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Preparation of Mesoporous Organically Modified Titanium Materials and their Activity in the Oxidation of Cyclohexene

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Abstract Mesoporous organically modified Ti-MCM-41 materials were synthesised 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 tested in the oxidation of cyclohexene using conventional heating and microwaves. The microwave assisted protocol was found to enhance reaction rates and selectivities to the epoxide, reducing the times of reaction from 24 to less than 1 h at comparable activities (60–80% conversion).

Keywords Ti-MCM-41 · Organic functionalisation · Cyclohexene oxidation · Microwaves

1 Introduction

Geometrically regular mesoporous materials have lately aroused great interest among scientific researchers on account of their high potential for practical applications in catalysis, adsorption, and separation as well as for medical, ecological and nano-technological uses [1–13]. Heterogeneous catalysis of organic reactions on porous inorganic solids has proved highly useful in both laboratory syntheses and modern industrial chemical processes. Nowadays, it is widely employed for the production of fuels, the manufacturing and processing of plastics, and the preparation of chemicals required for the development of new products. Micro- and mesoporous materials including silicas, aluminas, titanosilicates, aluminosilicates, aluminophosphates, clays and zeolites have been widely used as catalyst and supports for these purposes.

In 1992, researchers at Mobil Oil R&D discovered the M41S family of mesoporous silicates comprising of the MCM-41 (hexagonal), MCM-48 (cubic) and MCM-50 (layered) structures [14, 15]. Their advent opened up the potential to the preparation of porous solids with a uniform pore size within the mesopore range.

Also, the isomorphic replacement of Si with Ti in MFI and MEL zeolites has provided two new families of zeolites designated TS-1 and TS-2, respectively, which catalyse the selective oxidation of various organic compounds including alkanes, alkenes and alcohols with hydrogen peroxide. The preparation of β-zeolites containing isomorphous titanium has extended the use of microporous titanosilicates to the oxidation of larger organic molecules such as cycloalkanes and cycloalkenes. However, the pore diameters of these zeolites restrict their use to molecules with a kinetic diameter not greater than about 7 Å [16].

The epoxidation of olefins is important not only for the chemical industry (e.g. to obtain ethylene and propylene oxides), but also in Fine Chemistry [17]. The industrial production of ethylene oxide involves the oxidation of gaseous ethylene with oxygen or air on a silver catalyst [18]. This method is not particularly efficient with alkenes containing allyl or other reactive C–H bonds as it provides complex mixtures of several compounds with a low

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selectivity to the epoxide. However, the method has been recently extended to other alkenes including butadiene, styrene, norbornene and *t*-butylene [19] that do not contain any reactive allyl bonds. Some of the resulting products (e.g. butadiene monoepoxide and styrene oxide) are potentially useful as fine chemicals and reaction intermediates.

The epoxidation of cyclohexene on Ti-substituted mesoporous solids is one of the most thoroughly studied reactions. The preparation of highly active and stable catalysts under various operating conditions using *t*-butylhydroperoxide (TBHP) as oxidant has been reported [20–22].

Microwaves have recently been the subject of extensive investigations and a numerous range of applications in organic synthesis can be found in the literature [23–29]. Microwave irradiation can reduce the time of reaction and the energy consumption in microwave assisted syntheses improving reaction yields and selectivities [30]. Overall, microwave-assisted reactions are quicker, safer and more efficient and environmentally benign, than the reactions carried out under conventional heating.

In this work, we have prepared various titanium organically modified silicates and investigated their performance in the epoxidation of cyclohexene as model reaction both under conventional heating and microwave irradiation to demonstrate the advantages of the microwave protocol.

2 Experimental

2.1 Synthesis of Materials

A Ti-MCM-41 material (Si/Ti $= 20$) was employed as support. The Ti-MCM-41 was prepared according to a previously reported hydrothermal procedure [31] using tetraethylorthosilicate (TEOS) and titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$) as silicon and titanium sources, respectively. Cetyltrimethylammonium bromide (CTAMBr) was employed as template.

The preparation of the organotitanium compounds was performed as follows: the support was impregnated with a solution of the titanium precursor, namely titanium (IV) isopropoxide (Ti-Is), butoxide (Ti-b), *tert*-butoxide (Ti-tB), 2-ethylhexyl oxide (Ti-H) and 2-ethylhexanediolate (Ti-D). The mixture was stirred at room temperature for 30 min. The aim was to obtain organotitanium materials with a fixed Si/Ti 10 ratio with various hydrophilic/hydrophobic and steric properties. Such properties were found to be closely related to the structure of the particular organotitanium (IV) compound used for impregnation. The impregnated materials thus obtained were heated under vacuum at 373 K prior to their use in the epoxidation reaction.

