The use of H_2O_2 over titanium-grafted mesoporous silica catalysts: a step further towards sustainable epoxidation†

Matteo Guidotti,*[a] Claudio Pirovano,[a] Nicoletta Ravasio,[a] Beatriz Lázaro,[b] José M. Fraile,[b] José A. Mayoral,[b] Bernard Coq[c] and Anne Galarneau[c]

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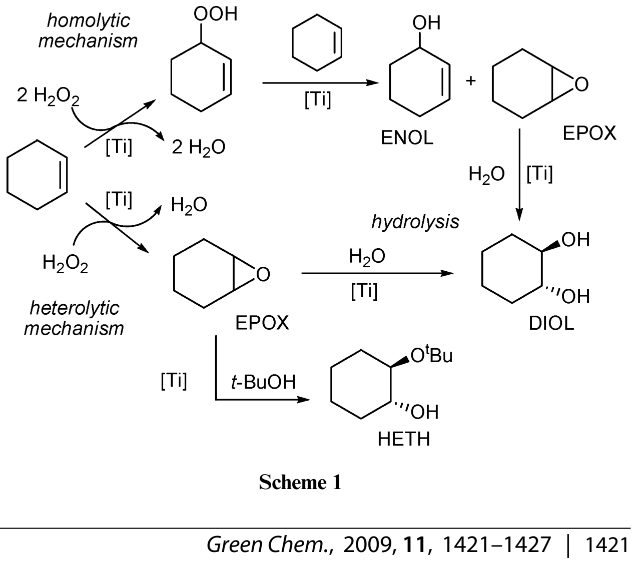
The epoxidation of cyclohexene with aqueous hydrogen peroxide over mesostructured $Ti(Cp)_2Cl_2$-grafted silica catalysts is described for the first time. Three kinds of Ti-containing systems with different textural properties have been employed: Ti/SiO_2, Ti/MCM-41 and Ti/MCM-48. A minimal local H_2O_2 concentration in the surroundings of Ti sites, obtained by a controlled dropwise addition of aqueous H_2O_2 (4.17 mmol H_2O_2 h^{-1} g_{cat}^{-1}), is crucial for an effective and highly selective epoxidation. Excellent selectivity (>98%) in cyclohexene epoxide is obtained at the end of the slow H_2O_2 addition in acetonitrile. Higher yields in epoxide are found over Ti/MCM-48 than over Ti/MCM-41 or Ti/SiO_2 thanks to better isolation, dispersion and stability of Ti(IV) sites.

Introduction

The post-synthesis modification of structured porous materials is a versatile and easily accessible method to prepare tailored catalysts with desired properties to be used in several domains. Thanks to this approach, the user can select the most suitable support, in terms of composition, morphology and stability, and graft or anchor on it the most appropriate catalytic centre (or centres), in terms of chemical species, loading, redox ability or acid/base character, hence achieving the 'ideal' heterogeneous catalyst.[1] In the case of the selective epoxidation of bulky alkenes, the single-site heterogeneous catalysts obtained by grafting titanium-containing precursors onto mesoporous silica materials have shown promising results.[2] The use of ordered and non-ordered solids with porosity in the range of the mesopores helps to circumvent the typical steric limitations of microporous titanosilicate zeolites, such as TS-1 (Ti-MFI) or Ti-BEA. Moreover, the careful dosing of the titanium precursor during the grafting allows an optimal dispersion and a good accessibility of the catalytically active sites.[3] Titanocene-derived systems found some interesting applications in the epoxidation of alkenes,[4,5] alcoholic unsaturated terpenes[6,7] or unsaturated fatty acid methyl esters.[8] Nevertheless, in all these examples, the epoxidation over the titanium-grafted systems has always been carried out successfully in the presence of *tert*-butyl hydroperoxide (TBHP) as the oxidant. In the presence of aqueous H_2O_2, Ti(IV) centres suffer hydrolysis, quickly form aggregates, lose their activity and, practically, undergo an irreversible deactivation. Such behaviour has been thoroughly followed by catalytic and spectroscopic evidences.[9–14] In addition, the higher hydrophilic character and the lower resistance to aqueous media of titanium-containing mesoporous silicates with respect to microporous titanosilicates (typically TS-1) is a further drawback to the extensive use of mesoporous catalysts.

The epoxidation of cyclohexene is a reaction of interest not only as a test oxidation to evaluate the activity of the catalysts and to discriminate between homolytic or heterolytic pathways taking place during the reaction[15] (Scheme 1), but also as a potential first step in the synthesis of adipic acid, according to a potential alternative route where cyclohexene epoxide replaces cyclohexanone.[16] So far, all the titanium-containing mesoporous



Scheme 1

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[a] CNR–Istituto di Scienze e Tecnologie Molecolari, IDECAT-CNR Unit, via Venezian 21, Milano, Italy. E-mail: m.guidotti@istm.cnr.it; Fax: +39 02 5031 4405; Tel: +39 02 5031 4428

[b] Instituto de Ciencia de Materiales de Aragón, IDECAT-CSIC Unit, Fac. Ciencias, Zaragoza, Spain

