



Microwave oxidation of alkenes and alcohols using highly active and stable mesoporous organotitanium silicates

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ABSTRACT

Mesoporous organically modified Ti-MCM-41 materials were synthesized employing different Ti precursors. Materials were found to possess improved properties in terms of stability, hydrophobicity and activity compared to the parent Ti-MCM-41, preserving their mesoporous structural order. The organically modified mesoporous materials were found to be very active and selective in the oxidation of various substrates including alcohols and alkenes under microwave irradiation using hydrogen peroxide. The materials were also highly stable and reusable up to four times preserving over 90% of their initial activity. The high activity and stability of the solids can be attributed to the higher Ti loading compared to the parent material as well as to an increase in hydrophobicity due to the organic functionalisation.

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1. Introduction

High surface areas and/or high active phase dispersions as well as fast mass transfer of the reactants and products to and from the catalytic sites are desirable materials properties. Materials designated as mesoporous molecular sieves have introduced a new degree of freedom in the conception of catalyst. They have monodispersed pore diameters in the mesopore range (2–50 nm), high surface areas and a stereoregular arrangement of these channels which mimics the liquid crystals formed by the surfactants used in their preparation [1,2]. Of particular interest are the materials that belong to the M41S family including MCM-41 and MCM-48 [3,4].

All siliceous mesoporous materials have a very limited range of applications due to the low acidity of the silanol groups on the surface. Nevertheless, the mesostructure pore lattice yields a clear advantage by providing enough space for the insertion of bulky active complexes. Many materials have been prepared using different possibilities of inclusion chemistry to introduce catalytically active species mesoporous silica guest materials. These include co-condensation of active species during the MMS synthesis or post-synthesis methods including ion exchange, impregnation, adsorption, grafting of reactive metal complexes, deposition of clusters or layers of metal oxides and grafting of silanes [1,2]. The

substitution of silica by different atoms in the inorganic framework of mesoporous molecular sieves has also been the subject of extensive studies, being Ti one of the major heteroatoms introduced in these mesoporous materials [5–10]. The introduction of Ti as heteroatom in the mesoporous M41S structure rendered materials with interesting oxidation properties [11–14].

On the other hand, the oxidation of primary and secondary alcohols to carbonyl compounds (corresponding aldehydes and ketones) is one of the simplest and most useful transformations in organic chemistry that is at the core of many synthetic routes due to the versatility of the carbonyl group as building block. These essential reactions have attracted the attention of considerable fundamental and applied research since the beginning of organic chemistry as a science [15–19].

However, in spite of this intensive research effort, alcohol oxidation processes are still far from being ideal from the environmental point of view and require more improvement. In particular, the oxidation of benzyl alcohol to benzaldehyde is an important organic transformation. Benzaldehyde is a very valuable chemical which has widespread applications in perfumery, dyestuff and agro chemical industries [20,21].

The selective and efficient epoxidation processes to obtain epoxides has also become very important, since the epoxides are versatile intermediates in the organic synthesis of fine chemical and pharmaceuticals.

Traditional methods based on the use of a stoichiometric amount of reagents, mainly heavy metal salts in high oxidation

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state (oxidation of alcohols) and peracids (oxidation of alkenes), are useful tools for laboratory scale preparation, but in industrial applications where serious problems related to the disposal of undesired by-product represent a strong drawback. Hence, the preparation of such intermediates using a safer and cleaner oxidising agent and a more active/selective, easily separable and reusable catalyst is of great practical importance [22,23].

Greener oxidation reagents including air and hydrogen peroxide are cheap and clean reagents suitable for bulk scale oxidation. The oxidation of various alcohols, including benzyl alcohol, has been investigated employing various Ti-MCM materials as catalysts [13,18,24,25]. However, Ti-M41S materials show very low catalytic activity compared to TS-1, Ti-beta and related zeolites due to the presence of a large number of silanol groups that promote the adsorption of the water produced as by-product in the reaction thus poisoning the catalytically active centres [14,26]. An increase in the hydrophobicity of Ti-M41S after functionalisation with organic moieties was reported to have a remarkable effect in the catalytic activity of such mesoporous materials in the oxidation of alkenes, alkanes and alcohols [16,27–31].

In this communication, we report the catalytic performance of Ti-organically modified Ti-MCM-41 materials in the oxidation of various alcohols and alkenes under microwave irradiation.

2. Experimental

2.1. Materials synthesis and methods

Ti-MCM-41 materials were synthesized as previously reported [32]. A Ti-MCM-41 material with a Si/Ti=20 ratio was prepared. The post-synthesis procedures involved the grafting of different titanium precursors on the Ti-MCM-41, including tita-

nium(IV) isopropoxide (Ti-Is), butoxide (Ti-B), *tert*-butoxide (Ti-tB), 2-ethylhexyl oxide (Ti-H) and 2-ethyl-1,3-hexanediolate (Ti-D) (Scheme 1). The preparation of the organically modified materials was carried out as follows: 2.5 g Ti-MCM-41 were placed in a round bottom flask with 20–25 mL isopropanol and then the exact quantity of the titanium precursor was added to the solution to obtain the desired Si/Ti 10 ratio. The mixture was then heated at 90–95 °C in a rotary evaporator for 2–3 h and the solid obtained was dried overnight in the oven at 50 °C.

