Zirconium containing mesoporous silicas: new catalysts for oxidation reactions in the liquid phase

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Zirconium containing mesoporous silicas are synthesized using hexadecylamine as surfactant; the new materials show very interesting properties as catalysts in liquid-phase oxidations with H_2O_2 and alkyl peroxides.

Liquid-phase oxidation by hydrogen peroxide or alkyl peroxides catalysed by transition-metal containing molecular sieves is a very interesting and promising field of research for the future. Catalysts with remarkable properties have been recently synthesized, particularly the titanium substituted silicalite-1 (TS-1) which catalyses the oxidation of a large family of organic molecules with H_2O_2.[1] Interesting results were also obtained over Ti, V, Cr or Sn containing zeolites or aluminophosphates.[2–5] However, the potential of such materials in liquid-phase oxidation is limited by the number of heteroelements that can be incorporated in the framework and by the relatively small pore opening of the structures.

There has been an important breakthrough with the recent discovery of M41S materials, a family of mesoporous aluminosilicates whose pore dimension can be varied between *ca.* 15 and 100 Å.[6] It has been reported that titanium and vanadium can be incorporated in these solids and that the corresponding materials were efficient catalysts for the oxidation of large and bulky substrates.[7,8] As these materials are amorphous, we may expect that incorporation of large cations in the silica walls will be favoured with respect to zeolites, at least because strains due to a crystalline framework are not present. In particular, Mo, W or Zr, which are known to be active as homogeneous catalysts, could generate new classes of catalysts when incorporated in mesoporous silicas. Attempts have been made to synthesize Zr containing silicalite-1, but the material possessed very low activity in hydroxylation of phenol with H_2O_2.[9]

In the present paper, we report on the synthesis of new Zr containing mesoporous silicas (Zr-MS), very active as catalysts in oxidation reactions with both H_2O_2 and *tert*-butyl hydroperoxide (TBHP) as oxidants.

Zr-MS samples were synthesized at room temperature using hexadecylamine as surfactant molecule. A solution containing 0.1 mol of tetraethyl orthosilicate and the required amount of zirconium isopropoxide was mixed with a second solution containing 0.03 mol of hexadecylamine in 0.65 mol of ethanol and 3 mol of water. The gel was mixed for *ca.* 30 min and aged under static conditions for 12 h. The solid was recovered by centrifugation, washed abundantly with distilled water and air-dried. In order to remove the organics, 1 g of dried solid was dispersed in 100 ml of ethanol and the mixture refluxed for 1 h under vigorous stirring. The solid phase was recovered by filtration, washed with cold ethanol and the extraction procedure was repeated once. Finally, the amine-free sample was dried overnight at 80 °C and subsequently calcined in air at 500 °C for 6 h.

For comparison in catalytic tests, a Ti containing mesoporous silica was synthesized following the same recipe using tetrabutylorthotitanate instead of zirconium isopropoxide.

Extracted samples were characterized using conventional techniques. N_2 adsorption–desorption isotherms were collected at 77 K using a Catasorb apparatus. Samples were preliminarily outgassed at 250 °C for 10 h.

Catalytic tests were carried out in a round-bottomed flask equipped with a condenser and a magnetic stirrer. Products were analysed by gas chromatography using a Tenax GC 60/80 nickel column.

Table 1 lists the chemical composition and some characteristics of the various samples. For all samples, the Zr content was very close to that originally introduced in the precursor gel.

Table 1 Chemical composition and structural parameters of the samples

	Si/Zr				
Sample	Gel	Product	S/m² g^{-1}	Φ_p[a]/Å	V/cm³ g^{-1}
1	1000	724	865	38	0.6
2	100	128	1049	33	0.72
3	50	46	887	36	0.65
4	25	26	886	36	0.6
5	15	17	1022	33	0.68

[a] Φ_p is the mean pore diameter and V the mesopore volume measured at p/p_0 = 0.5 in the N_2 isotherm.

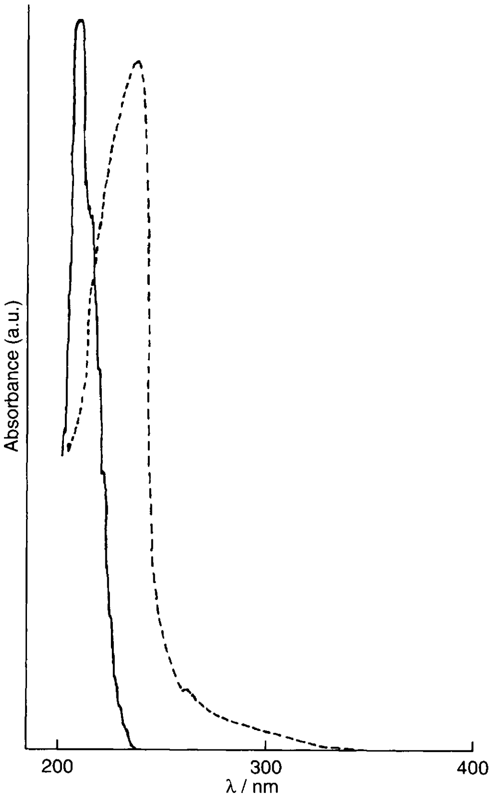

Fig. 1 UV–VIS spectra of Zr-HMS (sample 4) (—) and ZrO_2 (- - -). Spectra were collected on a Perkin Elmer Lambda 9 spectrometer.