2.2 Structural Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Siemens D5000 diffractometer (40 kV, 30 mA) using a nickel filtered CuK_α radiation ($\lambda = 1.5418$ Å) over a 2θ range from 1.8-10° (step size $1° \text{ min}^{-1}$).

Thermal analysis was performed by simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) of the solids using a Setaram Setsys 12 instrument. α-Al_2O_3 was employed as reference material. Solids were heated from 303 to 1173 K at a heating rate of 10 K min^{-1} in a stream of carrier gas (air or argon, 50 mL min^{-1}).

The elemental analysis of the parent Ti-MCM-41 was conducted at the Centre Nationale de la Recherche Scientifique in Vernaison (France). The experimentally determined Si/Ti ratio (19.5) was in good agreement with the Si/Ti value in the synthesis gel.

Diffuse reflectance infrared fourier-transform spectra (DRIFT) were recorded on a Bomen MB-Series IR spectrometer equipped with an "environmental chamber" (Spectra Tech P/N 0030–100) placed in the diffuse reflectance attachment (Spectra Tech, Collector). KBr was used as reference. The resolution was 8 cm^{-1} and 256 scans were averaged to obtain the spectra in the 4,000-400 cm^{-1} range. Samples were mixed with KBr to 15 wt%, placed in the environmental chamber cell with a 20 mL min^{-1}, flow of nitrogen, heated to 373–573 K, and held at this temperature for 1 h prior to spectrum measurement.

Scanning electron microscopy (SEM) micrographs were recorded on a JEOL JSM-6490LV. Samples were Au/Pd coated on a high resolution sputter SC7640 at a sputtering rate of 1,500 V per minute, up to 7 nm thickness.

Transmission electron microscopy (TEM) micrographs were recorded on a FEI Tecnai G^2 fitted with a CCD camera for ease and speed of use. The resolution is around 0.4 nm. Samples were suspended in ethanol and deposited straight away on a copper grid prior to analysis.

Diffuse reflectance UV–Vis spectra were recorded on a Varian CAREY-1E UV–Vis spectrophotometer, operating in the ABS photometric mode, in the 190-800 nm range wavelength range. Si–MCM-41 was employed as reference material.

Nitrogen adsorption measurements were carried out at 77 K using an ASAP 2000 volumetric adsorption analyzer from Micromeritics. The samples were outgassed for 24 h at 473 K under vacuum ($P < 10^{-2}$ Pa) and subsequently analysed. 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 N_2 physisorption isotherms and the Barret-Joyner-Halenda (BJH) formula. The cumulative mesopore volume V_{BJH} was obtained from the PSD curve.

2.3 Catalytic Tests

2.3.1 *Liquid Phase Epoxidation Under Conventional Heating*

The epoxidation of cyclohexene was conducted in a batch reactor consisting of a 50 mL two-necked round bottomed flask. A typical experiment was performed as follows: 4 mL (40 mmol) cyclohexene, 0.6 mL (3 mmol) *t*-butyl-hydroperoxide (TBHP, 5.0–6.0 M in decane), 10 mL dichloromethane and 0.1 g catalyst were heated in an oil bath at 308 K, under continuous stirring. The epoxidation of cyclohexane was also investigated using 35% v/v hydrogen peroxide (0.4 mL, 3 mmol) in *t*-butanol (10 mL) under similar conditions.

Small aliquots were periodically withdrawn from the reaction mixture, filtered off to remove the unwanted solids and analysed using a Gas Chromatograph (GC) HP 5890 Series II fitted with an HP-101 methyl silicone fluid capillary column and a flame ionisation detector (FID).

2.3.2 *Liquid-Phase Epoxidation Under Microwave Irradiation*

The microwave-assisted epoxidations were conducted on a PC controlled CEM-Discover microwave reactor. A typical microwave experiment was performed as follows: 1 mL (10 mmol) cyclohexene, 0.15 mL (0.8 mmol) TBHP, 1 mL of dichloromethane and 0.025 g of catalyst were placed on a microwave tube and irradiated at 300 W for 60 min under continuous stirring. Small aliquots of the final mixture were filtered off and analysed in a similar way to that of the conventional heating experiments.

The reaction products were characterised using chromatographic standards and GC-mass spectrometry (MS). The elution sequence was as follows: dichloromethane, cyclohexene, TBHP, cyclohexene oxide, 2-cyclohexen-1-one and 2-cyclohexen-1-ol.