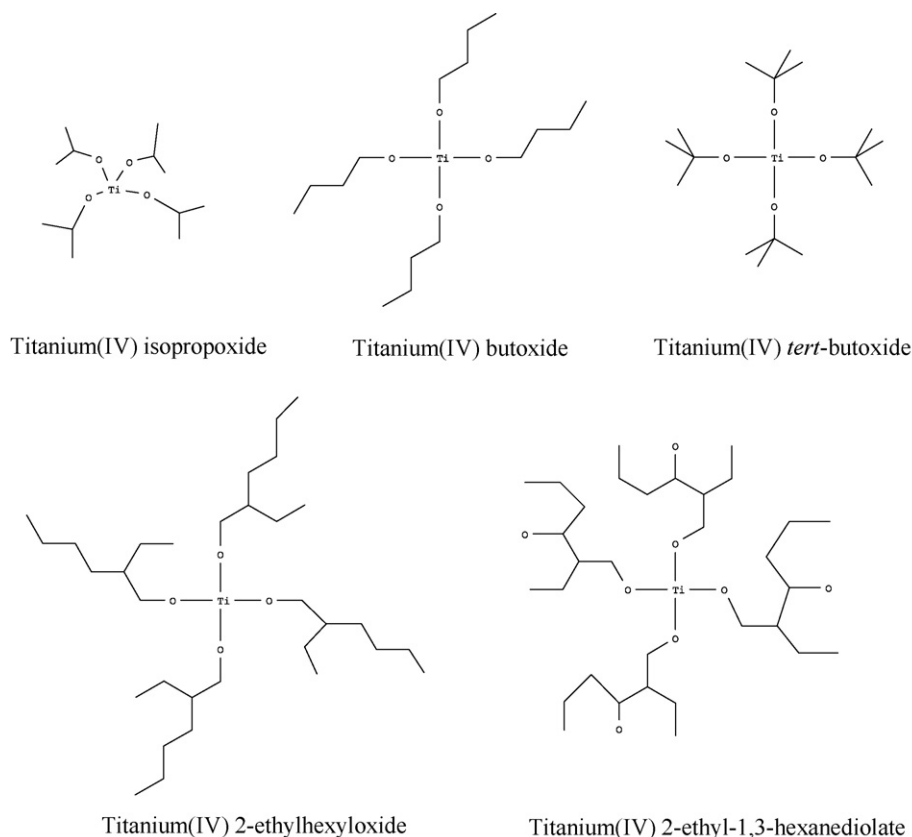
2.2. Materials characterisation

Powder X-ray diffraction patterns (XRD) were recorded on a Bruker AXS diffractometer with Cu K α ($\lambda = 1.5418 \text{ \AA}$), over a 2θ range from 1° to 10°, using a step size of 0.1° and a counting time per step of 4 s. High-resolution patterns were obtained using a step size of 0.01° and a counting time per step of 20 s.

Nitrogen adsorption measurements were carried out at 77 K using an ASAP 2010 volumetric adsorption analyzer from Micromeritics. The samples were outgassed for 2 h at 100 °C under vacuum ($p < 10^{-2} \text{ Pa}$) and subsequently analyzed. The linear part of the BET equation (relative pressure between 0.05 and 0.22) was used for the determination of the specific surface area. The pore size distribution was calculated from the adsorption branch of the N₂ physisorption isotherms and the Barret–Joyner–Halenda (BJH) formula. The cumulative mesopore volume V_{BJH} was obtained from the PSD curve.

The diffuse reflectance UV–vis spectra were recorded with an UV–vis Jasco V550 Diffuse Reflectance Spectrophotometer in the 200–800 nm range using Si-MCM-41 as a reference.

Microwave experiments were carried out in a CEM-DISCOVER model with PC control and monitored by sampling aliquots of



Scheme 1. Structures of the different organotitanium precursors.

reaction mixture that were subsequently analyzed by GC/GC–MS using an Agilent 6890N GC model equipped with a 7683B series autosampler fitted with a DB-5 capillary column and an FID detector. Experiments were conducted on a closed vessel (pressure controlled) under continuous stirring. The microwave method was generally power controlled. The samples were irradiated with the maximum power output (300 W) and different temperatures were reached depending on the reaction and/or the catalyst. Reaction products were also identified and confirmed by ^1H NMR using a JEOL 400 spectrometer operating at 400.13 MHz. Chemical shifts were calibrated using the internal SiMe_4 resonance.

A typical catalytic test was performed as follows: 2 mmol 1-buten-3-ol, 4 mmol H_2O_2 , 2 mL acetonitrile and 0.05 g of catalyst were microwaved at 300 W (100–110 °C) for 15 min. Products were analyzed by GC using an Agilent 6890N GC model equipped with a 7683B series auto sampler. The response factors of the main reaction products were determined with respect to the starting materials from GC analysis using known compounds in calibration mixtures of specified compositions.

3. Results and discussion

3.1. Structural and textural properties

XRD patterns of the titanium-grafted materials exhibited the characteristic diffractions of the hexagonal M41S phase (Fig. 1) [3,4]. Grafted materials exhibited a slight decrease in intensity of the main diffraction lines but the structural order of the materials was preserved as demonstrated in XRD longer scan patterns (Fig. 1, inset). These results were in good agreement with those reported by Igarashi and Tatsumi et al. in the preparation of similar organically modified Ti-MCM-41 materials [27,30].

