Preparation of metal-incorporated MSU mesoporous silica molecular sieves. Ti incorporation *via* a totally non-ionic route

Stephen A. Bagshaw,* Francesco Di Renzo and François Fajula

Laboratoire de Materiaux Catalytiques et Catalyse en Chimie Organique, Ecole Nationale Superieure de Chimie de Montpellier, UMR 5618 CNRS, 34053 Montpellier, France

A totally non-ionic pathway to mesoporous Ti-MSU-silicas is reported, wherein the incorporation of Ti into the silica framework proceeds *via* the hydrolysis of a chemically modified Ti–alkoxide species which permits control over the rate of hydrolysis of the metal precursor, thus allowing stoichiometric titanium incorporation up to approximately 5 mol%.

The recent discovery of synthetic routes to templated mesostructured molecular sieve materials (M41S, HMS)[1,2] has opened new areas of enquiry into the mechanisms of formation,[3] diversification of the structures of such materials[4] and application in catalysis.[5] A new family of templated mesoporous materials was recently reported by Pinnavaia and coworkers[6] wherein non-ionic inorganic precursors are templated by non-toxic, biodegradable, non-ionic polyethylene oxide (PEO) based surfactants producing novel MSU-oxide families of materials.[6,7] These materials differ fundamentally from MCM-41 and HMS materials in their method of preparation, mechanism of formation and in their pore architectures. MSU materials differ further from cubic MCM-48 and 'cage-like' SBA-2 materials[1,8] in that their pore architectures are totally non-symmetric, being constructed from three-dimensional arrays of randomly interconnecting long 'worm-like' pores of regular diameter. Such a three-dimensional pore structure may have significant benefits in practical catalytic applications of mesoporous materials by reducing the probability of pore blockage[9] and increasing the number of reactive surface defect sites.

M41S materials are synthesised under high temperature and pH conditions, HMS under high pH conditions. MSU-silicas on the other hand are synthesised under ambient temperature and neutral pH reaction conditions. Under these particular conditions the chemistry involved in the formation of the silica network is very different to that of M41S and HMS. In terms of how this applies to metal incorporation, the hydrolysis of transition metal alkoxides under these conditions is virtually instantaneous, while the rate of hydrolysis of the silica precursor remains low. In order to incorporate catalytically important metal atoms into a templated silica framework therefore, the rate of hydrolysis of the metal precursor must be rendered within the same order of magnitude as that of the silica precursor. The substitution of catalytically important metal atoms into the network of mesoporous MSU-silicas has thus posed interesting synthetic challenges. We herein report on the controlled incorporation of Ti into MSU-silica through modification of the rate of hydrolysis of a Ti-precursor *via* chemical manipulation of a Ti–alkoxide species.

In the current report we marry the concept of non-ionically templated mesostructures with the hydrolytic control of a Ti^{IV} bis(ethyl acetoacetato) diisopropoxide (Ti-bis) species to produce Ti-substituted MSU-silicas. Two different commercially available polyethylene oxide surfactants were employed. Silicon tetraethoxide (TEOS) and Ti-bis were obtained from Aldrich Chemicals. The amount of Ti-bis added to the reagent mixture was varied from 1 to 10 mol%. Elemental analyses of the calcined materials indicated near stoichiometric incorporation of Ti in the final products. The physico-chemical characteristics of the as-prepared and calcined materials are presented in Table 1.

In a typical synthesis, a solution of a PEO surfactant was prepared under moderate stirring, in deionized (DI) water. The temperature of the solution was slowly raised to just below the cloud point of the surfactant.[11] Surfactant concentrations were typically 5 mass% and the temperature was 323 K. The appropriate mass of Ti-bis was added rapidly to the required mass of TEOS in an air-tight, heat-proof vessel. This solution was then stirred at approximately 353 K overnight in order to induce oligomerisation between the Si and Ti species. The Si–Ti solution was then cooled to room temperature and added at once to the stirred surfactant solution. The resulting pale yellow suspension was stirred slowly. After 24–48 h the reaction was stopped and the pale yellow solid was filtered, washed thoroughly with DI water and dried overnight in air at 353 K. Removal of the occluded surfactant and any remaining unhydrolysed organic ligands was achieved through calcination in air at 823 K for 4 h.

