One step synthesis of highly active and selective epoxidation catalysts formed by organic–inorganic Ti containing mesoporous composites

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Ti-MCM-41 materials with methylated silicons have been prepared in one step synthesis; the resultant organic–inorganic composites are highly stable and present the highest activity and selectivity ever reported on Ti containing mesoporous catalysts for the epoxidation of olefins using organic peroxides.

The synthesis of molecular sieve mesoporous materials[1] have expanded the possibilities of zeolites and zeotypes, opening new possibilities in the fields of adsorption and catalysis.[2] Postsynthesis treatments devoted to prepared inorganic–organic composites have been carried out by silylating MCM-41 and MCM-48 materials, and in this way their stability, adsorption and catalytic properties have been improved.[3–7] Following the methodology used in sol–gel chemistry to functionalize amorphous silica, organically functionalized mesoporous silicas have been prepared by the co-condensation of tetraethoxysilane and organoalkoxysilanes in the presence of surfactant templates.[8] This method has been successfully extended to the introduction of thiol, amine, epoxide, imidazole and alkyl functionalities.[9] Taking this into account, and the fact that titanium containing molecular sieves increase their activity and selectivity by a postsynthesis silylation,[5,10] prompted us to prepare by direct synthesis, in one step, organic–inorganic self-assembled Ti-MCM-41 materials. Here, we will show that the process is successful, resulting in epoxidation catalysts much more active and selective than any similar materials reported up to now.

The synthesis of organo-silica containing Ti-MCM-41 materials were carried out with gels having the following molar compositions: $(1 - x)$ $Si(OCH_3)_4 : x\ CH_3Si(OCH_2CH_3)_3 : 0.26$ TMAOH : 0.15 CTABr : 24.3 $H_2O : y\ Ti(OCH_2CH_3)_4$ where x was varied from 0.15 to 0.35 and y between 0.0166 and 0.0075 (Table 1). Crystallisation was performed at 135 °C for 24 h in Teflon lined stainsteel autoclaves. The final solids were recovered by filtration, washed with water and dried at 60 °C, overnight. The occluded surfactant was removed by a two step extraction procedure. First, the solid was refluxed in a solution of 0.05 M H_2SO_4 in ethanol for 1 h. Then, the remaining occluded surfactant was extracted by refluxing the solid in a 0.15 M solution of HNO_3 in heptane–ethanol (52 : 48) over 24 h. In both steps, a liquid/solid ratio of 50 was used.

The materials before and after surfactant extraction were characterized by XRD, ^{29}Si MAS NMR, UV–VIS, IR spectroscopies and elemental analysis. The catalytic epoxidation of cyclohexene with *tert*-butylhydroperoxide (TBHP) on the Ti organosilica containing MCM-41 catalysts was carried out at 60 °C using an olefin/TBHP molar ratio of 4 and a liquid/catalyst ratio fixed at 20 (m/m). Aliquots of the reaction mixture were withdrawn at different reaction times and analysed by GC.

$Si(OCH_3)_4$ (TMOS) was chosen as the silica source because the structural order of the organo-silica MCM-41 samples obtained by using this precursor is superior to those of samples obtained using $Si(OEt)_4$ (TEOS).

The XRD patterns of samples prepared in the presence of different concentrations of $MeSi(OEt)_3$ (MTEOS) shown in Fig. 1, indicate that there is a limit for the incorporation of organosilica entities in the MCM-41 structure. It was found that the maximum MTEOS/Si ratio, for which a well ordered material is obtained, occurs at a value at 0.35.

Elemental analysis of the samples (Table 1) indicates that the C/N ratio is always > 19, which is the expected value if only CTA^+ filled the pores, and consequently this is an indication that CH_3Si groups are also incorporated into the MCM-41 structure. This assumption has been further established by ^{29}Si MAS NMR and IR spectroscopy. The ^{29}Si MAS NMR spectra of the methyl containing Ti-MCM-41 materials show four signals centred at −110, −100, −90, −65 and −55 ppm that can be assigned, respectively, to $Si(OSi)_4$ [Q_4], $HOSi(OSi)_3$ [Q_3], $(HO)_2Si(OSi)_2$ [Q_2], $MeSi(OSi)_3$ [MQ_3] and $MeHOSi(OSi)_2$ [MQ_2] environments around silicon.[11] The integrated intensity of $MQ_2 + MQ_3$ signals increases as the MTEOS concentration is increased in the synthesis gel, indicating that there is correspondence between the MTEOS concentration in the gel and the incorporation of CH_3Si groups in the final organosilica material. The presence and stability of CH_3Si

Table 1 Synthesis gel compositions for preparing methyl-tethered-Ti-MCM-41 in a single step synthesis

	Synthesis gel			Elemental analysis (wt.%)		
	Silica source					
Sample	TMOS	MTEOS	Ti/Si	C	N	C/N
1	1[a]	0	0.0075	33.28	2.29	16.95
2	0.75[a]	0.25	0.0075	33.78	2.07	19.04
3	0.85	0.15	0.0075	33.84	1.95	20.25
4	0.75	0.25	0.0075	34.33	1.98	20.23
5	0.65	0.35	0.0075	33.14	1.87	21.16
6	0.5	0.5	0.0075	—	—	—
7	0.75	0.25	0.0111	33.91	2.04	19.39
8	0.75	0.25	0.0166	33.84	1.95	20.25

[a] TEOS.