Nitrogen adsorption isotherms of the Ti organomodified materials confirmed the structural quality of the grafted Ti-MCM-41 compared to the parent Ti-MCM-41 (Fig. 2). The materials exhibited the characteristic mesoporous type IV profile. At $p/p_0 > 0.2$ the

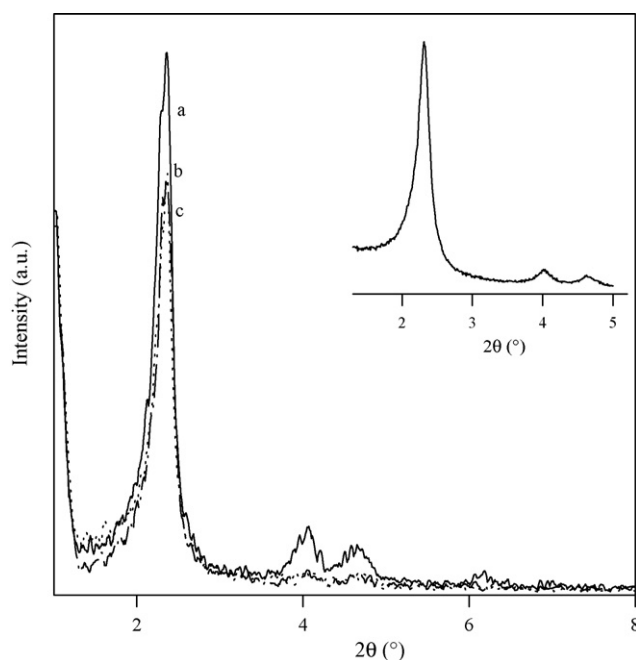


Fig. 1. XRD diffraction patterns of different Ti-MCM-41 materials: (a) Ti-MCM-41; (b) Ti-tB and (c) Ti-D. Inset corresponds to the XRD longer scans pattern of the Ti-D material.

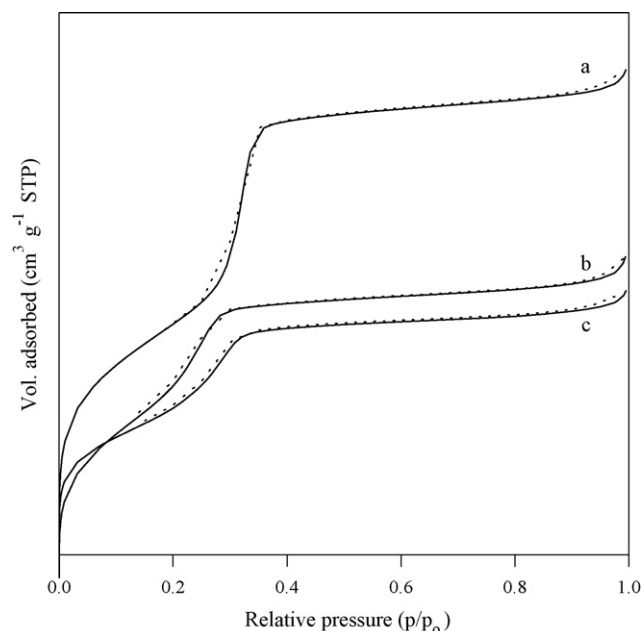


Fig. 2. N_2 physisorption profiles of (a) Ti-MCM-41; (b) Ti-tB; (c) Ti-D; (d) 3rd reused Ti-tB in the oxidation of benzyl alcohol.

isotherms have a sharp inflection characteristic of capillary condensation within the mesopores. The BET surface area (S_{BET}), mesopore diameter (D_{BJH}) and cumulative pore volume (V_{BJH} , in the range 10–400 Å) of the Ti organomodified MCM-41 materials are summarised in Table 1. The BET surface area (S_{BET}), and pore volume decreased for organically modified materials compared to the Ti-MCM-41 as expected. Interestingly, a substantial reduction of both the unit cell parameter (a_0) and the pore diameter were found when increasing the size of the grafted moieties (from Ti-tB to Ti-D) due to the repulsive interaction between organic groups plus the interface or inorganic–organic double layer and pore blockage in the mesoporous materials [33]. The BJH plot gives a remarkably wide pore size distribution depending on the material. Thus, an increase in the size of the grafted titanium group decreased the pore size from 23 Å (parent material) to 14 Å (Ti-D, Scheme 1), where the material starts to be mostly microporous. Consequently, the wall thickness (ϵ) was found to increase as most of these molecules may be grafted on the silanol groups on the walls, increasing the materials hydrophobicity.