[c] Institut Charles Gerhardt Montpellier, UMR 5253 CNRS/UM2/ENSCM/UM1, ENSCM, 8 rue de l'Ecole Normale, 34296, Montpellier, France

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Table 1 Characteristics of titanocene-grafted silica catalysts (calcined samples)

Samples	Symmetry	Ti(wt%)^a	$S_{BET}{}^b$/m^2 g^{-1}	V^c/mL g^{-1}	$D_{BdB}{}^d$/nm	$d_{XRD}{}^e$/nm	SC^f/Ti nm^{-2}
MCM-41	hexagonal	—	990	0.76	3.7	4.17	—
Ti/MCM-41	hexagonal	1.68	935	0.66	3.5	4.16	0.23
MCM-48	cubic	—	1163	0.96	3.6	3.79	—
Ti/MCM-48	cubic	1.49	997	0.54	3.4	3.64	0.19
SiO_2	none	—	527	0.83	7.9	n.d.^{g}	—
Ti/SiO_2	none	1.85	492	0.78	7.8	n.d.	0.47

^{a} Titanium content (determined by ICP-AES). ^{b} BET surface area. ^{c} Mesoporous pore volume. ^{d} Pore diameter (determined by Broekhoff and deBoer method). ^{e} d-spacing of the first XRD peak. ^{f} Titanium surface concentration (Ti atom per square nanometre). ^{g} Not determined.

catalysts have proved to be rather poor in the cyclohexene epoxidation with a 'sustainable' oxidant such as H_2O_2. In fact, rapid deactivation of the catalyst, limited cyclohexene conversion, bad oxidant efficiency or quick hydrolysis and leaching of the titanium species out of the catalysts are the main problems met by several groups during the study on this kind of system.[10–13,17] Remarkably better results have been obtained by applying the method of slow dropwise addition of H_2O_2 to the reaction mixture, thus increasing the yield of cyclohexene epoxide formation with respect to the addition at once of the oxidant.[9,15,18,19] In particular, some of us have highlighted the positive role of the slow addition of aqueous hydrogen peroxide not only in terms of reduced H_2O_2 decomposition into oxygen and water, but also of lower degree of titanium leaching and enhanced catalyst stability.[20]

In the present work, our aim is to extend the successful experimental methodology of the slow addition of H_2O_2 to the cyclohexene epoxidation over titanocene-grafted ordered mesostructured silica catalysts. Particular efforts will be devoted to the optimisation of the performance in the presence of this particular class of catalysts, to the improvement of the catalyst stability throughout recycling and reuse, as well as to the maximization of the selectivity to the desired epoxide.

Results and discussion

Characterisation of the catalysts

Three kinds of titanocene-grafted silica solids, with different textural properties, were chosen as catalysts: Ti/SiO_2, with a non-ordered network of mesopores, Ti/MCM-41, with an ordered one-dimensional array of mesopores with hexagonal symmetry, and Ti/MCM-48, with an ordered three-dimensional network of mesopores with cubic symmetry (Table 1).

Grafting titanocene in the presence of triethylamine in chloroform on mesostructured silicas and amorphous silica leads to a slight decrease in pore volume and surface area for SiO_2 and MCM-41 and a larger decrease for MCM-48. After calcination of titanocene-grafted silicas, pore volume and surface area decreased by about 10% after calcination, for SiO_2 and MCM-41, and by 40% in pore volume and 14% in surface area for MCM-48, respectively. The examination of the X-ray diffraction pattern (Fig. 1) and of the nitrogen sorption isotherms (Fig. 1-SI) of the ordered mesostructured silicas show that their structure is maintained.† Moreover, ordered mesoporous silicas show a remarkable stability after catalytic tests in the presence of aqueous H_2O_2, as revealed by their almost unchanged XRD pattern and nitrogen sorption isotherm, with even a slight increase in pore volume for MCM-48, as for amorphous silica,