Powder X-ray diffraction (XRD) patterns of the as-synthesised Ti-MSU-silica samples exhibited single peaks of moderate intensities, identical in form to those reported for pure MSU-

Table 1 Physicochemical properties of Ti-MSU-silicas

				d_{100}/nm				
Sample	Surfactant	Mass %	Mol% Ti	As prepared	Calcined	SA/m^2 g^{-1}	d_p/nm	V_p/ml g^{-1}
Ti(1)-MSU-2[a]	$C_{10}Ph(EO)_{10}$[b]	5	1	4.6	4.6	940	2.7	0.61
Ti(1.5)-MSU-2	$C_{10}Ph(EO)_{10}$	5	1.5	4.6	4.6	1100	2.4	0.78
Ti(2)-MSU-2	$C_{10}Ph(EO)_{10}$	5	2	4.9	4.6	1000	2.3	1.35
Ti(5)-MSU-2	$C_{10}Ph(EO)_{10}$	5	5	4.9	4.6	940	2.1	0.57
Ti(10)-MSU-2	$C_{10}Ph(EO)_{10}$	5	10	5.2	p.c[e]	1000	2.5	0.93
Ti(5)-MSU-1[c]	$C_{15}(EO)_{12}$[d]	10	5	5.2	4.9	950	3.0	n.o[f]
MSU-2 silica	$C_{10}Ph(EO)_{10}$	5	0	6.3	6.0	850	3.5	0.80

[a] MSU-2 designation applied to materials prepared from alkyl–phenyl PEO surfactants. [b] Triton N-101. Union Carbide product obtained from Aldrich Chemicals. [c] MSU-1 designation applied to materials prepared from alkyl–PEO surfactants. [d] Tergitol 15-S-12. Product kindly supplied by Union Carbide Corp. [e] p.c = Partial collapse of d_{100} XRD signal. [f] n.o = Not obtained.

silicas.[6] The d_{100} spacings for the respective as-prepared and calcined samples are presented in Table 1. In agreement with results for HMS[2] and MSU-silica materials,[6] the intensities of the XRD patterns increased after removal of the template by calcination in air at 823 K. A shift to lower d_{100} values from those of siliceous MSU-silica was observed when the transition metal atoms were incorporated into the structure, but little further change was observed as the Ti content was increased.

N_2 adsorption isotherms (Fig. 1) were also similar to those reported for siliceous MSU-silica, exhibiting single step isotherms characteristic of materials possessing regular pores in the lower mesoporous size region. The N_2-desorption isotherms showed no hysteresis, suggesting that the architectures of individual pores are uniform, with no 'bottle-necking' of the pore structure. Average pore diameters, calculated from the N_2-desorption isotherm using the BJH model,[12] are presented in Table 1 and show a decrease in pore size with increasing Ti content. This result, along with the XRD data suggests that as the Ti content is increased, the cell parameter remains more or less constant while the wall thickness increases. Therefore, either the space occupied by the micelles is reduced during synthesis, or the pore walls increase in thickness during calcination.

Ti speciation was investigated using diffuse-reflectance UV–VIS spectroscopy of calcined samples. The intensities of the spectra of all the Ti-containing samples were at least an order of magnitude greater than those of the pure silica samples, indicating the incorporation of a photoactive species within the given samples. Calcined Ti(1%)-MSU exhibited a sharp transition at 245 nm [Fig. 2(*a*)]. Increasing the concentration of Ti introduced a shoulder at 225 nm and a strong peak at 245 nm [Fig. 2(*b*)], while calcined Ti(5%)-MSU exhibited a broad absorption with two discernible maxima at 260 and 300 nm [Fig. 2(*c*)]. UV–VIS spectroscopic investigations of Ti incorporated in Ti-silicalite and HMS frameworks[13] have suggested that transitions around 220 nm are characteristic of isolated Ti atoms in symmetric tetrahedral sites. We assign the 245 nm band to isolated tetrahedrally coordinated Ti atoms in poorly symmetric environments, possibly the pore surface where one or more ligands are water or OH groups. As the Ti concentration increases to *ca.* 2 mol%, Ti atoms become incorporated within the silica framework of the pore walls, with an accompanying increase in coordination symmetry, thereby explaining the increase in the intensity of the 225 nm absorption.

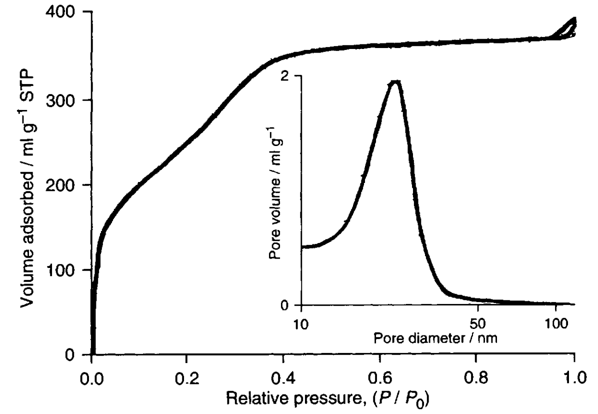

Fig. 1 Nitrogen adsorption–desorption isotherms for calcined Ti(2)-MSU-2 silica. Isotherms were obtained with a Micromeritics ASAP 2000 at 77 K after degassing at 473 K for 4 h. (Inset) BJH pore size distribution calculated from N_2-desorption branch.