UV–vis DRS spectra of the grafted Ti-MCM-41 are shown in Fig. 3. Ti-MCM-41 showed bands at ca. 210, 265 and 305 nm due to isolated titanium in tetrahedral coordination and two presumably different hexacoordinated titanium extraframework environments [34–36]. The grafted materials exhibited more intense bands (Fig. 4, inset) due to the incorporation of the Ti organic species onto the Ti-MCM-

Table 1

Hexagonal unit cell parameter ($a_0 = 2d_{100}/\sqrt{3}$), textural properties [surface area (S_{BET} , $\text{m}^2 \text{g}^{-1}$), mesopore diameter (D_{BJH} , Å), mesopore volume (V_{BJH} , mL g^{-1}) and wall thickness ($a_0 - D_{\text{BJH}}$, ϵ)] of various organomodified mesoporous Ti-MCM-41 materials

Catalyst	d_{100} (Å)	a_0 (Å)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	D_{BJH} (Å)	V_{BJH} ($\text{cm}^3 \text{g}^{-1}$)	ϵ (Å)
Ti-MCM-41	38	44	926	24	0.63	20
Ti-Is	38	43	877	21	0.53	22
Ti-B	38	43	930	19	0.12	24
Ti-tB	38	47	900	20	0.21	32
Ti-H	37	44	741	<18	0.05	^a
Ti-D	35	46	515	<15	0.04	^a

^a The materials were mostly microporous.

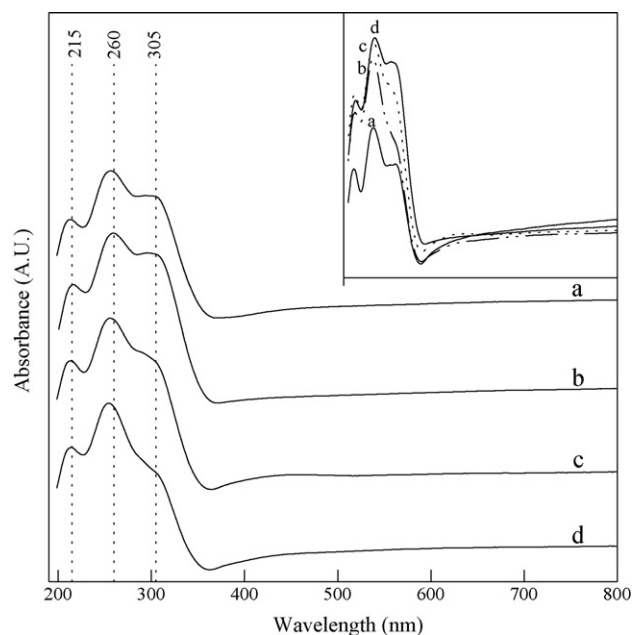


Fig. 3. UV-vis spectra (offset) of various Ti-MCM-41 modified materials: (a) Ti-MCM-41; (b) Ti-tB; (c) Ti-H; (d) Ti-D. The inset (top-right) corresponds to the four different materials in the same scale.

41 support. The main bands were also slightly shifted to lower wavelengths (205 and 260 nm) for the organically modified materials, indicating a change in environment in the structure of the Ti species. In addition, the absence of 330 nm peaks indicated that anatase was not present in significant amounts in our mesoporous Ti-MCM-41 samples [37], in good agreement with Raman results (not shown) that corroborated the absence of anatase crystallites. The presence of anatase would have reduced by decomposition the effective concentration of H_2O_2 in the oxidations [38].

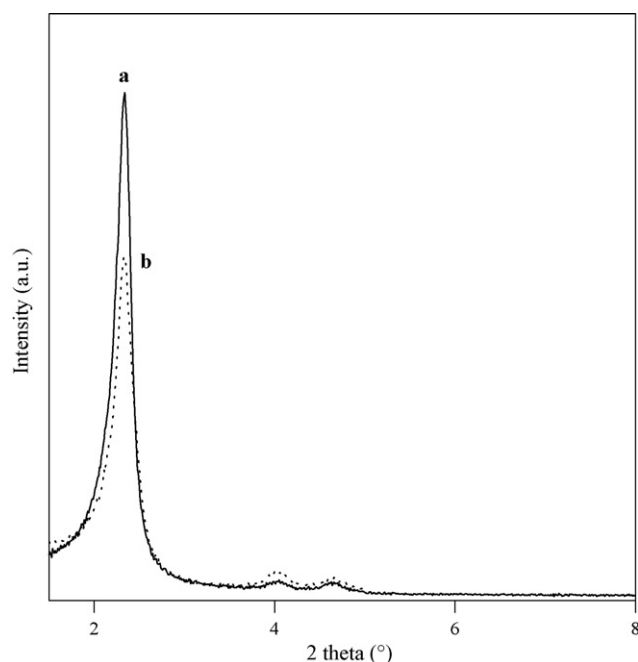


Fig. 4. XRD diffraction patterns of (a) Ti-tB fresh material and (b) Ti-tB reused in the oxidation of limonene (two reuses).

DRIFT spectra of the organically Ti-MCM-41 samples (not shown) exhibited the typical infrared absorption bands of M41S materials [39]. The grafting of the organic moieties on the silanol groups can be observed in the spectra as a decrease in intensity in the Si-OH stretching band (3740 cm^{-1}), as well as by the presence of the typical C-H stretching ($3000\text{--}2850\text{ cm}^{-1}$) and bending ($1350\text{--}1500\text{ cm}^{-1}$) vibrational bands. The decrease in intensity of the silanol bands implies an increase in the hydrophobicity of the surface. The presence of Ti within the samples was confirmed by the presence of a strong absorption band at ca. 960 cm^{-1} arising from the Si-O-Ti stretching vibration [12,16].

