditions that are commonly found in catalytic applications. Strategies have been developed to increase the Si/Al up to 5.5 in hydroxide media using combinations of organic structure-directing agents (OSDAs), and this material has been shown to be active for the MTO reaction.

Pure-silica LTA (ITQ-29) was first reported in 2004 and was synthesized in fluoride media using a combination of methylated julolidine (Figure 1) and tetramethylammonium fluoride as well as structural information.

Easily produced LTA shows compositional flexibility and catalytic activity

Pure-silica Aluminosilicate Titanosilicate

Published: November 5, 2015

DOI 10.1021/acs.chemmater.5b03579
Chem. Mater. 2015, 27, 7774–7779
Chemistry of Materials

Figure 1. Methylated julolidine (left) and Kryptox 222 (right).

...ulolidine molecules that form dimers through π−π stacking and that the initial OSDA concentration is critical to achieving this assembly and avoiding the formation of competing phases, such as AST. Additionally, the use of TMA is required, as it favors the formation of sodalite cages, part of the LTA structure. A method to synthesize germanosilicate LTA using a large polycyclic crown ether with the trade name Kryptox 222 (Figure 1) has been demonstrated, but this material required the use of germanium, lowering the material’s hydrothermal stability.

We have recently demonstrated the synthesis of AlPO₄ SAPO, and germanosilicate LTA using a large triquaternary OSDA, but we were unable to make pure-silica LTA with this OSDA, despite considerable efforts. During our investigations with related mono- and diquaternary imidazolium OSDAs, we identified an easy to prepare monoquaternary imidazolium OSDA capable of forming pure-silica as well as aluminosilicate and titanosilicate LTA in fluoride media across a wide compositional range and under relatively simple synthesis conditions (AlPO₄·LTA and germanosilicate LTA have been previously reported using monoquaternary imidazolium OSDAs different from the one used here, and a similar benzylimidazolium OSDA has been used in pure-silica systems to prepare ITW, MFI, and MTW). The aluminosilicate material has been evaluated for the MTO reaction and shows interesting product selectivities. Additionally, the crystal structures of the as-made and calcined materials were solved using single-crystal X-ray diffraction, providing information about the occluded organics and fluoride as well as structural information.

2. EXPERIMENTAL SECTION

2.1. OSDA Synthesis. Reactions were conducted in flame-dried glassware under an atmosphere of argon. All reagents were purchased from commercial sources and used as received. All chemicals were reagent grade unless otherwise specified. Liquid NMR spectra were recorded on Varian Mercury spectrometers.

A 500 mL flask was charged with 1,2-dimethylimidazole (11.60 g, 121.0 mmol, 98%, Aldrich), 4-methylbenzyl chloride (15.46 g, 121.0 mmol, 98%, Aldrich), and toluene (125 mL, Fisher). The flask was fitted with a reflux condenser and heated to reflux for 15 h. The reaction was cooled to 25 °C, and the resulting solids were filtered and washed with ethyl acetate (3 × 50 mL) to give the OSDA (24.10 g, 98% yield) as a white solid. 1H NMR (500 MHz, CD3OD): δ 7.08 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.8 Hz, 2H), 7.34 (s, 3H), 3.87 (s, 3H), 2.67 (s, 3H), 2.39 (s, 3H). 13C NMR (126 MHz, CD3OD): δ 144.8, 138.8, 130.7, 129.5, 127.6, 126.2, 122.4, 121.1, 51.2, 34.1, 19.7, 8.4.

The OSDA was then converted to hydroxide form using hydroxide exchange resin (Dowex Marathon A, hydroxide form) in water, and the product was titrated using a Mettler-Toledo DL22 autotitrator using 0.01 M HCl as the titrant. The OSDA was wash with ethyl acetate (3 times).