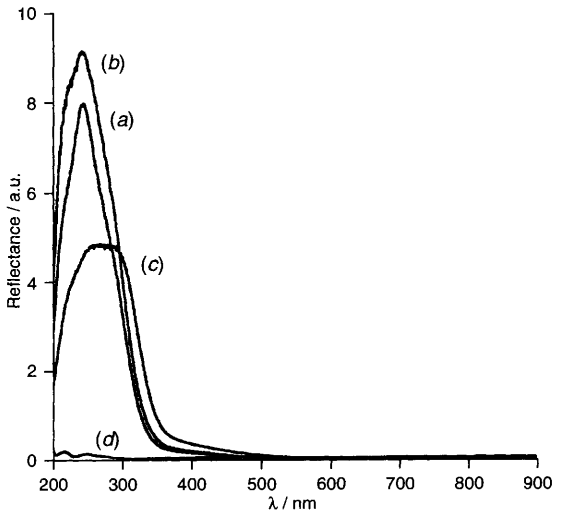

Fig. 2 UV–VIS diffuse reflectance spectra of calcined Ti(1)-MSU (*a*), Ti(2)-MSU (*b*) and Ti(5)-MSU-2 silicas (*c*), MSU-2 silica (*d*). Spectra were obtained with a Perkin-Elmer Lambda 14 spectrometer equipped with a Labsphere RSA PE 20 reflectance accessory.

Accepted assignments of the 300 nm absorption are to either six-coordinate Ti where at least two of the ligands are not framework oxygens, or to partially condensed Ti–O–Ti species.[13] Therefore, increasing the Ti concentration to 5 mol% appears to induce Ti–O–Ti oligomerisation. The absence of a well defined absorption at 330 nm indicates that crystalline TiO_2 phases are not formed, however after calcination the absorption extends into this region suggesting the possible formation of TiO_2 clusters grafted to the silica surface. Further increasing the Ti concentration of Ti-MSU to 10 mol% induces the formation of well defined extra-framework TiO_2 species, but the templated structure of the silica framework is retained.

The results for Ti incorporation into a mesoporous templated silica described herein are in good agreement with those recently reported for Ti incorporation into HMS[13] suggesting that the Ti species in these new materials are the same as those observed in Ti-HMS materials. We suggest however, that the method and mechanism of formation and the pore architecture of the final products differ fundamentally from those of M41S and HMS materials and offer advantages in preparation costs, environmental compatability and catalytic reactivity. Oxidation reactions are currently under investigation in order to verify the proposed catalytic benefits of the Ti-MSU structure.

S. A. B. acknowledges Air Liquide and ELF-Aquitaine of France for Post-doctoral sponsorship.

References

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
2 P. T. Tanev and T. J. Pinnavaia, *Science*, 1995, **267**, 865.
3 C. Y. Chen, H. X. Li, S. L. Burkett and M. E. Davis, *Microporous Mater.*, 1993, **2**, 27.
4 G. Huo, D. I. Margolese, U. Ceisla, P. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schuth and G. D. Stucky, *Nature*, 1994, **368**, 317.
5 W. Zhang, J. Wang, P. T. Tanev and T. J. Pinnavaia, *Chem. Commun.*, 1996, 979.
6 S. A. Bagshaw, E. Prouzet and T. J. Pinnavaia, *Science*, 1995, **269**, 1242.
7 S. A. Bagshaw and T. J. Pinnavaia, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1102.
8 Q. Hou, R. Leon, P. M. Petroff and G. D. Stucky, *Science*, 1995, **268**, 1324.
9 U. Ciesla, S. Schacht, G. D. Stucky, K. K. Unger and F. Schuth, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 541.
10 D. M. Anotelli and J. Y. Ying, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2014.
11 M. R. Porter, *Handbook of Surfactants*, 2nd edn., Blackie, London, 1994.
12 S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, 2nd edn., Academic Press, London, 1982.
13 S. Gontier and A. Tuel, *Zeolites*, 1995, **15**, 601.

Received, 10th July 1996; Com. 6/04868D