Improving epoxide production using Ti-UVM-7 porous nanosized catalysts†

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**Nanosized Ti-UVM-7 materials with a hierarchical system of
pores at two different length scales have been prepared through
a one-pot procedure by using a simple template agent; the cata-
lytic activity and selectivity of the resulting materials in bulky
olefin epoxidation by organic peroxides are the highest reported
to date.**

Both academic and industrial researchers are showing increas-
ing interest in titanium containing porous silicas because of
their catalytic properties. Indeed, microporous zeolites like
TS-2 and Ti-β,[1] in which titanium atoms isomorphously
replace some of the silicon atoms, were found to be effective
catalysts in the selective oxidation of a variety of organic com-
pounds (as had been already noticed for the related TS-1
zeolite).[2] Notwithstanding this, the activity of this type of
materials (with medium pore size) is limited to substrates with
small molecules. But the research was boosted by the discovery
of the mesoporous M41S and related solids, which, having
large pore sizes, might be efficient in the oxidation of bulky
substrates.[3] Hence, a diversity of materials with variable struc-
tural frameworks (Ti-MCM-41, hexagonal; Ti-MCM-48,
cubic; Ti-HMS, wormhole-like) has been characterised in
recent years.[4] However, when compared to the above-named
zeolites, the activity and selectivity of these mesoporous cata-
lysts are not as high as expected. It has been stated that factors
such as low titanium content (whose dispersion in the silica net
is not always under control), low hydrophobicity, and large
particle size could account for this relatively poor behaviour.[5]

We report here on Ti-UVM-7, new titanium–silicon mixed
oxides having bimodal pore systems (mesoporous–large meso-
porous or mesoporous–macroporous), which, as set out below,
are found to be very efficient catalysts in olefin epoxidation. Ti-
UVM-7 materials are prepared by a one-pot surfactant-
assisted procedure, which is a modification of the so-called
atrane route.[6] It has been recently applied to the preparation
of bimodal mesoporous silicas, and procedural details are
described elsewhere.[7] Now we show how these bimodal meso-
porous silicas can be modified to admit titanium contents in
the final material as high as 20% (*i.e.* Si/Ti = 5, in atoms),
while maintaining the features of the parent mesophase. This
results in well dispersed titanium centers having high accessi-
bility and, in turn, enhanced catalytic activity.

As shown by the results, our synthesis strategy is particu-
larly efficient in overcoming problems like those which in ref.
5 are associated with the comparatively low catalytic activity
of the titanium-containing mesoporous silicas. In fact, the
use of atrane precursors has proved to be very efficient in har-
monising the hydrolytic reactivity of the Si and Ti source spe-
cies,[6] which favours the chemical homogeneity in the resulting
materials (Ti dispersion; no segregation of TiO_2 crystalline
phases) while facilitating the incorporation of high amounts
of Ti atoms in the catalyst. Whereas EPMA data offer some
support for these considerations, UV-Vis spectroscopy pro-
vides confirmation that substitution of Ti for Si occurs isomor-
phously as well as the dispersion of Ti in the framework.
Indeed, the diffuse reflectance UV-Vis spectra of Ti-UVM-7
calcined samples (Fig. 1) show an intense band at *ca.* 214–
220 nm, which is typically assigned to a ligand to metal charge
transfer involving isolated and tetrahedrally coordinated Ti
atoms.[8] This supports the theory that isolated tetrahedral Ti
environments are the majority catalytic sites even for materials
with high titanium contents (although five and six-coordinated
Ti entities could be present in low proportions).

On the other hand, the comparatively high hydrophobicity
of the Ti-UVM-7 pore walls also contributes to their catalytic
performances.[5] In practice, by using silatrane precursors
(whose hydrolytic processes occur quickly in comparison with
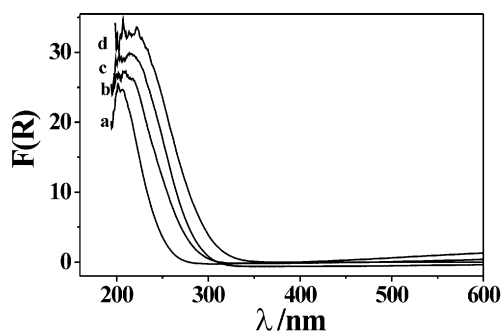
Fig. 1 UV-Vis spectra of (a) sample 1, (b) sample 2, (c) sample 4, (d) sample 6.