2.2. Microporous Material Synthesis. All reactions were performed in 23 mL Teflon-lined stainless steel autoclaves (Parr Instrument Co.). Reactions were performed statically or tumbled at 43 rpm using spits built into convection ovens. Syntheses were performed at 125, 140, 150, 160, or 175 °C. The silicon source was tetraethyl orthosilicate (TEOS, 99.9% Si(OCH2CH3)₄, Strem). The germanium source was germanium oxide (99.99% GeO₂, Strem). Tetramethylammonium hydroxide pentahydrate was purchased from Sigma-Aldrich (97%).

2.2.1. Germanosilicates. Gels for germanosilicate reagents were prepared by adding germanium oxide to a solution of OSDA in water directly in the 23 mL Teflon liner. This mixture was stirred at 15 °C for 5 min or until the germanium oxide dissolved into the solution. TEOS was then added, and the reaction vessel was capped and stirred for an additional 12 h to hydrolyze the TEOS. The reaction vessel was then uncapped, and a stream of air was blown over the gel while it was mechanically stirred until the required excess of water and hydrolyzed ethanol had been evaporated. In certain cases, the gel was put under vacuum to remove small amounts of residual water, when evaporation failed to remove the required amount of water. Hydrofluoric acid was then added in a dropwise fashion to the gel, the gel was quickly stirred with a Teflon spatula, and the Teflon liner was sealed into the stainless steel autoclave and put into the oven. The reactors were opened every 6–7 days to assess reaction progress. After homogenizing, a small sample was successively washed with DI H₂O (2 × 10 mL) and acetone/methanol (1:1, 3 × 10 mL), and the PXRD pattern was inspected. All reactions were monitored for at least 1 month or until a crystalline product was observed.

2.2.2. Synthesis of Pure-Silica Materials. Pure-silica materials were prepared in the same manner as that for germanosilicate materials except that the addition of GeO₂ was omitted.

2.2.3. Synthesis of Aluminosilicate LTA. Aluminosilicate materials were prepared in the same manner as that for germanosilicate materials except that the addition of GeO₂ was omitted and aluminum isopropoxide was used as the aluminum source (99.9%, Aldrich).

2.2.4. Synthesis of Titanosilicate LTA. Titanosilicate materials were prepared in the same manner as that for germanosilicate materials except that the addition of GeO₂ was omitted and titanium(IV) butoxide (97%, Aldrich) was used as the titanium source.

2.2.5. Characterization. Powder X-ray diffraction (XRD) patterns were collected using a Rigaku Miniflex II diffractometer and Cu Kα radiation. 13C, 19F, 27Al, and 29Si solid-state NMR were performed using a Bruker DSX-500 spectrometer (11.7 T) and a Bruker 4 mm MAS probe. The spectral operating frequencies were 200.2, 125.7, 74.6, and 82.7 MHz for 13C, 19F, 27Al, and 29Si nuclei, respectively. Spectra were referenced to external standards as follows: tetramethylsilane (TMS) for 1H and 13C, SiF₄ and GeF₄, and Si nuclei, respectively. Peaks were integrated using the T-G profile method. Argon physical adsorption isotherms were performed at 77 K using a Quantachrome Autosorb iQ and were collected using a Micromeritics ASAP 2010 instrument. Samples (0.01–0.06 g) were placed in an alumina crucible and heated at 1 K/min in a flowing stream (0.667 cm³/s) composed of 50% air (Air Liquide, breathing grade) and 50% argon (Air Liquide, UHP).
carried out. The last 5 ps of the trajectory is used to compute an average energy of the system. This same calculation is carried out for the isolated zeolite and the isolated OSDA. All computations were conducted using the previously reported method. The Dreiding force field was used in the GULP molecular modeling program to calculate the stabilization energies.

2.4. MTO Reaction Testing. Aluminosilicate LTA samples were also tested for their performance in the methanol-to-olefins (MTO) reaction. Prior to reaction testing, samples were calcined in breathing-grade air by initially holding them at 150 °C for 3 h (at a heating rate of 1 °C/min) before heating the samples further to 580 °C for 6 h (again at a 1 °C/min heating rate) to convert them to their proton forms. Calcined samples were then pelletized, crushed, and sieved. Particles between 0.6 and 0.18 mm were supported between glass wool beds in an Autoclave Engineers BTR8, Jr. SS-316 tubular, continuous flow reactor.

