

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^{1,2} since the first reports on MCM-41 type solids.³ 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.⁶ 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

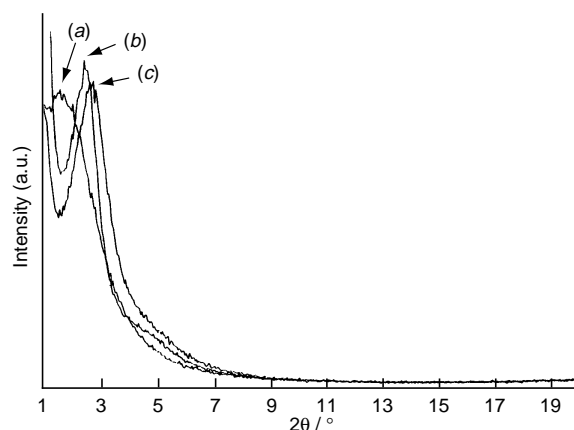


Fig. 1 Powder X-ray diffraction patterns of (a) SiZr50A, (b) SiZr50B and (c) SiZr25B calcined at 540 °C

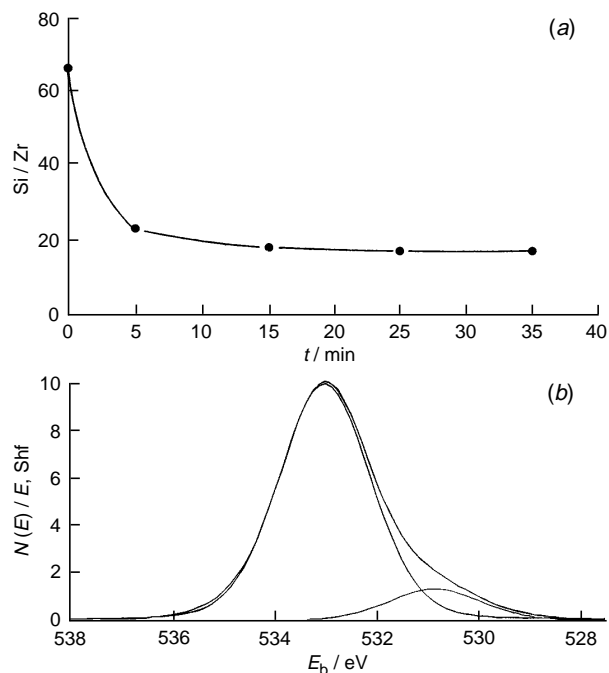


Fig. 2 (a) Variation of the Si/Zr ratio in sample SiZr25B as determined by depth profile analysis using XPS as a function of time of etching; (b) O 1s XPS spectrum of SiZr5B

Table 1 Textural parameters of prepared samples

Sample	S_{BET} (540 °C)/m ² g ⁻¹	$\Sigma V_p^{a/}$ cm ³ g ⁻¹	S_{BET} (800 °C)/m ² g ⁻¹	$dp(\text{av.})^b$ (540 °C)/Å	$dp(\text{av.})$ (800 °C)/Å	% shrinkage ^c	D^d (540 °C, air)/Å
SiZr50A	1140	0.788	—	27.5	—	—	34.1
SiB	1157	1.000	985	30.2	22.5	5.2	9.9
SiZr50B	1302	0.923	1072	27.6	24.2	4.3	12.5
SiZr25B	1386	0.879	876	24.6	20.4	12.4	12.0
SiZr5B	973	0.687	700	27.5	23.8	5.2	16.3

^a At $P/P_0 = 0.97$. ^b Calculated using the Cranston and Inkley method. ^c Reduction in lattice parameter a_0 after calcination at 540 °C. ^d Pore wall thickness, D , after calcination at 540 °C; $D = a_0 - d_p(\text{av.})$, and $a_0 = 2d_{100}/\sqrt{3}$.