3.2. Catalytic activity

3.2.1. Oxidation of alcohols

The oxidation of benzyl alcohol was initially performed under conventional heating (20 mmol benzyl alcohol, 15 mmol H_2O_2 , 0.1 g catalyst, 120°C). Results showed that poor conversions of starting material (<40%) were obtained after 24 h of reaction regardless of the catalyst employed in the reaction. The use of microwaves as novel and cleaner reaction tool has been reported to reduce the reaction times and energy consumption together with an increase in yields and selectivity in some cases [40,41]. Table 2 summarises the main results for the oxidation of benzyl alcohol under microwave irradiation using different Ti-MCM-41 materials. The blank reaction (in the absence or catalyst) gave a very small conversion (<5%) of starting material.

The microwave irradiation protocol afforded moderate to very good conversions of benzyl alcohol with almost complete selectivities to benzaldehyde (Table 2) at remarkably short times of reaction. Organically modified materials performed twice as better as the parent Ti-MCM-41 material without a significant decrease in the selectivity to benzaldehyde (Table 2). Only small quantities of R-epoxymethylbenzene and benzoic acid were found. Of note were the activity trends observed for the grafted Ti-MCM-41. The activity increased with an increase of the size and content of the organic groups, reaching a maximum for the Ti-tB and Ti-H materials (Table 2, entries 4–6). Nevertheless, the activity in the transformation of benzyl alcohol was reduced with bigger organic groups (e.g. Ti-D and Ti-isooctyl not shown owing to its poor activity) due to the less accessible active centres surrounded by organic groups, in good agreement with results reported by Igarashi et al. [30]. Interestingly, the selectivity to benzaldehyde was not significantly affected. The titanium leaching was checked after the reaction. Although Ti-MCM-41 materials were proved to leach (6 ppm Ti were found in the reaction mixture after the reaction as determined by ICP), the organomodified titanium materials were found to be more stable and lower quantities of Ti were present in

Table 2

Catalytic activity [total conversion (X_T , mol%) and selectivity to benzaldehyde (S_{benz} , %) of various Ti organomodified mesoporous materials in the oxidation of benzyl alcohol with H_2O_2 under microwave conditions^a

Entry	Catalyst	X_T (mol%)	S_{benz} ^b (%)
1	Blank	<5	–
2	Ti-MCM-41	40	>99
3	Ti-Is	60	>99
4	Ti-B	67	>99
5	Ti-tB	>95	>95
6	Ti-H	89	>95
7	Ti-D	78	>95

^a 20 mmol benzyl alcohol, 15 mmol H_2O_2 , 0.1 g catalyst, 200 W, 30 min, $130\text{--}140^\circ\text{C}$.

^b The rest to 100 is due to the formation of R-epoxymethylbenzene and benzoic acid.

solution (<2 ppm). These results were similar to those reported by Igarashi et al. [30].

We then tested the mesoporous materials in the oxidation of 1-buten-3-ol. Conventional heating experiments provided very low conversions of starting material (<20%) after 24 h of reaction compared to microwave runs in which relatively good conversions of benzyl alcohol were achieved under similar reaction conditions in a short period of time (15–30 min). Results are summarised in Table 3. Despite its poor activity, the parent Ti-MCM-41 gave a relatively low selectivity to the epoxide, with increasing quantities of the triol obtained at longer reaction times (>70% selectivity after 30 min of reaction) arising from the ring opening of the epoxide. This ring opening can either take place on the weak acid active sites present in the Ti-MCM-41 materials or under acidic conditions. Compared to the parent material, the organically modified mesoporous catalysts provided excellent activities and selectivities to the epoxide. The activity of the materials was not significantly affected by the organotitanium compound grafted onto the mesoporous silicate, with Ti-tB, Ti-H and Ti-D exhibiting a similar activity (Table 3, entries 5–7). This fact suggests the transformation of relatively

Table 3

Catalytic activity [total conversion (X_T , mol%) and selectivity to 1,2-epoxybutan-3-ol (S_{epoxy} , %), 1-buten-3-one 1 (S_{ketone} , %) and 1, 2, 3-butanetriol (S_{triol} , %)] of various Ti-MCM-41 mesoporous materials in the oxidation of 1-buten-3-ol with H_2O_2 under microwave irradiation^a

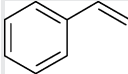
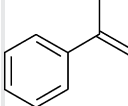
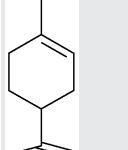
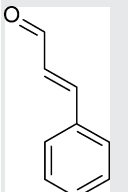
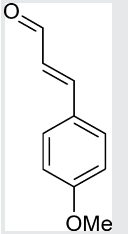
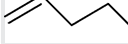
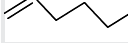
Entry	Catalyst	X_T (mol%)	S_{epoxy} (mol%)	S_{ketone} (mol%)	S_{triol} (mol%)
1	Blank	<10	>99	–	–
2	Ti-MCM-41	26	65	20	15
3	Ti-Is	75	85	15	–
4	Ti-B	85	81	17	2
5	Ti-tB	>99	>90	<10	–
6	Ti-H	86	93	7	–
7	Ti-D	90	>90	<10	–

^a 2 mmol 1-buten-3-ol, 4 mmol H_2O_2 , 2 mL acetonitrile, 0.05 g catalyst, 300 W, 15 min, 100–110 °C (temperature max. 140 °C).

small compounds is not strongly influenced by the modification of the materials (including a reduction in the pore sizes) whereas the reaction of rather bulky compounds including substituted aromatic substrates is restricted in materials with pore constraints.