† Electronic supplementary information (ESI) available: experimental
details of the catalytic tests and data analysis including $\ln[(\alpha+c)/(\alpha/(1+c))]$ *vs.* *t* plots. See http://www.rsc.org/suppdata/nj/b2/
b205856c/

Table 1 Selected synthetic and physical data for Ti-UVM-7 bimodal porous materials

Sample	Si/Ti[a]	Si/Ti[b] (solid)	d_{100}/ nm	S_{BET}/ m^2 g^{-1}	Small pore size[c] /nm	Large pore size[c] /nm	Small pore volume/cm^3 g^{-1}	Large pore volume/cm^3 g^{-1}	R_0/mol epox. (mol Ti)$^{-1}$ min^{-1}	$k* \times 10^2$/ min^{-1}	$k_2 \times 10^3$/ min^{-1} M^{-1}
1	80	68	4.19	1125	3.16	57.2	1.08	1.53	9.2 ± 0.5	1.85 ± 0.07	3.5
2	60	52	4.20	1075	2.97	66.5	0.98	1.42	25 ± 1	6.60 ± 0.07	12.3
3	50	45	4.01	1077	3.15	62.5	0.97	1.48	11.0 ± 0.5	3.32 ± 0.07	6.20
4	40	32	4.02	1045	3.17	55.1	1.02	1.46			
5	30	26	4.10	1094	2.85	55.0	0.95	1.38			
6	10	5	4.13	1070	2.83	70.0	0.85	1.01			

[a] Starting mixture. [b] Values averaged from EPMA of *ca.* 50 particle agglomerates. [c] BJH pore sizes estimated from the isotherms adsorption branch.
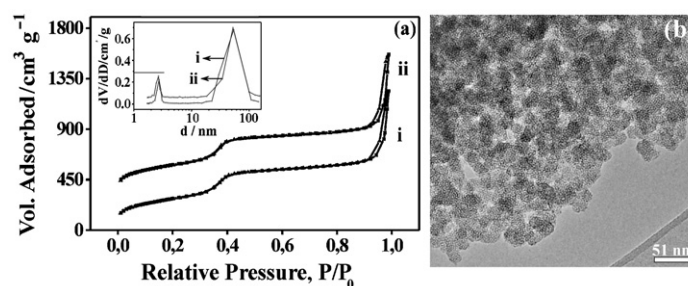
Fig. 2 (a) N$_2$ adsorption–desorption isotherms (i and ii curves are shifted for clarity) of (i) sample 4, (ii) sample 2. In the inset are represented the pore size distributions from the desorption branches. (b) Representative TEM image of Ti-UVM-7 materials (sample 2).

those characteristic of TEOS),[6] we favour a high polymerization degree in the resulting silica network. In effect, ^{29}Si NMR results show that there is a very low proportion of Q^3 silicon environments in the net (Q^3/Q^4 = 0.25). In this way, the modified atrane procedure allow us to directly obtain Ti-UVM-7 hydrophobic catalysts without need for silylation or related post-treatments of the surface.[9]

Finally, the high site accessibility in Ti-UVM-7 catalysts should correlate to the characteristics of their pore systems. In accordance with N$_2$ adsorption–desorption experiments, these materials really include bimodal pore systems with very high pore volumes (see Table 1). In fact, the N$_2$ adsorption–desorption isotherms (Fig. 2a) show, in all cases, two well-defined steps. The first one, characteristic of MCM-41 like solids, must be generated by the template effect of the surfactant. The second, at a high relative pressure, corresponds to the filling of the large pores. In practice, the nature of these pore systems can be understood with the help of XRD and TEM results. As can be observed (Fig. 2b), these catalysts consist of micro-agglomerates (*ca.* 5 μm) of soldered primary mesoporous nanoparticles, which generate a non-ordered system of large pores (on the border between meso- and macro-pores). Hence, this new nanosized nature is the fingerprint of Ti-UVM-7 catalysts.

The catalytic activity of these materials was measured in the epoxidation reaction of cyclohexene (CE) with *tert*-butylhydroperoxide (TBHP) at 60 °C. In a typical experiment, 150 mg of solid catalyst, 59.2 mmol of CE and 13.8 mmol of TBHP were magnetically stirred under atmospheric pressure. Aliquots of 1 μL were monitored for CE and epoxide by gas chromatography (HP6890). The results shown in Fig. 3 clearly indicate that catalyst activity and selectivity increase with increasing Ti content, reaching a maximum for the Si/Ti = 52 molar ratio, and then decreasing. Adherence to the integrated second-order rate equation $\ln[(\alpha + c)/(\alpha/(1 + c))] = k*(t - t_0) = k_2cr$ [BuOOH]$_0(t - t_0)$,[10]‡ is apparent

in all reactions; the rate constant $k*$ is obtained directly from the linear plots $\ln[(\alpha + c)/(\alpha/(1 + c))]$ *vs. t*. The catalyst activities, $R_0 = k*$ $n_{CE}/(n_{CE}/n_{t\text{-BuOOH}} - r)/n_{Ti}$ (where n_{CE}, $n_{t\text{-BuOOH}}$ and n_{Ti} are the initial mol numbers of CE, TBHP and Ti, respectively) are shown in Table 1.