Moreover, comparison of the Zr content before and after the extraction procedure revealed that Zr species were not removed in boiling ethanol. The specific surface areas as well as the mesoporous volumes (measured at $p/p_0 = 0.5$ in the N_2 isotherm) do not strongly depend on the zirconium content and are comparable to those reported in the literature for various mesoporous silicas. The mean pore diameter Φ_p also does not significantly change with the chemical composition, indicating that samples are thermally stable and do not contain large amounts of extrawall species. The pore distribution curves are very similar to those reported for HMS[7] and MCM-41.[6]

X-Ray diffraction patterns of the samples exhibited a single broad line at $2\theta \approx 2.3°$. (100) and (200) reflections were not resolved as already reported for mesoporous silicas prepared with primary alkylamines. This was attributed to small scattering domains as compared to the hexagonal parent MCM-41. Owing to the X-ray line width, we did not observe any correlation between the position of the peak and the Zr content.

The dispersion of Zr^{4+} cations in the silica matrix was studied by UV–VIS spectroscopy (Fig. 1). All samples exhibited a single narrow band at *ca.* 205 nm and showed the absence of ZrO_2 oxide species within the mesopores. As for titanium, this absorption may be attributed to a transition having charge-transfer character involving isolated Zr^{IV} species. More studies on the coordination of such species are in progress and will be reported in a forthcoming paper.

Table 2 Oxidation of various substrates over Zr-HMS (sample 4) and Ti-HMS

Catalyst	Substrate	Oxidant	Ox/S	Ox (%)	Product (%)
Zr-HMS	aniline	H_2O_2	0.2	98	100[a]
Ti-HMS	aniline	H_2O_2	0.2	97	100
Zr-HMS	cyclohexane	H_2O_2	0.05	72	67(22)[b]
Ti-HMS	cyclohexane	H_2O_2	0.05	90	60(4)
Zr-HMS	norbornylene	TBHP	3	92	20(80)[c]
Ti-HMS	norbornylene	TBHP	3	95	70(30)
Zr-HMS	2,6-DTBP	H_2O_2	6	90	80[d]
Ti-HMS	2,6-DTBP	H_2O_2	6	95	95

Data were collected after 3 h reaction. Ox (%) and Product (%) are the selectivities in oxidant and product, respectively. Products were: [a] azoxybenzene and azobenzene, [b] cyclohexene (cyclohexanediol), [c] 2,3-epoxynorbornane (norborneol) and [d] 2,6-di-*tert*-butyl-1,4-benzoquinone.

Some of the samples have been tested as catalysts in the oxidation of organic molecules wtih H_2O_2 or TBHP. The molecules were chosen on the basis of preliminary catalytic data obtained over titanium containing mesoporous silicas. Results are summarized in Table 2, which clearly shows that Zr containing mesoporous silicas are active catalysts and that the activity is similar to that obtained over Ti-MS. Owing to their large pore diameter, Zr-MS as well as Ti-MS can catalyse the oxidation of large substrates like norbornylene or 2,6-di-*tert*-butylphenol (2,6-DTBP). It is interesting to note that both ZrO_2 and Zr impregnated mesoporous silica showed very low activities for these reactions, confirming that the dispersion of Zr atoms is a necessary condition for the catalytic activity.

Whilst the activities of Zr-MS and Ti-MS are similar, differences are observed in the product selectivities, particularly in the case of epoxidation reactions. For both norbornylene and 2,6-DTBP, the selectivity in alcohol at the end of the reaction is higher over Zr-MS. Additional catalytic reactions are now in progress to confirm these differences and to elucidate the mechanism of the reaction.

We have shown that zirconium containing mesoporous silicas can be easily synthesized at room temperature using a primary amine as surfactant molecule. Zirconium atoms are highly dispersed in the silica matrix, as shown by UV–VIS spectroscopy. These samples showed interesting properties as catalysts in the liquid-phase oxidation of organic molecules with alkyl peroxides.

References

1 B. Notari, *Catal. Today*, 1993, **18**, 163.
2 A. Corma, P. Esteve, A. Martinez and S. Valencia, *J. Catal.*, 1995, **152**, 18.
3 A. Tuel and Y. Ben Taârit, *Appl. Catal. A: Gen.*, 1993, **102**, 201.
4 J. D. Chen, M. J. Haanepen, J. H. C. van Hooff and R. A. Sheldon, *Stud. Surf. Sci. Catal.*, 1994, **84**, 973.
5 N. K. Mal, V. Ramaswamy, S. Ganapathy and A. V. Ramaswamy, *Appl. Catal. A: Gen.*, 1995, **125**, 233.
6 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Breck, *Nature*, 1992, **359**, 710.
7 P. T. Tanev, M. Chibwe and T. J. Pinnavaia, *Nature*, 1994, **368**, 321.
8 K. M. Reddy, I. Moudrakovski and A. Sayari, *J. Chem. Soc., Chem. Commun.*, 1994, 1059.
9 M. K. Dongare, P. Singh, P. P. Moghe and P. Ratnasamy, *Zeolites*, 1991, **11**, 690.

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