Table 4

Comparison of the catalytic activity of Ti-tB in the oxidation of various alkenes using conventional heating compared to microwave irradiation

Substrate	Microwave irradiation ^a		Conventional heating ^b	
	X_T (mol%)	S_{epoxide} (mol%)	X_T (mol%)	S_{epoxide} (mol%)
	>99	20 ^c	90	35 ^c
	80	13 ^c	72	<10 ^c
	>99	85	87	>99 ^d
	75	>99	65	>99
	85	>99	62	>99
	>90	>99	40	>99
	90	>99	<35	>99

^a 5 mmol substrate, 6 mmol H_2O_2 , 2 mL acetonitrile, 0.05 g catalyst, 300 W, 30 min, 100–120 °C.

^b 5 mmol substrate, 6 mmol H_2O_2 , 2 mL acetonitrile, 0.05 g catalyst, 24 h, 100 °C.

^c The difference in selectivity to 100 corresponds to benzaldehyde.

^d 1,2-epoxy-limonene was the major product obtained.

Interestingly, only minor quantities of the ketone and traces of the triol were obtained under the reaction conditions using acetonitrile as solvent. We believe shorter times of reaction combined with a potential acetonitrile solvation or neutralisation (of the weak acid sites on the Ti supported materials) effect afforded such improved selectivity to epoxidation, in good agreement with previously reported results [30]. The materials leaching had a similar effect in samples as reported in the previous reaction (4–8 ppm vs. 1–2 ppm leaching for the Ti-MCM-41 and the organically modified materials, respectively).

3.2.2. Oxidation of alkenes

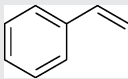
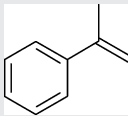
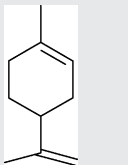
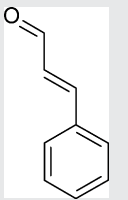
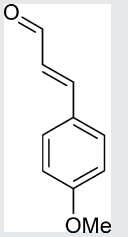
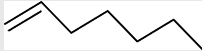

Various substrates were then screened in the oxidation of alkenes with H_2O_2 under microwave irradiation and conventional heating using different Ti-MCM-41. A preliminary screening of the grafted mesoporous titanosilicates in the oxidation of various alkenes showed the Ti-*t*B was the most active material for the oxidation of rather bulky substrates. Data for the oxidation of various aromatic and linear alkenes using Ti-*t*B as catalyst comparing both the microwave and the conventional heating protocols is summarised in Table 4. The use of microwaves reduced times of reaction (from 24+ h to 30 min) as well as increased the conversion of starting material in the oxidation under relatively similar reaction conditions.

A wide range of substrates were successfully oxidised to the respective epoxides in high selectivities under microwave irradiation (Tables 4 and 5, entries 3–7). Interestingly, the oxidation of (α -methyl)styrene gave high selectivities to benzaldehyde and acetophenone, respectively, and only small quantities of the epoxides (<20%) were found. Similar results have been also reported by Nur et al. using Ti supported manganese oxide materials [42]. The catalysts were very selective to the epoxide formation in the double bond present within the cyclohexene ring to give the 1,2-epoxy-limonene in the oxidation of limonene. Minor quantities of carveol (trans 2-cyclohexene-1-one, 2 methyl-5-(1-methylethenyl), carveone (ketone) and the 8,9 epoxy-limonene were also detected. The product distribution, activities and selectivities observed are in good agreement with those reported by Cagnoli et al. for Ti-MCM-41 materials [38]. In a similar way as it was found in the oxidation of alcohols, the addition of acetonitrile as solvent in the oxidation of the aromatic substrates seemed to be critical in order to achieve high selectivities to the epoxides. Microwave runs in the absence of acetonitrile provided lower selectivities to epoxides under the same reaction conditions.

The organically modified Ti-MCM-41 materials were also very active and selective in the epoxidation of linear alkenes (Table 5, entries 6 and 7).

The Ti leaching in the reactions was found to be very similar to that reported in the oxidation of alcohols.