The value of $R_0 = 25 \pm 1$ mol (epoxide)/(mol (Ti) × min) means that the Ti-UVM-7 material containing a Si/Ti molar ratio of 52 has the greatest potential as an epoxidation catalyst
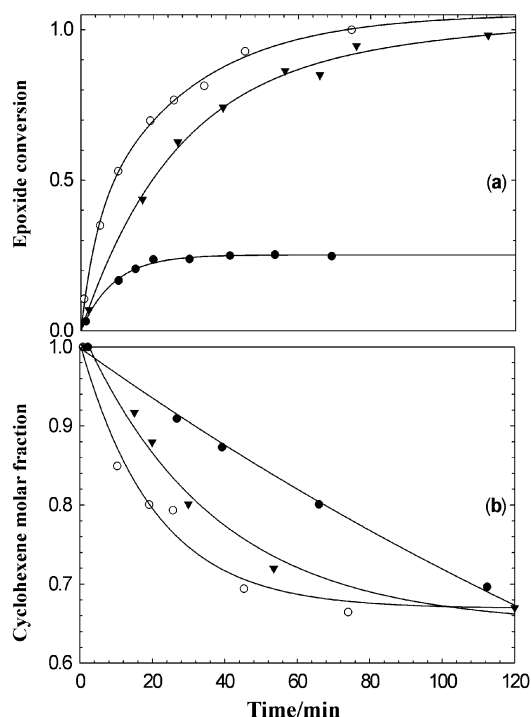
Fig. 3 Concentration *vs.* time curves for (a) epoxide, and (b) cyclohexene for catalysts with different Ti contents: (○) [Ti] = 3.12 × 10^{-4} (sample 2), (▼) [Ti] = 3.59 × 10^{-4} (sample 3), (●) [Ti] = 2.40 × 10^{-4} (sample 1) mol (g of catalyst)$^{-1}$.

‡ Where $r = 1$, the CE:TBHP stoichiometric coefficient ratio, $c = r^{-1} \times$ [CE]$_0$/[TBHP]$_0 - 1$, and k_2 is the second-order rate constant of the epoxidation reaction.

when TBHP is used as the oxidant, the selectivity to the epoxide being close to 100% at a level of conversion of 100%. Such results are the best ever reported using Ti-based catalysts for epoxidation processes.[9,11] Moreover, as mentioned above, this excellent performance is achieved without any need for post-synthesis surface modifications to improve the hydrophobic surface character, which simplifies the catalyst preparation.

In short, factors such as a good dispersion of Ti atoms, controlled Ti environment geometry, low concentration of silanol groups (*i.e.* relatively high hydrophobicity of the surface), and, especially, the high site accessibility due to the nanometric pore length, are responsible for the noteworthy catalytic improvement achieved with Ti-UVM-7 catalysts. Very likely, the synthesis strategy here presented might be extended to the preparation of a diversity of materials of catalytic interest.

Experimental

In a typical synthesis leading to the Ti-UVM-7 sample 3 (see Table 1), 4.23 g of CTMABr (CTMABr = cetyltrimethyl-ammonium bromide) were added at $60\,^{\circ}C$ to a solution containing 23 mL of 2,2′,2″-nitrilotriethanol (hereinafter TEAH3) and 0.045 and 0.0009 mol of the silatrane and titanatrane derivatives of TEAH3, respectively (*e.g.* in the form of M(TEA)(-TEAH$_2$), M = Si or Ti, and TEA meaning the fully deprotonated ligand).[6] Then, 180 mL of water were slowly added with vigorous stirring at $50\,^{\circ}C$. A white suspension resulted. This mixture was aged at room temperature for 2 h. The resulting powder was collected by filtration, washed with water and ethanol, and air-dried. To prepare the final porous material, the as-synthesised solid was calcined at $500\,^{\circ}C$ for 5 h. Summarised in Table 1 are the main synthesis variables and physical data. In all cases, the molar ratio of the reagents in the mother solution was adjusted to 2 Si:x Ti:7 TEAH3:0.52 CTAMBr:180 H$_2$O.

All samples were characterised by electron probe microanalysis (EPMA, Philips SEM-515), XRD techniques (Seifert 3000TT diffractometer using CuK$_\alpha$radiation), TEM (Hitachi H9000NAR microscope operating at 300 kV), UV-Vis diffuse reflectance spectroscopy (UV-250 1 PC Shimadzu instrument), ^{29}Si MAS NMR (Varian Unity-300 spectrometer tuned at 59.59 MHz) and N$_2$ adsorption–desorption isotherms (Micromeritics ASAP2010 analyzer).

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