All catalysts were dried at 150 °C in situ in a 30 cm³/min flow of 5% Ar/95% He for 4 h prior to the reaction. The reactions were conducted at 400 °C in a 10% methanol/inert flow. Methanol was introduced via a liquid syringe pump at 5.4 μL/min into a gas stream of the inert blend at 30 cm³/min. The reactant flow had a weight hourly space velocity of 1.3 h⁻¹. In a typical run, 200 mg of dry catalyst was loaded. Effluent gases were evaluated using an on-stream GC/MS (Agilent GC 6890/MSD5793N) with a PLOT-Q capillary column installed. Conversions and selectivities were computed on a carbon mole basis.

2.5. Crystal Structure Analysis of LTA. The crystal structure of three different LTA samples was solved using single-crystal X-ray diffraction; details are given in the Supporting Information, including sample description, structural information, and CIF files.

3. RESULTS AND DISCUSSION

The OSDA that we identified to make ITQ-29 is shown in Figure 2, and the synthesis results are shown in Table 1. A number of different synthesis conditions are included in the table to show how the optimal conditions were found for LTA. As is typical for fluoride-mediated reactions, the total organic content was held constant for all syntheses. We first found LTA as a product in germanium-containing syntheses (perhaps not surprising, as germanium is known to favor the formation of double four rings [D4Rs] and the entire LTA structure can be formed from D4Rs). Additionally, it was found that the formation of LTA was favored at lower temperatures, as BEC formed instead at higher temperatures in germanosilicate systems.

The synthesis of pure-silica LTA was favored by either seeding the syntheses or by adding a small amount of TMAOH (one, but not both, of these factors was necessary; see Table 1). The addition of TMAOH helped form pure-silica LTA, but it was added in small amounts to avoid the formation of AST. Additionally, lower synthesis temperatures helped to avoid the formation of competing phases. The water content was held constant for all syntheses, as the ratio used is easy to obtain in these types of reactions. Using this new OSDA, the synthesis of ITQ-29 is much simpler than previously reported, as the new methodology has a much higher water content and a lower amount of TMA, avoiding the competing formation of AST. While the use of fluoride media may provide some limitations to large-scale implementation, we do not believe that they will be insurmountable.

Powder X-ray diffraction (PXRD) of as-made and calcined pure-silica LTA are shown in Figure 3. It was confirmed by ¹³C CP-MAS NMR that both the OSDA and TMA were occluded intact in the as-made material (Figure 2). The calcined material was characterized by argon and nitrogen adsorption isotherms (Supporting Information, Figures S1–S3), and the results are consistent with the expected values. The argon adsorption isotherm shows a sharp, low-pressure transition, consistent with well-defined 8MRs. The ²⁹Si BD NMR of the calcined material (Figure 4) reveals a single resonance at −113.3 ppm, consistent with the single T-site in the LTA structure. The ¹⁹F NMR of the as-made material (Figure 5) shows a single resonance at −39 ppm, assigned to fluoride occluded in D4Rs.

