Highly ordered cubic mesoporous aluminosilicates were synthesized using PEO_{106}PPO_{70}PEO_{106} triblock copolymer and aluminosilicate sols containing Si–O–Al bonds, which are obtained by dissolving Na-A type zeolite in HCl, under mild acidic conditions (pH 1.9–3.2).

The discovery of ordered mesoporous silicas (MSs) has led to a considerable interest in the development of various ordered mesoporous materials. The high surface area and large pore sizes of ordered mesoporous aluminosilicates (MASs) have considerable potential for use as catalysts for conversion of high-molecular-weight petroleum fractions, which have high diffusion resistance through the micropores of conventional zeolites. Many research efforts have focused on developing MASs with a high content of Al tetrahedrally coordinated in the framework and with high hydrothermal stability. Recently, some methods for the preparation of MASs with short-range zeolitic building units have been reported. These methods are based on the use of protozeolitic nanoclusters, zeolite seeds prepared by a bottom-up approach from zeolite synthesis solutions. The zeolite seeds are presumed to consist of zeolite primary and secondary structural building subunits, which provide Si–O–Al bonds originating in zeolite building units.

Li et al. and Yang et al. have reported the synthesis of MASs using an aluminosilicate ester (sec-BuO)_{2}AlOsi(OEt)_{3}. Aluminosilicate ester contains two alkoxide functionalities, one on the Si side and the other on the Al side, which may allow construction of a continuous Si–O–Al linkage. Inagaki et al. have prepared MCM-41 type MASs containing fragments of the structure of ZSM-5 zeolite using a filtrate of ZSM-5 dissolved by alkaline treatment. On the other hand, our group has used zeolite LTA crystals dissolved in a HCl solution as both Al and Si precursors. This method proceeds in two steps: (1) zeolite LTA crystals are dissolved in a HCl solution to produce a homogeneous solution containing Al and Si sources, and (2) a PEO_{106}PPO_{70}PEO_{106} triblock copolymer (Pluronic F127) coassembles with the inorganic species in the presence of an organic base tetramethylammonium hydroxide (TMAOH), followed by hydrothermal treatment. We note that the first step mentioned above is very important as it provides a Si–O–Al bond originating from a zeolite building unit.

In this study, we have developed two-step synthesis of well-ordered MASs under relatively mild acidic conditions. In the first step, zeolite nanoblocks are prepared by a top-down approach using zeolite crystals by dissolution of LTA in HCl solution at carefully controlled concentration. In the second step, we combine the above solution and aqueous Pluronic F127 solution in the absence of TMAOH to carry out the self-assembly process. We also describe the influence of pH on the mesostructure of products.

In a typical preparation, 0.5 g of Pluronic F127 was dissolved in 130 g of deionized water with stirring at room temperature for 15 min. In parallel with the above procedure, 1 g of zeolite LTA powder was added to 11.2 mL of 2.2–3.0 M HCl solution, and the mixture was stirred at room temperature for 10 min to obtain a transparent solution. The LTA-dissolved HCl solution was added to the aqueous Pluronic F127 solution and then stirred for an additional 1 h at room temperature. Then, the resulting mixture was aged without stirring at 100°C for 20 h. The white precipitated product was collected by centrifugation, washed with deionized water, and then dried in air. Calcination was performed at 600°C for 5 h to remove the template. The final products are designated as X-MS or X-MAS, where X is the pH value of the final solution (shown in Table 1).

The crystal structure of mesoporous materials prepared using the LTA-dissolved HCl solutions was characterized by wide-angle XRD. All products show no diffractions attributable to the LTA structure, indicating that the framework was composed of an amorphous phase. From EDX and ICP analyses, it was found that 1.4-MS is made of pure silica. The removal of Al from the zeolite lattice occurs during the dissolution under strongly acidic conditions. A complete dealumination results in complete Si–O–Al bond dissociation. The LTA-dissolved HCl solution contains entirely distinct Al and Si species. Thus, the pure silica framework of 1.4-MS suggests an absence of interaction between the Al species and Pluronic F127. Free Al^{3+} could not interact the protonated PEO segments and silicate species and could not enter the silica matrix. The calcined 1.4-MS has an ordered mesostructure with a d spacing of 14.7 nm.