3 Results and Discussion

Both the Ti-MCM-41 (Si/Ti = 20) parent material and the organically modified materials (Si/Ti = 10) exhibited the typical XRD patterns of mesoporous MCM-41 materials [14, 15]. Grafted materials exhibited a slight decrease in intensity and broadening of the main diffraction lines but the structural order of the materials was preserved as demonstrated in XRD longer scan patterns (Fig. 1).

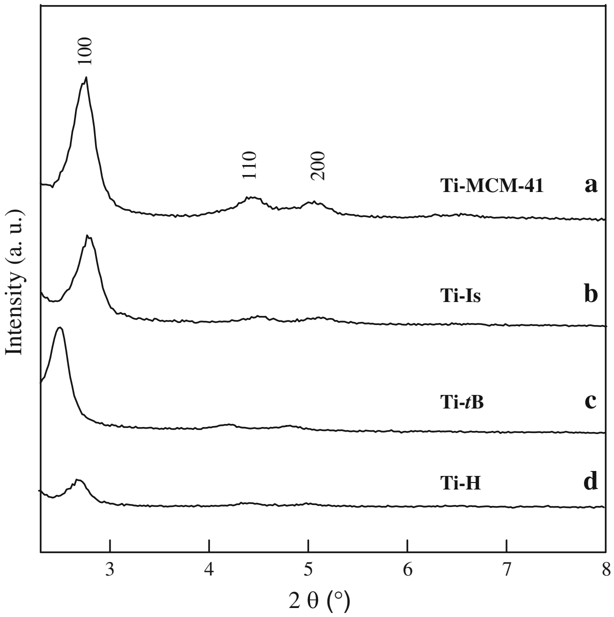


Fig. 1 XRD patterns of the modified Ti-MCM-41 solids: a—parent Ti-MCM-41; b—Ti–Is; c—Ti-tB; d—Ti-H

The effect of the incorporation of various organotitanium compounds onto the Ti-MCM-41 was similar for all titanosilicates. Interestingly, the unit cell size (a_0), in the 43–47 Å range, was not significantly altered in the modified materials with respect to the parent MCM-41 (Table 1). These results were in good agreement with those reported by Igarashi and Tatsumi et al. [32, 33] in the preparation of similar organically modified Ti-MCM-41 materials.

The modified MCM-41 titanosilicates studied exhibited the type IV isotherms, characteristics of mesoporous materials with a steep increase at p/p_o of around 0.2, from the capillary condensation within mesopores. The slope of the isotherms in this region suggests a lack of uniformity in pore size (Fig. 2).

Table 1 Hexagonal cell dimension ($a_0 = 2d_{100}/\sqrt{}3$), textural properties [surface area (S_{BET}, $m^2\ g^{-1}$), pore diameter (D_{BJH}, Å), mesopore volume (V_{BJH}, $mL\ g^{-1}$) and BET constant (C_{BET})] and wall thickness ($\varepsilon = a_0 - D_{BJH}$) of the Ti-MCM-41 mesoporous materials

Material	a_0 (Å)	S_{BET} ($m^2\ g^{-1}$)	D_{BJH} (Å)	V_{BJH} ($mL\ g^{-1}$)	C_{BET}	ε (Å)
Ti-MCM-41	44	926	24	0.63	78	20
Ti-Is	43	877	21	0.15	38	22
Ti-b	43	930	19	0.12	30	24
Ti-tB	47	900	20	0.21	32	27
Ti-H	44	741	<18[a]	0.05	18	–
Ti-D	46	515	<18[a]	0.04	22	–

