Preparation of highly ordered Fe-SBA-1 and Ti-SBA-1 cubic mesoporous silica via sol-gel processing of silatrane

Walairat Tanglumlert, Toyoko Imae, Timothy J. White, Sujitra Wongkasemjit

The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand
Graduate School of Science and Technology, Keio University, Yokohama 223-8522, Japan
School of Materials Science and Engineering, Nanyang Technological University, Singapore

Abstract
Silatrane prepared from fumed silica and triethanolamine (TEA) was used as a precursor for the sol-gel synthesis of M-SBA-1 (M=Fe and Ti) at room temperature using cetyltrimethylammonium bromide as a template, and dilute solutions of ferric chloride and titanium glycolate as metal sources. Powder X-ray diffraction (XRD) showed the mesoporous materials to be well-ordered cubic structures, while N2 adsorption/desorption measurements yielded high surface areas. Diffuse reflectance UV–visible spectroscopy demonstrated that iron (Fe3+) and titanium (Ti4+) were incorporated in the framework of the calcined materials to loadings of 6 wt.% Fe and 10 wt.% Ti without perturbing the ordered mesoporous structure.

1. Introduction
In mesoporous materials of the SBA family, phases with a three-dimensional pore system are advantageous for catalytic applications, compared to one-dimensional pore arrays, because of the thicker walls, greater pore diameters and improved hydrothermal stability with respect to reference materials such as MCM-41 [1–3]. Moreover, metal substituted mesoporous architectures are attractive for catalytic reactions involving molecules that are sterically excluded from the channels of microporous zeolites [4–6]. Recently, several metal ions including Ti4+, Cr6+, Mo5+, V5+ and Fe3+ have been successfully incorporated into the frameworks of mesoporous silicas [7–11]. In particular, Ti-substituted molecular sieves (Ti4+), such as TS-1, Ti-beta and Ti-MCM-41 have displayed excellent catalytic properties in selective oxidation reactions when using aqueous hydrogen peroxide as the oxidant [12–14]. Iron-containing mesoporous materials (Fe3+), such as Fe-SBA-1, Fe-MCM-41, and Fe-HMS have also been extensively studied because of their unique catalytic enhancement of hydrocarbon oxidation, selective reduction, acylation and alkylation reactions [2,3].

In an earlier report, the successful synthesis of SBA-1 mesoporous silica via a sol-gel process using silatrane was described [15]. Here, this approach is extended to the preparation of highly ordered M-SBA-1 (M=Fe and Ti) cubic mesoporous silicas, and the structural and physical properties of these materials evaluated.

2. Methodology

2.1. Materials
Fumed silica (SiO2, 99.8%) (Sigma-Aldrich), titanium dioxide (TiO2) (Carlo Erba), triethanolamine (TEA) (Carlo Erba), tetraethylenetriamine (TETA) (FACAI, Thailand), ethylene glycol (J.T. Baker, USA), acetonitrile (Labscan, Asia), ferric chloride (FeCl3) (Sigma-Aldrich), hexadecyltrimethylammonium bromide (C16TMAB) (Sigma-Aldrich), H2SO4 (Labscan, Asia) and NaOH (Labscan, Asia) were used without treatment.

In this synthesis, solution A was prepared by adding C16TMAB (0.44 g) to water (30 ml) and stirring for 0.5 h to obtain a clear solution. Solution B was prepared by dissolving silatrane precursor (5 mmol, 1.4 g), synthesized following the procedure described in references [16], in 14 ml of 0.3 M H2SO4 and NaOH (1.7 mmol, 0.068 g) by stirring for 0.5 h. The required amount of metal precursor, titanium glycolate synthesized according to Ref. [17], or FeCl3, was added to solution B and stirring continued for 0.5 h. Solution B was then added to the solution A under vigorous stirring that continued for 4 h. Water...
(30 ml) was added to this mixture before aging for 2 days at room temperature to form a white precipitate. The product was filtered, washed with distilled water, and dried at room temperature overnight. The template was removed by calcination (560 °C/6 h) in a Carbolite Furnace (CFS 1200) at a heating rate of 0.5 °C/min.