The role of the OSDA was studied computationally. TGA analysis (Figure S5) shows that two molecules are occluded per unit cell of LTA. This knowledge and the fact that the OSDA is too large to fit in the small sodalite cage mean that two molecules of OSDA are occluded in each α-cage. Molecular dynamics calculations showed that the stabilization energy was an advantageous −16.9 kJ/(mol Si), and the conformation of the OSDA is shown in Figure 6. The molecular modeling agrees well with the occupancy determined by TGA, as the stabilization energy is only −7.36 kJ/(mol Si) if a single OSDA is occluded per cage. For methylated julolidine, a maximum stabilization energy of −14.27 kJ/(mol Si) and an average stabilization energy of −13.03 kJ/(mol Si) were found (a detailed discussion is given in the Supporting Information). The molecular modeling shows that the conformation of the methyl groups in the occluded julolidine OSDA is most likely different than has been previously reported since the most stable conformation in the α-cage is with the methyl groups pointing away from the dimerization complex (Figure S7), not toward the complex (Figure S8), as was assumed based on the single-crystal structure of the pure OSDA. The molecular modeling also agrees with previous studies that found AST as the product if the methylated julolidine did not dimerize properly, as the stabilization energy for a single OSDA per cage is only −6.35 kJ/(mol Si), reinforcing the idea that dimerization of the julolidine OSDA to form a supramolecular complex is key to the formation of LTA. The molecular modeling shows how the relatively simple OSDA used in this work is able to fill such a large cavity (Figure 6), in a similar manner to the supramolecular assembly formed from methylated julolidine, although π–π stacking is not claimed in the present situation.

The pure-silica, as-made materials (with and without TMA in the synthesis) as well as the calcined material were studied using single-crystal X-ray diffraction (results, including the CIF file, are in the Supporting Information). In the as-made material containing TMA, the structure analysis confirms that TMA is
present in the sodalite cages (although not all are occupied) and that the carbon atoms are completely disordered. The cages are symmetrical, so there is no reason that long-range order of the OSDA with respect to the LTA structure should be expected. It was also found that the fluoride location could be resolved to the D4Rs in both as-made materials; the preferential location of fluoride in D4Rs has been often reported and is normally given as one reason that fluoride-mediated syntheses lead to many structures containing D4Rs. The OSDA was completely disordered with respect to the LTA structure in both as-made materials, and even lowering the symmetry of the structure did not help to resolve the location. As the large $\alpha$-cage of LTA is very symmetrical, it is unlikely that the organic would adopt any long-range conformational order between cages, so this result is also expected, but it means that the single-crystal analysis cannot be used to confirm the results of the molecular modeling study.

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Figure 3. Powder X-ray diffraction patterns of as-made (lower) and calcined (upper) pure-silica LTA. The inset image is of the calcined material with the intensity increased to show the reflections more clearly.

Figure 4. $^{29}$Si MAS NMR of calcined Si-LTA.

Figure 5. $^{19}$F NMR of as-made silica LTA. Spinning sidebands are marked with an asterisk (*).

Figure 6. Conformation of the OSDA in LTA determined by molecular modeling demonstrating how it is able to fill the large $\alpha$-cage.
The robustness of the new synthesis method was demonstrated by preparing Bronsted acidic LTA. Aluminosilicate LTA was synthesized in fluoride media over a wide product compositional range (product Si/Al = 12–42; see Table 1). In the calcined sample containing the largest amount of aluminum (Si/Al = 12), it was shown by $^{27}$Al MAS NMR that nearly all of the aluminum is tetrahedral and therefore incorporated in the framework (Figure S10). Four different samples of LTA with product Si/Al = 12, 33, 38, 42 were studied with the MTO reaction, and the results are compared to SSZ-13, SAPO-34, and aluminosilicate RTH in Table 2 (full reaction profiles are given in the Supporting Information). The time-dependent reaction profiles for each material are different, and data are listed in Table 2 for comparison at around 50 min time on stream. Additional data points are provided for SSZ-13, SAPO-34, and RTH, as those materials had longer lifetimes than the LTA samples tested. Geometrical properties of the three frameworks tested for the MTO reaction are given in Table 3.