[a] The materials were mostly microporous

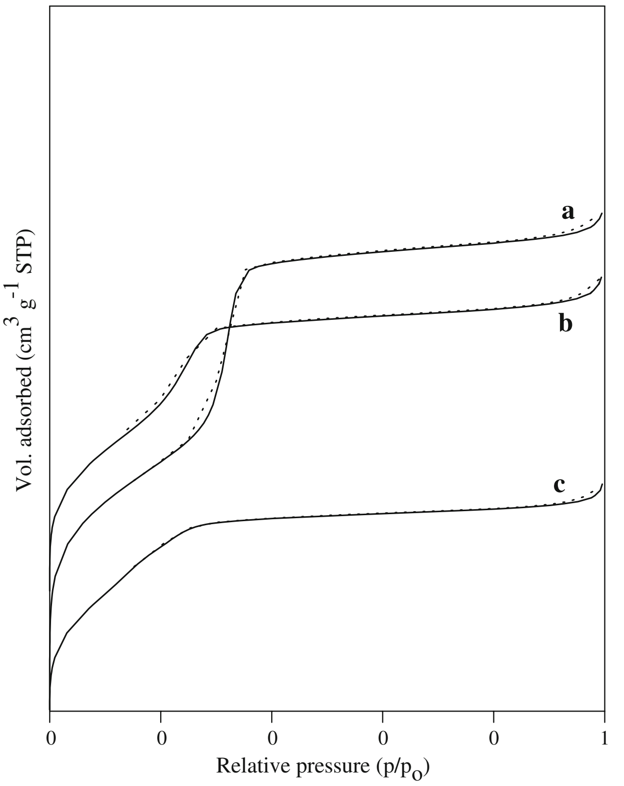


Fig. 2 N_2 physisorption profiles of a—Ti-MCM-41; b—Ti-H; c—Ti-D

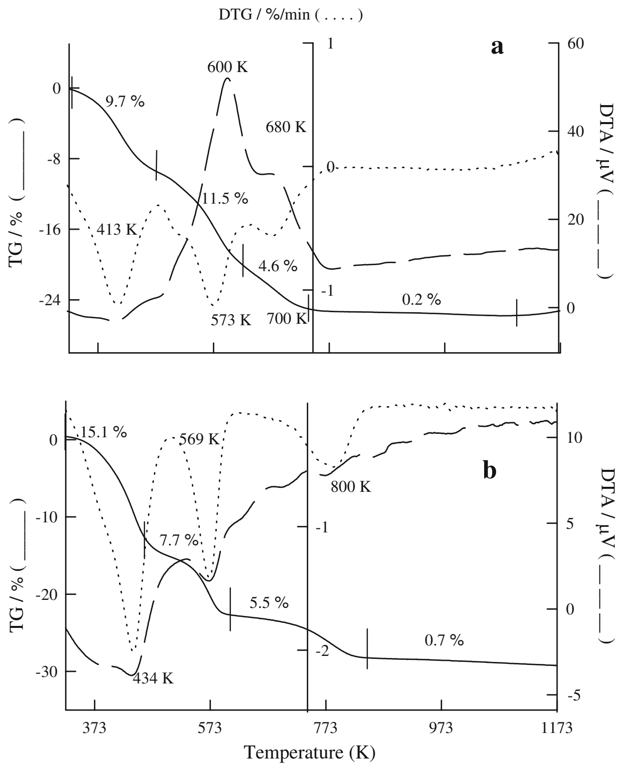


Fig. 3 TG, DTG and DTA curves of the Ti-H in (**a**) oxidizing atmosphere (air) and (**b**) inert atmosphere (argon)

Pore size distribution (PSD) curves showed a width at half-height of 4-7 Å. The cumulative pore volume of the solids was calculated over the range 15-400 Å. Table 1 summarises the main textural properties of the mesoporous grafted Ti materials.

In general, the modified titanosilicates exhibited inferior textural properties compared to the parent Ti-MCM-41. Only a small decrease in such properties was found for the materials modified with small organotitanium compounds (e.g. Ti-b). In the particular case of the grafting of bulky organic Ti species, the mesopore volumes were considerably decreased (e.g. 0.04 and 0.05 for Ti-D and Ti–H, respectively) and the pore diameters were found to be within the micropore range (Table 1).

The thermal analysis of the mesoporous materials revealed variable mass losses. The mass loss profile was similar to all materials regardless of the organotitanium precursor employed in their preparation. Figure 3 shows the TG, DTG and DTA curves for the Ti-H in air and argon. The organically modified titanium silicate exhibited a weight loss of ca. 9.7% below 473 K which can be correlated to the removal of physisorbed water and traces of 2-propanol from the grafting step on the catalysts surface (Fig. 3). The weight losses in the 473-623 K range (11.5% total mass loss) can be ascribed to the decomposition and oxidation of the organic grafted moieties on the materials in view of the exothermic peak (ca. 600 K) found in the DTA curve. A third mass loss was observed in the 623-700 K range, which can be attributed to both the decomposition and oxidation of the remaining grafted organic species as well as to the oxidation of carbonaceous species directly generated on the materials surface. A small weight loss (ca. 0.2%) was found above 700 K as a result of the removal of water produced in the formation of siloxane bonds by condensation of neighbouring silanol groups [31].

The TGA-DTA results were in good agreement with the DRIFT spectra obtained at different temperatures. DRIFT spectra of the organically Ti-MCM-41 samples showed the typical infrared absorption bands of M41S materials (Fig. 4); [34]. The grafting of the organic moieties on the silanol groups can be observed in the spectra as a decrease in intensity of the Si-OH stretching band (3,740 cm^{-1}), as well as by the presence of the typical C–H stretching (3,000-2,850 cm^{-1}) and bending (1,350–1,500 cm^{-1}) vibrational bands of aliphatic organic species (Fig. 4). The decrease in intensity of the silanol bands implies an increase in the hydrophobicity of the surface.