2.3. Characterization

The mesoporous products were characterized using a Rigaku X-ray diffractometer (XRD) with patterns accumulated at a scan speed of 1°/s using CuKα radiation over the range of 2θ = 1.5°–8°. M-SBA-1 mesopore order was directly examined using a JEOL 2010F transmission electron microscope (TEM). Specific surface area and average pore size were determined by the Brunauer–Emmett–Teller (BET) method with a Quantasorb JR instrument. Diffuse reflectance UV–visible spectroscopic measurements were recorded on a Shimadzu UV-2550 spectrometer fitted with an ISR-2200 integrating sphere attachment from 200–600 nm referenced to BaSO4. Electron spin resonance (ESR) spectra were measured at the X-band, ~9 GHz, on a JEOL JES-RE2X spectrometer.

3. Results and discussion

Higher metal (Ti4+, Fe3+) incorporation in SBA-1 has been attributed to a surfactant silica assembly mechanism, in which the mesophase forms under acidic conditions via an S+X−I+ pathway (S, X and I correspond to surfactant, halide and inorganic species, respectively). As silatrane is a water soluble alkoxide, hydrolysis to silicate generates...
Table 1

Physical and crystallographic characteristics of M-SBA-1 (M=Fe³⁺, Ti⁴⁺) mesoporous materials as a function of metal loading

<table>
<thead>
<tr>
<th>Material Designation</th>
<th>Metal Doping (wt.%)</th>
<th>BET surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Average pore diameter (nm)</th>
<th>Crystallographic properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-1</td>
<td>0</td>
<td>1435</td>
<td>0.75</td>
<td>2.12</td>
<td>d₁₀₀ (nm) 3.62, a₀ (nm) 8.09</td>
</tr>
<tr>
<td>Ti 6%</td>
<td>6</td>
<td>1101</td>
<td>0.91</td>
<td>2.11</td>
<td>d₁₀₀ (nm) 3.65, a₀ (nm) 8.16</td>
</tr>
<tr>
<td>Fe 6%</td>
<td>6</td>
<td>1062</td>
<td>0.54</td>
<td>2.10</td>
<td>d₁₀₀ (nm) 3.68, a₀ (nm) 8.23</td>
</tr>
<tr>
<td>Ti 2%</td>
<td>2</td>
<td>1101</td>
<td>0.57</td>
<td>2.07</td>
<td>d₁₀₀ (nm) 3.71, a₀ (nm) 8.30</td>
</tr>
<tr>
<td>Fe 4%</td>
<td>4</td>
<td>1029</td>
<td>0.56</td>
<td>2.17</td>
<td>d₁₀₀ (nm) 3.77, a₀ (nm) 8.43</td>
</tr>
<tr>
<td>Ti 6%</td>
<td>6</td>
<td>880</td>
<td>0.51</td>
<td>2.34</td>
<td>d₁₀₀ (nm) 3.80, a₀ (nm) 8.51</td>
</tr>
</tbody>
</table>

*Lattice parameters a₀ were calculated based on the formula a₀=√3d₁₀₀.

Transmission electron microscope lattice images (Fig. 4A and B) of representative Ti-SBA-1 and Fe-SBA-1 crystals demonstrates that regular mesopore arrays had formed, and exclude the presence of metal segregation, as this would be readily detected due to the greater electron scattering powder of Fe/Ti compared to Si.

Conclusions

Silatrane obtained from the Oxide One Pot Synthesis (OOPS) process is a highly reactive precursor for the preparation of transition metal-bearing SBA-1 mesoporous materials. It has been demonstrated that the SBA-1 framework can accommodate up to 6 wt.% Fe and 10 wt.% Ti without perturbing mesopore order. Dilation of the mesoporous lattice with metal loading is consistent with crystalchemical framework replacement of Si⁴⁺ by Fe³⁺/Ti⁴⁺ and the predominant retention of the metals in tetrahedral co-ordination to oxygen. However, to maintain charge balance as Fe³⁺ replaces Si⁴⁺ some edge-sharing octahedral FeO₆ clusters may be present as suggested by ESR spectroscopy.

Acknowledgements

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References