Table 5
Catalytic activity [total conversion (X_T , mol%) and selectivity to the epoxides (S_{epoxide} , mol%)] of Ti-*t*B in the oxidation of various alkenes

Entry	Substrate	Reaction conditions	X_T (mol%)	S_{epoxide} (mol%)
1		5 mmol styrene, 6 mmol H_2O_2 , 0.05 g catalyst, 300 W, 30 min, 110 °C (max temp. 130 °C)	>99	<10
2		5 mmol α -methylstyrene, 6 mmol H_2O_2 , 0.05 g catalyst, 300 W, 30 min, 115 °C (max temp. 140 °C)	80	<10
3		5 mmol limonene, 6 mmol H_2O_2 , 2 mL acetonitrile, 0.05 g catalyst 300 W, 30 min, 100 °C (max temp 140 °C)	>99	75
4		2 mmol trans-cinnamaldehyde, 6 mmol H_2O_2 , 2 mL acetonitrile, 0.05 g catalyst, 300 W, 30 min, 100 °C (max temp 140 °C)	75	>99
5		2 mmol trans-anethol, 6 mmol H_2O_2 , 2 mL acetonitrile, 0.05 g catalyst, 300 W, 30 min, 100 °C (max temp 140 °C)	85	>99
6		2 mmol 1-heptene, 6 mmol H_2O_2 , 0.05 g catalyst, 300 W, 15 min, 120 °C (max temp 150 °C)	>99	>99
7		2 mmol 1-decene, 6 mmol H_2O_2 , 0.05 g catalyst, 300 W, 15 min, 110 °C (max temp 140 °C)	>99	>99

The improved activity of the organically modified mesoporous materials is believed to be due to a combination of the increase in Ti loading together with an increase in hydrophobicity in the materials after the grafting of the organic moieties on the Si-OH groups. In particular, the effect of the size of the organic moieties does seem to affect the activity of the catalysts in the oxidations, reaching a maximum for the Ti-tB and decreasing for bigger organic moieties (Ti-H, Ti-D and Tables 2 and 3) as expected according to their increasing microporosities. This effect is particularly obvious in the oxidation of bulky compounds including substituted aromatic substrates in which Ti-H and Ti-D exhibited inferior activities that may be correlated to pore size constraints.

However, Ti-Is and Ti-B materials have indeed very similar textural properties to those of Ti-tB despite their lower activities. We believe the superior activity of Ti-tB may be correlated to its improved hydrophobicity through a better coverage of the MCM-41 surface, reduced repulsive interaction between the organic groups and higher titanium stability (in the *tert*-butyl environment) that did not significantly influence the textural properties of the catalyst.

The use of acetonitrile as solvent seemed to also have an effect on the selectivity to the epoxides. In general, microwave runs in the absence of acetonitrile provided lower selectivities to epoxides under the same conditions regardless of the reaction substrate (epoxide selectivity for 1-hexene and 1-heptene were also affected at longer times-over 20 min-of microwave irradiation).

3.2.3. Materials reusability

Further experiments were performed to ensure the heterogeneous nature of the catalysed reactions. A hot filtration test was performed as follows: the catalyst was filtered off after 5 min of microwave irradiation (30% conversion). The reaction mixture without catalyst was then further microwaved for 30 additional minutes and finally quenched. No significant changes in conversion (<10% increase in conversion) were observed, excluding the presence of major quantities of Ti leached species in solution, in good agreement with the traces of Ti (1.2–1.8 ppm) found for the different organotitanosilicates by ICP-MS.

The catalyst reusability was also investigated under the optimized conditions. Results have been included in Tables 6 and 7 for the particular examples of the oxidation of benzyl alcohol and the oxidation of 1-heptene. The catalyst was filtered off after each reaction run, washed with methanol, dried at 80 °C and subsequently reused in another catalytic cycle. Despite a slight increase in the time of reaction required for quantitative conversion (Table 6), the catalysts were reusable up to four times preserving more than 90% of the initial catalytic activity.

The reused solids were also fully characterised after the oxidation reactions. Examples of reused materials in the oxidation of alcohols (e.g. oxidation of benzyl alcohol) and alkenes (e.g. oxidation of limonene) are shown in Figs. 4–6. The reused organically modified Ti-MCM-41 exhibited identical XRD patterns to those of the fresh catalysts, implying that the structural order of the materi-

Table 6
Catalyst reusability studies of Ti-tB in the oxidation of benzyl alcohol^a

Reuse	Conversion (mol%)	S _{benz} ^b (mol%)
1	>95	>95
2	95	>95
3	90	>95
4	87	>95

^a 20 mmol benzyl alcohol, 15 mmol H₂O₂, 0.1 g catalyst, 300 W, 30 min, 130–140 °C.

^b The rest to 100 is due to the formation of R-epoxymethylbenzene and benzoic acid.

Table 7
Catalyst reusability studies of Ti-tB in the oxidation of 1-heptene^a

Reuse	Conversion (mol%)	S _{epoxide} (mol%)
1	>99	>99
2	>95	>99
3	>90	>99
4	90	>99

^a 2 mmol 1-heptene, 6 mmol H₂O₂, 0.05 g catalyst, 300 W, 15 min, 110–120 °C (max temp. 150 °C).

als was preserved after the reaction. Only a small expected decrease in the intensity of the main (1 0 0) line was observed (Fig. 4). Diffraction lines at (1 1 0) and (2 0 0) were present in the reused material.

The nitrogen adsorption measurements confirmed the structural and textural properties of the materials remained almost unchanged after the oxidation with hydrogen peroxide (Fig. 5). The depicted isotherm of the Ti-tB material after its second reuse exhibited a similar profile to that of the parent material. The surface area was 602 m² g⁻¹ and a pore volume and pore size of 0.17 cm³ g⁻¹ and 23 Å, respectively, were found. These textural properties are very similar to those of the fresh material (Table 1, Ti-tB).