**Table 1.** Preparation and physicochemical properties of ordered mesoporous materials prepared using LTA-dissolved HCl solutions

<table>
<thead>
<tr>
<th>HCl/M</th>
<th>Yield (%)</th>
<th>Si/Al</th>
<th>d [nm]</th>
<th>d_{p} [nm]</th>
<th>S_{BET} [m^{2}/g]</th>
<th>V_{t} [cm^{3}/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4-MS</td>
<td>3.0</td>
<td>0.31</td>
<td>Al free</td>
<td>14.7</td>
<td>6.6</td>
<td>750</td>
</tr>
<tr>
<td>1.9-MAS</td>
<td>2.5</td>
<td>0.33</td>
<td>35</td>
<td>17.3</td>
<td>7.7</td>
<td>790</td>
</tr>
<tr>
<td>2.3-MAS</td>
<td>2.4</td>
<td>0.35</td>
<td>19</td>
<td>17.5</td>
<td>8.4</td>
<td>910</td>
</tr>
<tr>
<td>2.8-MAS</td>
<td>2.3</td>
<td>0.36</td>
<td>13</td>
<td>17.7</td>
<td>8.4</td>
<td>870</td>
</tr>
<tr>
<td>3.2-MAS</td>
<td>2.2</td>
<td>0.36</td>
<td>9</td>
<td>10.3</td>
<td>600</td>
<td>1.03</td>
</tr>
</tbody>
</table>

*Concentration of HCl solution used for dissolution of LTA zeolite. **g-Calcined product/g-LTA. †Lattice d spacing. ‡Pore diameter calculated by the Barrett–Joyner–Halenda method using adsorption branches. ‡Brunauer–Emmett–Teller (BET) surface area. Total pore volume calculated as the amount of N\textsubscript{2} adsorbed at a relative pressure of 0.99.
On the other hand, Al is incorporated into the mesoporous framework of products prepared under relatively mild acidic conditions. A decrease in the concentration of HCl resulted in a decrease in the Si/Al ratio of products, indicating that the amount of Al species incorporated in the framework had increased. The incorporation of Al in the silica matrix suggests that the zeolite nanoblocks are retained in the local structure of the zeolite. The aluminosilicate sol containing the Si–O–Al bonds was obtained by adjusting the HCl concentration and then used as a single-source molecular precursor of Si and Al. Al atoms were fixed in the zeolite nanoblocks and directly introduced into the mesostructure along with the nanoblocks. From yield evaluation, it is conjectured that most of silicates are consumed for formation of inorganic–inorganic composites. The SAXS patterns of the calcined products prepared at pH 1.9, 2.3, and 2.8 exhibit a well-defined single reflection peak at low 2θ angle, corresponding to a d spacing of greater than 17 nm, which is larger than that of the pure silica mesoporous 1.4-MS. The SAXS pattern of the calcined 3.2-MAS shows no reflection peak, indicating a disordered structure.

The porous structures of the products were investigated by N$_2$ adsorption/desorption measurements (Figure 1). All products calcined at 600 °C show typical type-IV curves with a hysteresis loop and sharp capillary condensation, both of which are ascribed to the uniform large cage-like mesopores. Table 1 summarizes the physical properties of ordered mesoporous materials prepared using solutions of LTA dissolved in HCl. The Si/Al ratio, d spacing, pore diameter, BET surface area, and pore volume changed, depending upon the pH of the final solution. With an increasing pH value, the capillary condensation steps were shifted to higher relative pressures. As revealed by pore size distribution, the pore size shows a clearly increasing trend with an increasing pH value.

As revealed by TEM image of 2.8-MAS (Figure 2), well-aligned cage-like mesopores were observed. Note that the Pluronic F127 has a very broad region in its binary temperature–concentration phase diagram over which a bcc phase is obtained. We speculate that the ordered structure is described by the bcc, likely Im 3 m symmetry, which is similar to that of MASs prepared using TMAOH in our previous study. The lattice constant and pore size are in good agreement with that calculated by the SAXS and N$_2$ sorption measurements.

The interactions between the inorganic species (I) and organic template (S) during self-assembly have a significant effect on the final mesostructure. The structure-directed assembly of mesoscopically ordered aluminosilicate by dilute Pluronic F127 under acidic conditions may occur by a pathway that involves a combination of electrostatic and hydrogen-bonding interactions (S$^+$H+X$^-$). X is the intermediated molecular species, Cl. At low pH, positively charged protonated aluminosilicate species interact preferentially with the more hydrophilic PEO segments to promote cooperative self-assembly. At high pH, the low H$^+$ concentration results in weaker interactions between the aluminosilicate precursor and the Pluronic F127. Thus, the absence of sufficiently strong interactions leads to the formation of a poorly ordered structure or wormhole-like disordered structure.

Under acidic conditions, the PPO segments are believed to exhibit more hydrophobicity than the PEO segments. Hydrogen bonding weakens with decreasing HCl concentration. The decrease in hydrogen bonding at the inorganic–organic interface may decrease the effective head group area and the interfacial curvature. In other words, the PEO segments become more hydrophobic, resulting in shorter lengths of PEO segments associated with the inorganic wall, increased hydrophobic domain volumes, and increased final mesopore sizes.

The authors thank Associate Prof. J. Hayashi (Kansai Univ.) for N$_2$ sorption measurements.

References and Notes
6. A synthetic zeolite Na-A in a powdery form was purchased from Wako Pure Chemical Industries and used without further purification and any ion exchange treatment. Pluronic F127 was purchased from Sigma-Aldrich Chemical Co. and used as received.