Surface characterisation of zirconium-doped mesoporous silica

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Zirconium-doped mesoporous silicas of mole ratio Si/Zr from 50 to 5 are Lewis-acid catalysts, with a linear correlation between the zirconium content and total acidity.

Much attention has been devoted to the synthesis of new mesoporous materials using surfactants as templates since the first reports on MCM-41 type solids. Mesoporous silica displays a hexagonal arrangement of cylindrical channels with diameters that vary between 16 and >100 Å, partially overcoming the small pore dimension limitations of zeolites. The low acidity of siliceous MCM-41 can be enhanced by isomorphous substitution of e.g. Al or Ti IV for Si3–5 which specifically increases the number of Lewis-acid sites. The presence of Zr IV may also increase the acidity but, in addition, its invariable oxidation state may be an advantage compared with e.g. substitution with Ti IV, in particular with regard to thermal stability.

The preparation of zirconium-containing mesoporous silica assisted by surfactant species (hexadecylamine) and its activity in redox catalysis has recently been described. We report here a synthesis of Zr-doped mesoporous silica using hexadecyltrimethylammonium as template, and describe the total acidity and types of acid site, and structural information derived from X-ray photoelectron spectroscopy (XPS) coupled with depth profile analysis.

Si/Zr MCM-41 type compounds were prepared by adding tetraethoxysilane and zirconium tetrapropoxide to an ethanol–propanol solution at room temperature. Si/Zr ratios of 5, 25 and 50 gave samples SiZr5B, SiZr25B and SiZr50B. The solution was stirred for 15 min and then added to an aqueous solution of hexadecyltrimethylammonium bromide (25 mass%), previously stirred at 80 °C for 30 min. The surfactant/(SiO2 + ZrO2) ratio was 0.5. For these samples, the pH was adjusted to 10.5 by addition of tetraethylammonium hydroxide. The resulting gels were stirred at 80 °C for 24 h and then at 25 °C for 48 h. The solids were recovered by filtration and washed with ethanol–propanol. A purely siliceous sample was prepared using the same experimental conditions (SiB). A further sample of Si/Zr ratio 50 was prepared, but the pH was adjusted to 2.8 by the addition of HCl (SiZr50A). All precursors were calcined in air at 540 °C, for 6 h. The ramp rate was 1 °C min–1. Complete removal of surfactant was confirmed by elemental and thermogravimetric analyses.

Fig. 1 shows the powder X-ray diffraction patterns of the calcined Si/Zr materials. In all cases, a single diffraction peak was observed, consistent with short-range hexagonal order. Indeed, transmission electron microscopy allows a roughly hexagonal arrangement of pores to be observed. Owing to the breadth of the diffraction line, no correlation between its position and the Zr content was apparent. Neither XRD nor UV spectroscopy showed evidence for zirconium oxide.

Chemical analyses indicated that the Si/Zr ratio in the calcined phases is the same as that in the initial mixture. However, in each case, the ratio of Si/Zr at the surface, as determined from XPS, is higher than this bulk ratio. This is expected, given the greater rate of hydrolysis of Zr alkoxides relative to that of Si alkoxides. Depth profile analysis of sample SiZr25B was performed by etching with an Ar+ gun, and observing the evolution of the Si/Zr ratio with time. After 5 min the surface ratio of 66 decreases to 23, and a constant value of 17 was reached after 15 min [Fig. 2(a)]. Single peaks were

![Fig. 1 Powder X-ray diffraction patterns of (a) SiZr50A, (b) SiZr50B and (c) SiZr25B calcined at 540 °C](image)

![Fig. 2 (a) Variation of the Si/Zr ratio in sample SiZr25B as determined by depth profile analysis using XPS as a function of time of etching; (b) O 1s XPS spectrum of SiZr5B](image)
observed for both Si 2p and Zr 3d_{5/2} and the percentage of oxygen remained constant at 63% throughout the etching treatment. The O 1s peak becomes asymmetric as the amount of Zr in the samples increases. Thus for ZrSi5B, O 1s can be deconvoluted into two components, indicating two different environments for oxygen, viz. Si–O–Zr (530.9 eV) and Si–O–Zr (530.9 eV) \[\text{Fig. 2(b)}\]. The intensity ratio of these two peaks closely matches the surface Si/Zr ratio. In such heteroatom-substituted analogues of siliceous MCM-41 materials, the question arises as to the true incorporation of the heteroatom.

Further, the binding energies of Zr 3d_{5/2} (183.1–183.6 eV) are higher than that of ZrO2 (182.2 eV) and are closer to that of ZrO2 –SiO2 materials. 7

All calcined compounds exhibited a reversible type IV nitrogen adsorption–desorption isotherm, with a sharp inflection at \(P/P_0 = 0.35-0.40\), as is typical for MCM-type mesoporous materials. Table 1 gives the textural parameters derived from the isotherms. Surface areas lie between 973 and 1376 m² g⁻¹. The average pore size of the silica-only compound after calcination at 800 °C is lower by 25% that of its value after calcination at 540 °C. Zirconium-doped samples are more resistant, the average pore size being reduced by 12–17%. Even after calcination at 800 °C, all materials retain their mesoporous character and a high surface area. The wall thicknesses of all zirconium-containing phases are higher than that of the purely siliceous analogue, in agreement with the incorporation of zirconium into the framework. The particularly strong increase in intensity of the two lower field resonances relative to that at \(\delta = 107.3\), –98.6 and –89.4. After calcination, the increase in intensity of the two lower field resonances relative to that at \(\delta = 107.3\) can be explained on the basis of the formation of Si–O–Zr bonds, as previously suggested for mixed ZrO2–SiO2 materials. 7

The 29Si MAS NMR spectra of as-prepared SiZr25B shows resonances at \(\delta = 107.3, -98.6\) and \(-89.4\). After calcination, the increase in intensity of the two lower field resonances relative to that at \(\delta = 107.3\) can be explained on the basis of the formation of Si–O–Zr bonds, as previously suggested for mixed ZrO2–SiO2 materials. 7

### Table 1 Textural parameters of prepared samples

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<thead>
<tr>
<th>Sample</th>
<th>(S_{BET}) (540 °C) m² g⁻¹</th>
<th>(\Sigma V_{p}) cm³ g⁻¹</th>
<th>(S_{BET}) (800 °C) m² g⁻¹</th>
<th>(d(p, av.)) (540 °C) Å</th>
<th>(d(p, av.)) (800 °C) Å</th>
<th>% shrinkage</th>
<th>(D) (540 °C, air) Å</th>
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</thead>
<tbody>
<tr>
<td>SiZr50A</td>
<td>1140</td>
<td>0.788</td>
<td>—</td>
<td>27.5</td>
<td>—</td>
<td>34.1</td>
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<tr>
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<td>1157</td>
<td>1.000</td>
<td>985</td>
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<td>22.5</td>
<td>9.9</td>
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<tr>
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<td>24.6</td>
<td>20.4</td>
<td>12.4</td>
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<tr>
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<td>700</td>
<td>27.5</td>
<td>23.8</td>
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