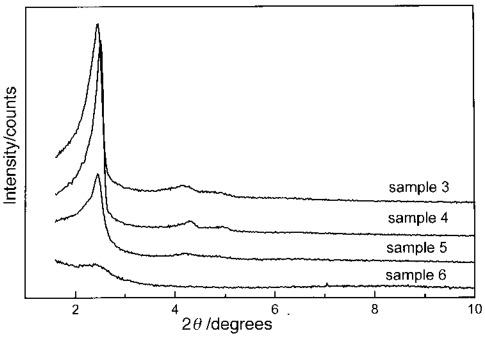

Fig. 1 XRD patterns showing the influence of the concentration of $MeSi(OEt)_3$ on the structural order of the methyl containing Ti-MCM-41 catalysts

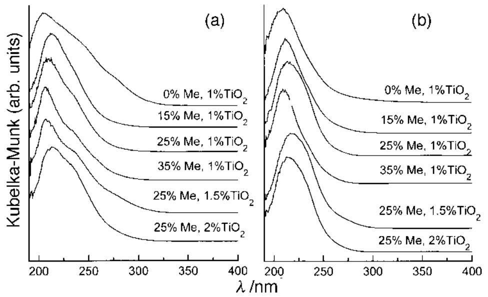

Fig. 2 UV–VIS DRS spectra of the methyl containing Ti-MCM-41 materials of as prepared (b) and extracted (b) samples

groups have been also studied by IR spectroscopy. The IR spectra of the sample heated under vacuum at different temperatures, show bands at 2974 and 1411 cm^{-1}, that can be assigned to methyl groups directly linked to silicon,[12] while, bands appearing at 2956, 2927 and 1464 cm^{-1} can be assigned to the CTA^+ cations located within the pores of the MCM-41 structure.[3] It is observed that the bands attributed to CTA^+ cations decrease in intensity with increased temperature, while bands assigned to methyl groups directly bonded to the silica wall remain nearly unchanged up to temperatures as high as 700 °C, indicating that the Si–C bond in the MCM-41 structure is highly stable to heat.

The UV–VIS spectra of the Ti containing inorganic–organic mesoporous silica materials for the as-prepared and extracted materials containing different methyl group concentrations on the silica walls are shown in Fig. 2(*a*) and (*b*), respectively where a narrow band centred at 220 nm, is taken as proof of Ti incorporation into the silica wall.[14,15] Also, when the UV–VIS spectra of the extracted samples is compared with those of the as-prepared samples, it was found that the 220 nm band is even narrower in the extracted samples than in the as-prepared materials. This indicates that Ti is located in a more distorted tetrahedral environment when the surfactant fills the pores of the MCM-41 structure, similarly to Ti-MCM-41 without any Si–C bonds.

The UV–VIS spectra for samples containing different amounts of Ti [Fig. 2(a) and (b)] in the synthesis gel showed that the 220 nm band becomes broader and a shoulder at 240 nm appears when the Ti content increases. However, after extraction all the samples show a very similar UV–VIS spectra, indicating that during extraction the tetrahedral coordination around the Ti centers becomes more regular.

The catalytic activity of the methyl containing samples for the epoxidation of cyclohexene pass through a maximum when *ca*. 25% of the silicon atoms are methylated. However, the selectivity to the epoxide decreases with increased methyl content, while the efficiency of TBHP increases with level of organic groups on the silica wall [Fig. 3(*a*)–(*c*)].

The production of epoxide calculated after 30 min of reaction was 10.6 mol min^{-1} (mol Ti)$^{-1}$ which gives an initial reaction rate, assuming a pseudo-first order reaction, of 21 mol min^{-1} (mol Ti)$^{-1}$ with a selectivity of 94% to the epoxide at a level of conversion of 98%. These results are, so far, the best ever obtained on Ti-MCM-41 incorporating Ti either by direct synthesis[16] or by anchoring titanocene[17] [0.4 and 2.1 mol min^{-1} (mol Ti)$^{-1}$ respectively], and they are much better than those obtained on titanium–silica cogels[18] [4.7 mol min^{-1} (mol Ti)$^{-1}$].

The inorganic–organic Ti-MCM-41 is highly stable in the presence of water and it represents one step forward in the preparation of epoxidation catalysts.

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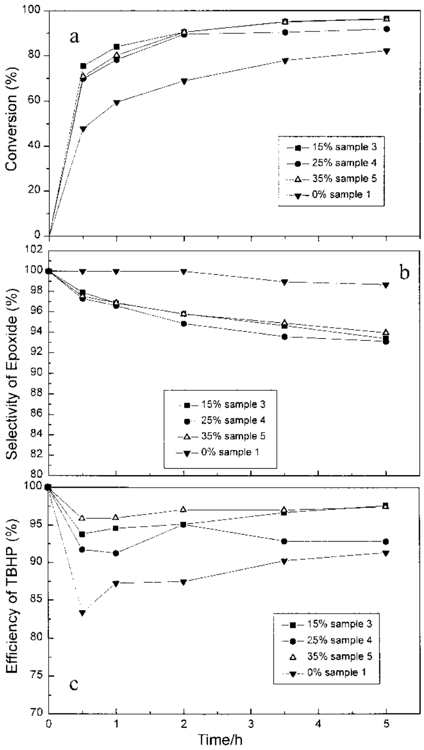

Fig. 3 Influence on the catalytic performance of the methyl concentration on the surface of the methyl containing Ti-MCM-41 catalysts; (a) catalytic activity, (b) selectivity to the epoxide and (c) efficiency of TBHP. *Reaction conditions*: 56.3 mmol of cyclohexene, 14.0 mmol TBHP, reaction temperature = 333 K and 0.3 g catalyst.

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