No remarkable differences were noticeable in TG/DTA profiles of the reused Ti materials (not shown) with respect to the fresh catalysts, excluding the presence of significant quantities of any adsorbed compounds.

The UV-vis spectra of the recycled materials are included in Fig. 6. The bands due to the different environments of the Ti species, that is, tetrahedral (framework, 210–220 nm) and octahedral (extraframework, 260–270, 300 nm) remained almost unchanged in the recycled materials (Ti-MCM-41 2nd reuse, Fig. 6) compared to those of the freshly prepared catalysts. The intensity of the bands was pretty similar for both reused-fresh organically modified mesoporous materials thus confirming the relatively low level of Ti leaching observed by ICP. The absorption band at ca. 960 cm⁻¹ in the DRIFT experiments was also present in the reused materials.

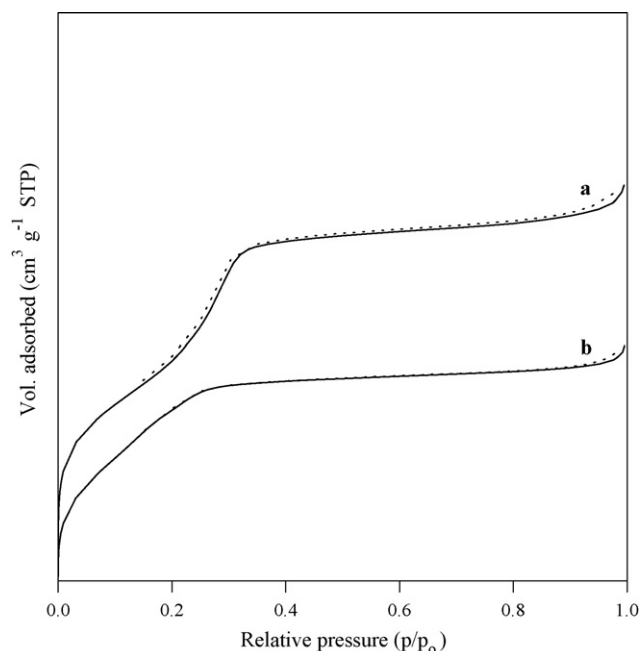


Fig. 5. N₂ physisorption profiles of (a) Ti-tB and (b) 3rd reused Ti-tB in the oxidation of benzyl alcohol.

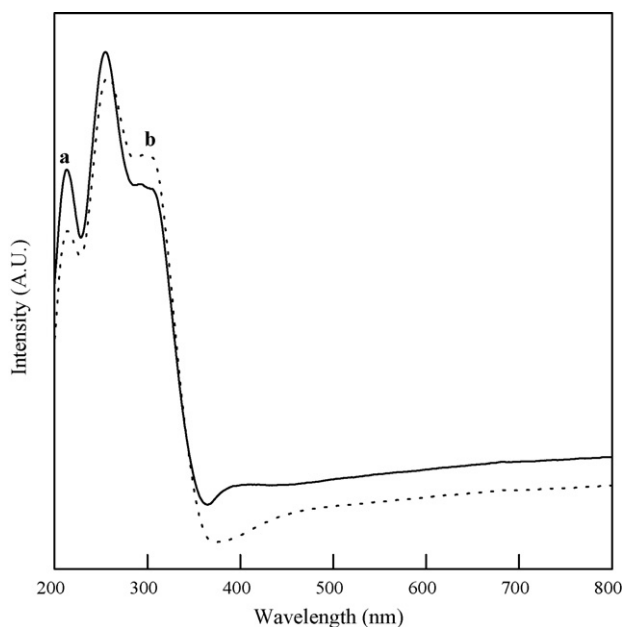


Fig. 6. UV-vis spectra of (a) Ti-MCM-41 (fresh catalyst) and (b) Ti-MCM-41 reused in the oxidation of limonene (two reuses).

Of note was the significant decrease and increase in intensity of the 210 and 305 nm bands, respectively. This fact suggests the partial extraction of the Ti atoms located in the mesoporous framework (tetrahedral coordination) during the reaction. These extracted titanium framework species were either found to be in octahedral coordination (more than 80% as pointed out by the deconvolution of the different bands not shown) or as leached species giving rise to increasing quantities of Ti in solution with reuses, in good agreement with ICP data.

We can conclude that both the Ti in tetrahedral coordination (framework) and the extraframework hexacoordinated Ti species are responsible of the catalytic activity of the organically modified mesoporous materials. The presence of increasing quantities of hexacoordinated Ti extraframework atoms in the functionalised materials seemed to have induced a synergetic effect that enhances the catalytic activity of the materials, in good agreement with results recently reported by Nur et al. [42]. The organic functionalisation rendered highly active and stable materials, contributing to a decrease of the Ti leaching during the various oxidations screened.

4. Conclusions

The preparation of organically modified Ti-MCM-41 materials was successfully accomplished. The incorporation of the Ti organic moieties on the surface increased not only the hydrophobicity and the stability of the materials but also enhanced their activity in various oxidation reactions. Low activities of the catalysts were found in the oxidation of alcohols and alkenes under conventional heating. In contrast, microwave irradiation afforded high conversions and selectivities to the desired products in a short period of time in the oxidation of different alcohols and alkenes. The materials were reusable up to four times preserving more than 90% of their initial activity.

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