The O–H vibrational bands and the broad band at 3,400 cm^{-1} due to the formation of hydrogen bonds and related to the presence of water and/or 2-propanol adsorbed at 373 K, were found to disappear with a further

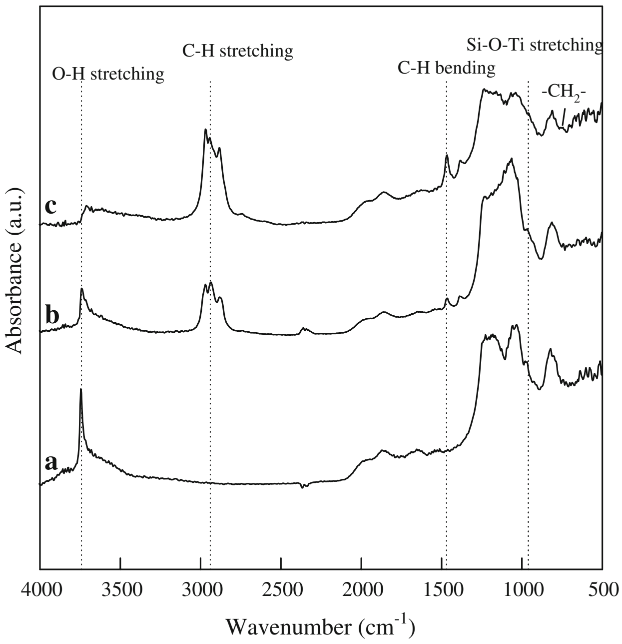


Fig. 4 DRIFT spectra (4,000–500 cm^{-1}, offset) of a—Ti-MCM-41; b—Ti-H; c—Ti-D

temperature increase (573 K). The Si–OH stretching band also increased in intensity as a consequence of the removal of the organic grafted compounds.

Skeleton vibrational bands (720–750 cm^{-1}) were also visible in the particular case of the grafted compounds with a longer alkyl chain (e.g. Ti-D). 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 [35, 36].

SEM micrographs of both parent and organically modified materials showed spherical particle morphology, similar to that previously reported by our group [37], for all materials regardless of their synthesis procedure.

TEM micrographs were also recorded and they are included in Fig. 5. The micrographs clearly show the highly ordered hexagonal array of mesopores in the materials (Fig. 5a), that was preserved after the organic modification with the titanium precursors (Fig. 5d).

Diffuse reflectance UV–Vis spectroscopy is a sensitive technique for detecting off-network Ti in zeolites [38–41]. UV–Vis DRS spectra of the grafted Ti-MCM-41 are shown in Fig. 6. Ti-MCM-41 showed bands at ca. 210 nm due to isolated titanium in tetrahedral coordination [41–44] and 265 and 305 nm due to partially polymerised Ti species in pentahedral or hexahedral titanium extraframework environments present in small TiO$_2$ nanodomains [39, 40, 45, 46]. The grafted materials exhibited more intense bands (Fig. 6, inset) due to the incorporation of the Ti organic species onto the Ti-MCM-

