ChemComm

Very high titanium content mesoporous silicas

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Received (in Cambridge, UK) 1st November 2000, Accepted 18th December 2000
First published as an Advance Article on the web 5th February 2001

Titanium content in mesoporous titanosilicate catalysts has been modulated up to a minimum Si/Ti value of 1.9 by using complexing agents able to coordinate both Si and Ti atoms and harmonize the reactivity of the resulting precursors avoiding subsequent phase segregation and leading to chemically very homogeneous materials.

The interest of titanium–silicon mixed oxides in petrochemistry is mainly related to their ability to catalyze olefin epoxidation.[1] Recently, maximum interest was focused, however, on microporous products in which titanium atoms isomorphously replace some of the silicon atoms. Indeed, it was found that zeolites such as TS-1, TS-2 and Ti-β are effective catalysts (although limited to substrates with small molecules) in the oxidation of a variety of organic compounds.[2] Hence, the discovery of the M41S materials opened a new way towards expanding the available pore size. Owing to their large pore-sizes, Ti-substituted MCM-41 materials might be efficient in the oxidation of bulky substrates. In 1994, Corma *et al.*[3] and Tanev *et al.*[4] published the first results on titanium substitution in MCM-41 silicas. Since then a considerable effort has been devoted to this subject.[5]

A major problem concerning the preparation of Si–Ti mixed oxides through sol–gel-derived techniques is to achieve an adequate balance between the hydrolysis and condensation processes affecting the titanium and silicon precursors. Insofar as the catalysts' efficacy substantially depends upon their purity and chemical homogeneity, phase segregation must be avoided.

We report here a new direct and reproducible surfactant-assisted procedure that has allowed us to prepare thermally stable mesoporous titanosilicate molecular sieves in which the Ti content in the framework can be modulated up to a minimum Si/Ti molar ratio value of 1.9. Such a limit value corresponds to a relative Ti content noticeably higher than those previously achieved by using surfactants (Si/Ti = 5.0)[6] or block-copolymers (Si/Ti = 3.9)[7] as supramolecular templates.

The procedure is based on the use of a cationic surfactant (CTAB = cetyltrimethylammonium bromide) as structural directing agent, and a complexing polyalcohol (2,2′,2″-nitrile-triethanol, hereinafter TEAH3) as the hydrolysis retarding agent for Ti species.[8] In a typical synthesis leading to the Si/Ti = 1.9 mesoporous solid, 0.80 g of NaOH (0.02 mol) were dissolved in a TEAH3 (21.55 mL, 0.1624 mol) solution containing 0.0126 mol and 0.051 mol of the titanatrane and the silatrane derivatives of TEAH3 (*e.g.* in the form of $[M(TEA)Cl]_2$ or M(TEA)OR (M = Si, Ti), R being an alkyl chain and TEA meaning the fully deprotonated ligand),[9] respectively, and 0.0116 mol of CTAB. Then, 155 mL of water were slowly added with vigorous stirring. A pale yellow suspension was formed after aging the mixture at 25 °C for 24 h. The resulting mesostructured powder was then collected by filtration, washed with water and ethanol, and air-dried. To obtain the final mesoporous material, the as-synthesized solid was calcined at 500 °C for 5 h under a static air atmosphere. The main synthetic variables and analytical data are summarized in Table 1. All samples were analyzed and characterized by electron probe microanalysis (EPMA, Philips SEM-515), XRD techniques (Seifert 3000TT diffractometer using CuKα radiation), TEM (Philips CM10 electron microscope), UV–Vis diffuse reflectance spectroscopy (Perkin-Elmer Lambda 9), IR spectroscopy (FTIR Perkin-Elmer 1750), and N_2 adsorption–desorption isotherms (Micromeritics ASAP2010).