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–Si (component at 533.0 eV) and Si–O–Zr (530.9 eV) [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 in the framework, as opposed to its presence as a segregated oxide phase. Here, the XPS signals of O 1s are at least 0.7 eV higher than that of ZrO₂ (530.2 eV), strong evidence in favour of the presence of framework zirconium. 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 ZrSiO₄ (183.3 eV). Preliminary results from extended X-ray absorption fine structure spectroscopy at the zirconium edge show the local structure to differ from that of ZrO₂, with evidence for silicon in the next nearest neighbour coordination shell.

The ²⁹Si MAS NMR spectra of as-prepared SiZr25B shows resonances at δ –107.3, –98.6 and –89.4. After calcination, the increase in intensity of the two lower field resonances relative to that at δ –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

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 observed for the synthesis under acidic conditions may be a result of the synthetic mechanism which controls the precipitation of a solid phase from the gel mixture.

IR spectra of calcined samples after adsorption of pyridine show a virtual absence of Brønsted acid sites, and an increasing number of Lewis-acid sites with an increase in the amount of Zr present. The origin of the Lewis acidity may be attributed to the presence of Zr^{IV} species with low coordination. Total acidity, determined by thermally programmed desorption of NH₃ follows the same trend, ranging between 0.17 and 0.77 mmol NH₃ g⁻¹. In particular, sample ZrSi5B is considerably more acidic than MCM-41 aluminosilicates.⁵ Confirmation of the

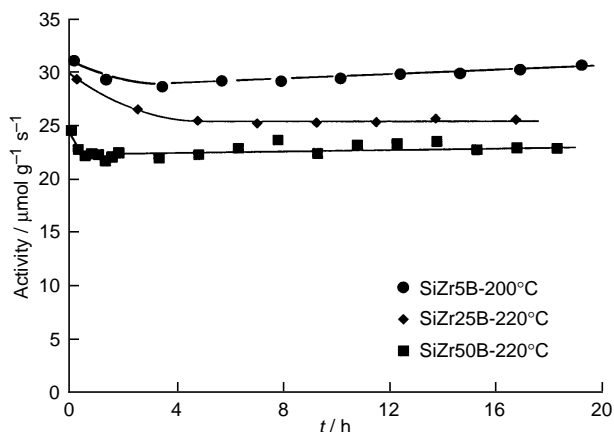


Fig. 3 Catalytic activity of SiZr50B, SiZr25B and SiZr5B for *iso*-propyl alcohol decomposition as a function of time on stream

acidic character of the zirconium-doped samples is provided by their activity in the decomposition of isopropyl alcohol. Whilst purely siliceous MCM-41 (sample SiB) is not active in this reaction, calcined Si/Zr samples displayed, in contrast, a high catalytic activity (30 μmol g⁻¹ s⁻¹ at 200 °C for sample SiZr5B) and a selectivity of 99% towards production of propene, which was maintained after 20 h of reaction (Fig. 3). Inasmuch as both the location and number of active sites are key factors in the observed catalytic properties, knowledge of the ion distribution is essential. In this respect, this study has demonstrated the important contribution that XPS can make in the study of heteroatom-substituted mesoporous materials.

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References

- N. K. Raman, M. T. Anderson and J. Brinker, *Chem. Mater.*, 1996, **8**, 1682.
- A. Sayari, *Chem. Mater.*, 1996, **8**, 1840.
- C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
- J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. C. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10 834.
- A. Corma, V. Fornes, M. T. Navarro and J. Pérez-Pariente, *J. Catal.*, 1994, **184**, 569.
- A. Tuel, S. Gontier and T. Teissier, *Chem. Commun.*, 1996, 651.
- M. Andrianainarivelo, R. Corriu, D. Leclercq, P. H. Mutin and A. Vioux, *J. Mater. Chem.*, 1996, **6**, 1665.
- R. W. Cranston and F. A. Inkley, *Adv. Catal.*, 1957, **9**, 143.

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