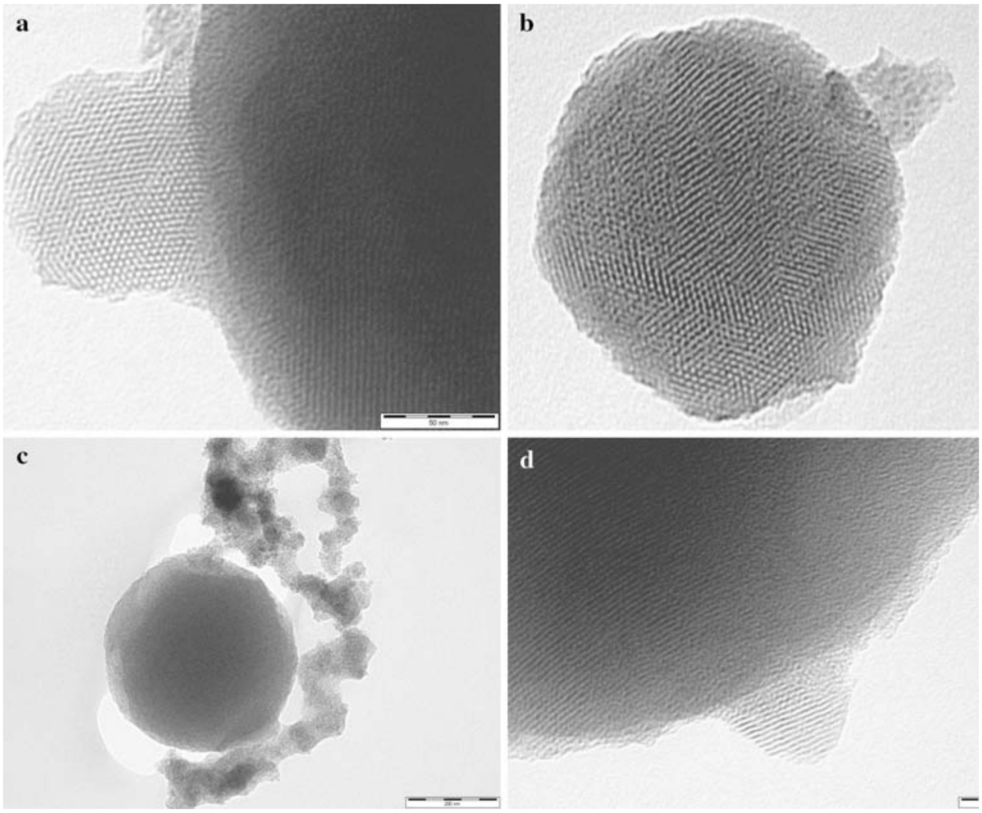


Fig. 5 HRTEM micrographs of (**a**, **b**) Ti-MCM-41 (×300,000, 50 nm); (**c**) Ti-H (×87,000, 200 nm) and (**d**) Ti-H (×300,000, 50 nm)

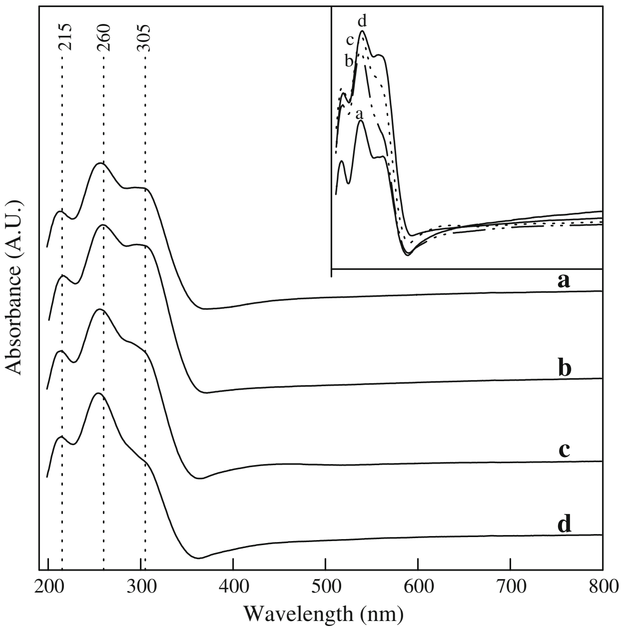


Fig. 6 UV–Vis spectra (offset) of various Ti-MCM-41 modified materials: a—Ti-MCM-41; b—Ti-tB; c—Ti-H; d—Ti-D. The inset (top-right) corresponds to the four different materials in the same scale

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, 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. [47].

The absence of a band at 330 nm suggests that MCM-41 titanosilicates form no anatase crystals at least, not to an appreciable extent. Therefore, most Ti atoms must be at isolated positions in the SiO_2 structure of the Ti-MCM-41.

3.1 Catalytic Activity

3.1.1 Liquid Phase Epoxidation of Cyclohexene Under Conventional Heating

Epoxidations are industrially important reactions affording the transformation of alkenes into oxygen-containing molecules as important intermediates and fine chemicals. The activity and selectivity of the grafted Ti silicates was tested in the epoxidation of cyclohexene as model reaction. TBHP and hydrogen peroxide were employed as oxidants. Dichloromethane and *t*-butanol were used as solvents in the epoxidation of cyclohexene with TBHP and H_2O_2, respectively, based on previously results [28]. Data is summarised in Tables 2 and 3. Cyclohexene oxide, 2-cyclohexene-1-ol, cyclohexanediol and 2-cyclohexene-1-one were found as major products in the epoxidation of cyclohexene using TBHP and H_2O_2, respectively, (Scheme 1).

No products were observed after 24 h in a blank reaction run in the absence of catalyst. TBHP decomposes to tert-butanol at TBHP decomposition was found to be very low (less 5%) under the relatively mild reaction conditions, so the contribution of TBHP decomposition can be considered almost negligible. The organically modified Ti-MCM-41 materials clearly exhibited improved activities and selectivities to the epoxide when using TBHP as oxidant with respect to the parent Ti-MCM-41 material (Table 2) as expected from its higher Ti content. Furthermore, a substantial increase in selectivity to the epoxide was found for the organically modified mesoporous materials (e.g. 80% and 83% for Ti-D and Ti-tB, respectively, Table 2). Minor quantitites of the 2-cyclohexene-1-ol and the cyclohexanediol were also found. The Ti-tB and Ti-H exhibited the best activities in the reaction compared to the other grafted titanosilicates. Smaller (Ti-Is, Ti-b) or bigger (Ti-D, Ti-isoctyl-not shown-) grafted organotitanium materials had lower activities suggesting such size of organotitanium was the optimum for an improved catalytic activity. We believe the hydrophobic/hydrophilic ratio and the size of the grafted titanium compounds, in terms of pore blockage, are the two key parameters to be correlated to the activity of the mesoporous modified titanosilicates.