Our synthesis strategy has been designed to avoid problems due to the great reactivity differences between the usual Ti and Si precursor species (such as alkoxides). Indeed, atrane complexes (*i.e.* complexes which include TEA-like species as ligands) are, in general, unstable but relatively inert towards hydrolysis. In practice, we have observed (Fast Atomic Bombardment coupled with Mass Spectrometry) that, once formed in the absence of water, both titanatrane and silatrane complexes do not react easily with water. In anhydrous solution, the majority species are the complexes $M(TEA)_2H_2$ and $MNa(TEA)_2H_2^+$ (M = Si or Ti). After water addition, both Si and Ti atrane complexes strikingly remain in solution in the majority form of the M(TEA)OH species. In this context, the most outstanding feature concerning the silatranes' and titanatranes' hydrolytic reactivity (when compared to the respective

Table 1 Selected synthetic, physical and catalytic data for some mesoporous titanosilicate samples

Sample	Si/Ti (precusor)	Si/Ti[a]	d_{100}/Å	BJH pore/Å	S_{BET}/m^2 g^{-1}	IR[b]	C_{ox}(%)[c]	Select.(%)[d]
1	∞	∞	37.5	25.6	1118	2.1	—	—
2	50.0	49.9(3)	40.0	28.0	1110	2.3	97	98
3	32.3	34.9(4)	41.8	28.5	1093	2.5	97	97
4	17.0	19.0(4)	41.2	26.5	959	3.0	—	—
5	10.0	8.3(3)	40.0	25.1	958	3.0	90	83
6	5.0	3.2(3)	38.6	22.0	725	3.0	44	68
7	4.0	1.9(3)	34.5	20.0	595	3.0	—	—

[a] Values averaged from EPMA of *ca.* 50 different particles (statistical esds in parenthesis). [b] Intensity ratio between the 960 and 800 cm^{-1} infrared bands. [c] Oxidant conversion. [d] Selectivity in cyclohexene epoxide.

DOI: 10.1039/b008810m

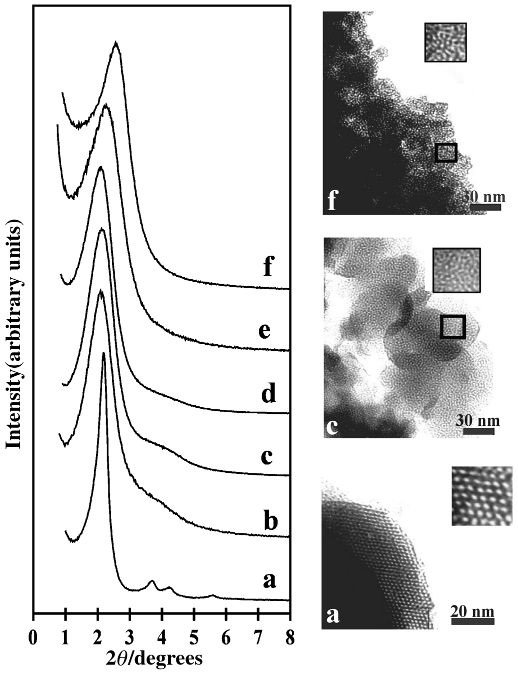

Fig. 1 XRD powder patterns of mesoporous titanosilicates and some selected TEM images: (a) sample 2; (b) sample 3; (c) sample 4; (d) sample 5; (e) sample 6; (f) sample 7.

alkoxides) is that silatranes are more labile than, for example, TEOS, whereas the contrary occurs in the case of titanatranes. Hence, the role of TEAH3, which acts in practice as a hydrolysis retarding agent for Ti species, is the key to achieve an adequate balance between the hydrolysis and subsequent condensation reactions affecting the precursors.

EPMA analysis shows that all the samples are chemically homogeneous (spot area *ca.* 1 μm) with a regular distribution of titanium and silicon atoms. Hence, the solids can be considered as monophasic products, and segregation of TiO_2 can be discarded. This is consistent with the absence of rutile or anatase peaks in the XRD patterns.