### Table 2. MTO Reaction Results at Maximum C$_2$ to C$_4$ Olefin Selectivity$^a$

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<th>Si/Al</th>
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<th>C$_2$-C$_4$ olefins</th>
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<th>propylene</th>
<th>butenes$^b$</th>
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<td>17</td>
<td>128</td>
<td>1.00</td>
<td>0.82</td>
<td>0.15</td>
<td>0.47</td>
<td>0.21</td>
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<td>0.10</td>
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<tr>
<td>RTH$^{23}$</td>
<td>29</td>
<td>48</td>
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<td>0.73</td>
<td>0.10</td>
<td>0.38</td>
<td>0.24</td>
<td>0.17</td>
<td>0.11</td>
</tr>
<tr>
<td>RTH$^{23}$</td>
<td>29</td>
<td>112</td>
<td>1.00</td>
<td>0.82</td>
<td>0.12</td>
<td>0.45</td>
<td>0.24</td>
<td>0.07</td>
<td>0.11</td>
</tr>
</tbody>
</table>

$^a$Full reaction profiles for each material can be found in the Supporting Information. $^b$Butenes include all isomeric butenes (but-1-ene, (Z)-but-2-ene, (E)-but-2-ene, and 2-methylpropene). $^c$Selectivity to all fully saturated hydrocarbons containing 1–4 carbon atoms. $^d$Selectivity to all 5 and 6 carbon species.

Some interesting comparisons can be made between the various frameworks. SSZ-13 and SAPO-34 show the highest maximum olefin selectivity and have a high selectivity to ethylene and propylene. RTH gives a lower selectively to ethylene but higher selectivity to propylene, butenes, and C$_3$ and C$_6$ products compared to that of CHA-type materials. Aluminosilicate LTA shows a relatively low selectively to ethylene and propylene, but it produces the highest selectively to butenes as well as C$_3$ and C$_6$ products. It is possible that the reaction selectivities and faster deactivation times are related to the larger cage size of LTA, as it shows the highest selectivity to higher carbon number products as well as the fastest deactivation. However, given the complexity of the MTO mechanism$^{22}$ and the influence of additional parameters (crystal size, Si/Al ratio, etc.), any explanation for the differences is only speculation without a more detailed study that systematically varies all parameters (if this can be achieved synthetically).

Lewis acidic LTA was prepared by the addition of titanium as a heteroatom (Table 1). The incorporation of titanium was studied through DR-UV spectroscopy (Figure 7), showing tetrahedral (framework) titanium. This material may have possible applications in low-temperature oxidations of small molecules, where the 8MR ring and large, spherical cage size may show advantages over larger pore materials such as TS-1 and Ti-BEA.

### 4. CONCLUSIONS

We have demonstrated a robust method to prepare pure-silica and heteroatom LTA. This method is able to reproducibly produce the LTA framework under conditions typical for fluoride-mediated microporous materials syntheses. The aluminosilicate material is an active catalyst for the MTO reaction and shows interesting product selectivities compared to those of other 8MR materials. Titanosilicate, Lewis acidic LTA can also be prepared using this method and may have possible applications where the 8MR ring and large, spherical cage size may show advantages over larger pore materials.

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$^{7778}$DOI: 10.1021/acs.chemmater.5b03579

Chem. Mater. 2015, 27, 7774--7779
ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmate.5b03579.

- Nitrogen and argon isotherms, $^{29}$Si NMR, TGA, $^{27}$Al NMR, details of molecular modeling, including julolidine conformation analysis, MTO reaction plots, SEM images, and details of crystal structure analysis (PDF)
- Crystalllographic data (CIF, CIF, CIF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to thank Chevron Energy and Technology Company for providing funding for this work. J.E.S. would like to thank the Department of Energy, Basic Energy Sciences, for grant DE-FG02-91ER13942. J.E.S. would like to thank the NDSEG for their support through a fellowship. M.W.D would like to thank the U.S. Department of Energy, Basic Energy Sciences, for grant DE-FG02-08ER16010. B.W.B. and J.E.S. contributed equally to this work.

ABBREVIATIONS

MR, membered-ring; MTO, methanol-to-olefins reaction; OSDA, organic structure directing agent; PXRD, powder X-ray diffraction; TGA, thermogravimetric analysis; TMA, tetramethylammonium

REFERENCES