Interestingly, the catalysts provided inferior activities and very different selectivities with the use of H_2O_2 as oxidant. The water generated in the decomposition of H_2O_2 (as well as that present in the 35% hydrogen peroxide solution) was found to contribute to the decrease in the selectivity to the epoxide at long times of reaction (Table 3). The cyclohexanediol was the main product (60–

Table 2 Total conversion (X_T, mol%) and selectivities to cyclohexene oxide (S_{epox}, %), 2-cyclohexene-1-ol (S_{ol}, %)and cyclohexanediol (S_{diol}, %) of various modified Ti-MCM-41 catalysts in the epoxidation of cyclohexene with TBHP

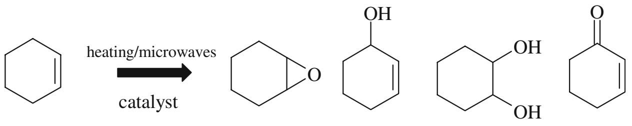
Catalyst	X_T (mol%)	S_{epox} (%)	S_{ol} (%)	S_{diol} (%)
Ti-MCM-41	48	66	17	16
Ti-Is	52	68	14	17
Ti-b	58	73	12	13
Ti-tB	64	83	12	<5
Ti-H	62	77	10	13
Ti-D	47	80	16	<5

Reaction conditions: 40 mmol cyclohexene, 3 mmol TBHP, 10 mL dichloromethane, 0.1 g catalyst, 308 K, 24 h. Traces of 2-cyclohexen-1-one (<5%) were also found

Table 3 Total conversion (X_T, mol%) and selectivities to cyclohexene oxide (S_{epox}, %), 2-cyclohexene-1-ol (S_{ol}, %), 2-cyclohexen-1-one (S_{one}, %) and cyclohexanediol (S_{diol}, %) of various modified Ti-MCM-41 catalysts in the epoxidation of cyclohexene with H_2O_2

Catalyst	X_T (mol%)	S_{epox} (%)	S_{ol} (%)	S_{one} (%)	S_{diol} (%)
Ti-MCM-41	26	<10	8	15	65
Ti-Is	34	32	12	12	43
Ti-b	49	<5	8	21	66
Ti-tB	32	<5	7	15	73
Ti-H	49	<5	10	24	60
Ti-D	57	<5	8	20	67

Reaction conditions: 40 mmol cyclohexene, 3 mmol H_2O_2, 10 mL *tert*-butanol, 0.1 g catalyst, 308 K, 24 h



Scheme 1 Reaction products obtained in the oxidation of cyclohexene under conventional heating and/or microwave irradiation using TBHP and H_2O_2

70% selectivity) arising from the hydrolysis of the cyclohexene oxide and only minor quantities of cyclohexene oxide were found. In any case, a similar peroxide decomposition (less 5%) was found for H_2O_2 under the reaction conditions.

A hot filtration test was performed to ascertain the truly heterogeneous nature of the epoxidation. Thus, the oxidation reaction was carried out with the organically modified Ti-MCM-41 at 308 K for 24 h using TBHP as oxidant. The catalyst was then filtered off from the hot reaction mixture and a small reaction aliquot was extracted and analysed. The mixture was then kept at the reaction temperature for a further 24 h and further investigated. No difference in composition between the two analyses was found, implying that no catalytically active Ti species were present in solution. The filtrate was also investigated by ICP-MS. A tiny <2 ppm leaching of total titanium amount (around 1 ppm Ti concentration in the supernatant) was found.

3.1.2 Liquid Phase Epoxidation of Cyclohexene Under Microwave Irradiation

The effect of the microwave power (Table 4) and the time of reaction (Table 5) were investigated in order to optimise the reaction conditions for the epoxidation of cyclohexene using both TBHP and H_2O_2. The conditions used in the microwave-assisted epoxidation of cyclohexene with TBHP (amount of catalyst and reagent volumes) were identical to those of the conventional reaction in the liquid phase with the exception of the volume of dichloromethane employed as solvent.