Selected low-angle XRD patterns of mesoporous samples are shown in Fig. 1. All solids show diffraction patterns with at least one strong reflection at low 2θ values, which is typical in mesoporous materials. Apart from this intense peak [associated with the (100) reflection if a hexagonal cell is assumed], in the patterns of solids whose titanium content is lower than that defined by the Si/Ti = 49.9 molar ratio, we can observe three other resolved small reflections [(110), (220) and (210)], which are characteristic of highly ordered hexagonal pore systems. Such an evolution indicates that incorporation of Ti in the silica-based hexagonal mesoporous framework (whatever its coordination may be) implies a progressive lowering of order in the pore array. TEM micrographs fully correlate to XRD observations. On the other hand, all materials give typical reversible type IV isotherms with one well defined step in their N_2 adsorption–desorption curves. Incorporation of Ti leads to a slight decrease of the BET surface area. This notwithstanding, high surface area values and unimodal pore distribution are retained even for the highest Ti contents.

Isomorphous substitution of Ti for Si in the framework has been confirmed by UV–Vis and IR spectroscopies. Thus, the UV–Vis spectra (Fig. 2) corresponding to samples with Si/Ti $\geqslant$ 34.9 show an absorption band at *ca.* 220 nm together with a small shoulder in the range 250–275 nm. In contrast, the spectra corresponding to samples with Si/Ti $\leqslant$ 19.0 present an additional band at *ca.* 300 nm whose intensity increases as the titanium content does. These results indicate that nearly all Ti occupies tetrahedral sites in the skeletal net until the Si/Ti = 34.9 molar ratio is reached.[10] Also for samples with Si/Ti $\leqslant$ 19.0, the presence of both tetrahedrally and octahedrally coordinated Ti atoms becomes evident. Nevertheless, even in this last case, the band at 220 nm remains as an intense signal in the UV–Vis spectra. This observation suggests that tetrahedral Ti environments are relevant even for very high titanium contents, although five- and six-coordinated Ti local environments (in the form of small clusters) could be involved in the titanosilicate walls.[11] On the other hand, the IR spectra of all the samples display one band at 960 cm^{-1} that can be assigned to the stretching mode of SiO_4 entities bonded to Ti atoms.[11] Moreover, the intensity ratio (see Table 1) between the bands at 960 and 800 cm^{-1} (SiO_4 symmetric stretching) increases with the titanium content, which is usually taken as proof of isomorphous substitution of Ti for Si.[10]

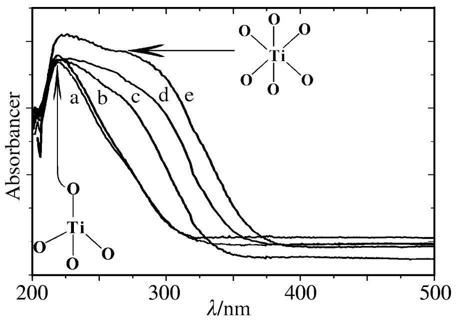

Fig. 2 Diffuse reflectance UV–Visible spectra of mesoporous titanosilicates: (a) sample 2; (b) sample 3; (c) sample 4; (d) sample 5; (e) sample 7.

The catalytic activity of these solids in the epoxidation of cyclohexene with TBHP (*tert*-butyl hydroperoxide) was tested in a stirred glass flask (at 343 K) by mixing 28.15 mmol of cyclohexene with 7.03 mmol of TBPH and 300 mg of catalyst. The results obtained after 3 h of reaction are summarized in Table 1. Such preliminary results seem to represent a significant performance improvement with respect to previous reports based on the use of mesoporous silica,[11] and are comparable to those provided by organo-silica-containing Ti-MCM-41 catalysts.[12] The maximum catalytic activity is maintained in the compositional range 34.9 $\leqslant$ Si/Ti $\leqslant$ 49.9, that is to say the range along which the number of tetrahedral Ti-sites is the highest. The increment in the Ti content implies a slow reduction both in conversion and selectivity related to both the proximity among the active Ti-sites and the growth of small nanodomains of TiO_2-like clusters.

In short, our results demonstrate that by using kinetically inert atrane molecular precursors it is possible to introduce catalytically active Ti-sites into mesoporous silicas. We consider that the atrane route can be extended to the preparation of a diversity of materials of catalytic interest[13]

This research was supported by DGES under grants PB98-1424-C02-01 and MAT2000-1387-C02-01. S. C. and J. E. H. thank the A.E.C.I. for doctoral grants.

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