Table 4 Influence of the microwave power and the time of reaction on the catalytic activity of Ti-MCM-41 in the epoxidation of cyclohexene with TBHP

Influence of microwave power (reaction time = 60 min)					
Power (W)	100		200		300
Conversion (mol%)	60		78		86
Influence of reaction time (microwave power = 300 W)					
Time (min)	5	15	30	60	180
Conversion (mol%)	<10	34	60	86	>95

Reaction conditions: 10 mmol cyclohexene, 0.8 mmol TBHP, 1 mL of dichloromethane, 0.025 g catalyst. A complete selectivity to cyclohexene oxide was obtained in all cases

Table 5 Total conversion (X_T, mol%) and selectivities to cyclohexene oxide (S_{epox}, %) of different Ti materials in the oxidation of cyclohexene with TBHP under microwave irradiation

Catalyst	X_T (mol%)	S_{epox} (%)
No catalyst	<10	>99
Commercial TiO_2	<10	>99
Ti-MCM-41	86	>99
Ti-Is	51	>99
Ti-b	63	>99
Ti-tB	64	>99
Ti–H	80	>99
Ti-D	66	>99

Reaction conditions: 10 mmol cyclohexene, 0.8 mmol TBHP, 1 mL of dichloromethane, 0.025 g catalyst, 300 W, 1 h

The microwave power had a remarkable effect on the reaction rate at a given reaction time. A power increase from 100 to 300 W resulted in a substantially increased conversion with TBHP (from 59% to 86%) and ensured a complete selectivity to the epoxide in all cases.

However, the activities with TBHP did not significantly increase with time after 60 min (86%, Table 4). The selectivity to cyclohexene oxide was found to be completely independent of the time of reaction.

Table 5 summarises a comparison of activities for the various catalysts screened in the epoxidation of cyclohexene with TBHP. The blank reaction and the commercial TiO_2 catalyst exhibited a similar very poor activity (ca. 8%). In general, the mesoporous Ti-MCM-41 materials exhibited relatively high conversions (>60%) with a complete selectivity to the epoxide. Of note was the high unexpected activity provided by the parent Ti-MCM-41 compared to the organically modified materials, with only Ti-H exhibiting comparable activity in the cyclohexene epoxidation. Such bizarre activity trend found in the microwave experiments may be related to the hydrophobic/hydrophilic character of the catalyst. It is well known that highly polar compounds or materials tend to readily heat under microwave irradiation while less polar substances including highly ordered crystalline materials are poor microwave absorbers [30]. The changes in physical properties (mainly an increase of the surface hydrophobicity) of the Ti-MCM-41 after functionalisation can have a dramatic influence on the susceptibility to microwave irradiation. We believe the decrease in free surface hydroxyls and therefore in hydrophilicity in the organomodified mesoporous materials rendered poorer microwave absorbers compared to the parent hydrophilic Ti-MCM-41 material and therefore a preferential heating promoting the reaction may have taken place. However, microwave absorption depends on several factors and can vary with both sample and temperature, making difficult the interpretation of results.

In any case, the rates of reaction were remarkably increased compared to those of the conventional liquid phase, reducing the time of reaction (from 24 to 1 h) as well as increasing the activities of the materials.

The tests conducted using H_2O_2 as oxidant under the same reaction conditions revealed the materials had a poor catalytic activity. The activities were considerably increased (~30–50%) with double quantities of catalyst (0.05 g). In any case, the activities were found to be inferior compared to those of the use of TBHP as oxidant. Such decrease in activities can be conditioned by the insufficient stirring provided by the microwave reactor that may lead to a poor mixing of the bi-phasic mixture (viz. cyclohexene, 35% w/v H_2O_2 and *t*-butanol).

4 Conclusions

Organically modified Ti-MCM-41 materials with improved hydrophilic/hydrophobic properties were successfully prepared. The activity of the catalysts was investigated in the liquid phase epoxidation of cyclohexene with TBHP or H_2O_2 under conventional heating and microwave irradiation. The grafted organotitanium silicates were found to be very active and selective to the formation of the cyclohexene oxide in the liquid phase oxidation of cyclohexene with TBHP under conventional heating. The reaction took +24 h to complete. The use of H_2O_2 provided lower activities and a switch in selectivity to 2-cyclohexen-1-ol.

The epoxidation under microwave irradiation was proved to be quicker compared to the reaction under conventional heating, reducing the time of reaction from 24 to less than 1 h to achieve comparable activities and improved selectivities to the epoxide. TBHP was proved to be a more efficient oxidant than H_2O_2.

In summary, the microwave-assisted protocol results in substantial time and energy savings, and in high yields to the target product. Microwaves can improve the green credentials of the catalytic epoxidation of cyclohexene.

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