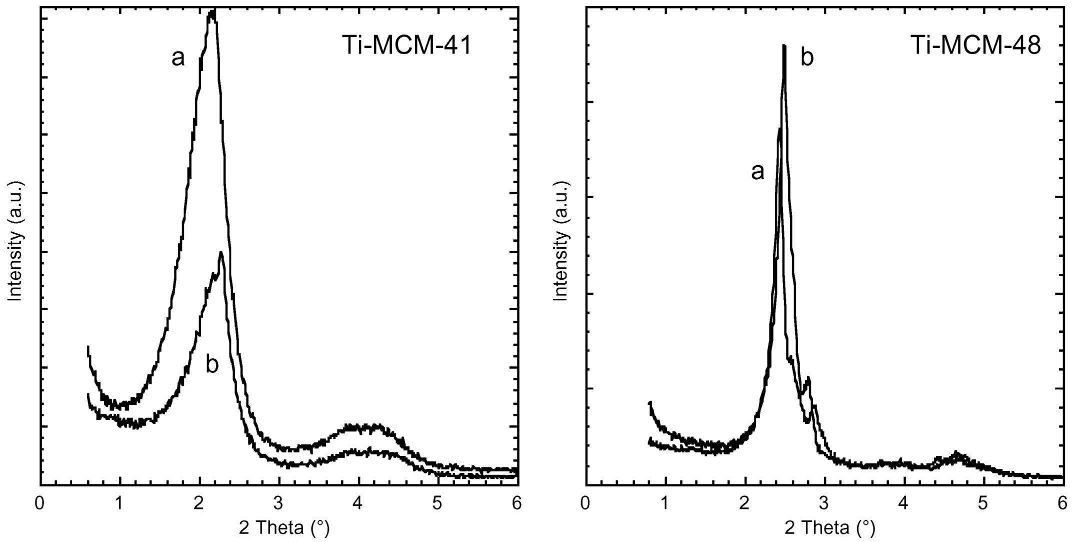

Fig. 1 XRD pattern of calcined Ti-MCM-41 (left) and Ti-MCM-48 (right) before (a) and after one-run of catalysis (b) in the presence of aqueous H_2O_2.

which could be likely due to some restructuring of the pores during the catalytic reaction (Fig. 1 and Fig. 1-SI).†

Catalysts, namely Ti/MCM-41, Ti/MCM-48 and Ti/SiO$_2$, were prepared with similar weight loading of titanium (1.68, 1.49, 1.85 wt%, respectively). However, considering the difference in surface area between ordered and non-ordered silicas (twice as high for ordered silica), to get a comparable surface dispersion of titanium, an additional catalyst was prepared on amorphous silica (Ti-d/SiO$_2$) with 0.93 Ti wt%. For Ti-d/SiO$_2$ the Ti surface concentration is 0.24 Ti nm^{-2}, similar to Ti/MCM-41 (0.23 Ti nm^{-2}) and Ti/MCM-48 (0.19 Ti nm^{-2}), whereas for Ti/SiO$_2$ it is 0.47 Ti nm^{-2} (Table 1). Actually, the concentration and dispersion of the Ti sites on the surface proved to be important in related solids.[15,18]

The dispersion of Ti in the three catalysts, Ti/MCM-41, Ti/MCM-48 and Ti/SiO$_2$, has been studied by UV-Vis DRS on calcined samples. Spectra of the mesostructured materials showed a sharp peak at about 240 nm, in agreement with highly dispersed titanium centres, and much narrower than similar spectra obtained from analogous solids prepared by Ti(O^{i}Pr)$_4$ grafting on amorphous silica.[21]

In particular, in Ti/MCM-41, Ti(IV) is very well dispersed on the surface and it is mainly present as isolated Ti in tetrahedral coordination (Ti maximum <260 nm). In Ti/MCM-48, Ti dispersion is larger, with additional Ti octahedrally coordinated (Ti Oh maximum between 260 and 290 nm). In Ti/SiO$_2$, the dispersion is broad with Ti maximum shifted to 300 nm (Fig. 2), probably due to a higher coordination of titanium, either octahedral or pentacoordinated. After catalysis in the presence of H$_2$O$_2$, the position of the Ti maxima does not significantly change for Ti/SiO$_2$ and Ti/MCM-48, the Ti species being in very stable environments in these two structures, and a slight broadening of the absorption peak arises for MCM-41, showing the formation of some Ti aggregates after catalysis (Fig. 2).

Deconvolution of the IR spectra does not allow any accurate determination of Ti dispersion and/or type of species (mono-, di-, tripodal)[20,22] due to the presence of structural Si–O–Si bands of silica materials around 1000 cm^{-1}, overlapping the Ti–O–Si band.

Table 2 Yield (*Y*) and selectivity (*S*) in cyclohexene epoxidation over titanocene-grafted silica catalysts in *tert*-butanol[a]

	EPOX		DIOL		HETH		TOT[d]
Catalyst	*Y*[b] (%)	*S*[c] (%)	*Y* (%)	*S* (%)	*Y* (%)	*S* (%)	*Y* (%)
Ti/SiO$_2$	15	29	26	50	11	21	52
Ti-d/SiO$_2$	27	41	20	31	18	28	65
Ti/MCM-41	22	48	0	0	24	52	46
Ti/MCM-48	24	46	0	0	28	54	52

[a] Catalyst (200 mg) pre-treated under vacuum at 140 °C for 12 h; cyclohexene : H$_2$O$_2$ (aq. 30%) = 5 : 1; cyclohexene : decane = 2.43 : 1; 5 mL *tert*-BuOH; 85 °C; batch reactor; H$_2$O$_2$ addition over 3 h; 4.17 mmol H$_2$O$_2$ h^{-1} g$_{cat}$$^{-1}$. EPOX: cyclohexene epoxide; DIOL: *trans*-cyclohexane-1,2-diol; HETH: *trans*-2-*tert*-butoxycyclohexanol. [b] Yield at the end of the H$_2$O$_2$ addition (3 h). [c] Selectivity at the end of the H$_2$O$_2$ addition (3 h). [d] Total yield to oxidised products.

Catalytic tests

The catalysts were first tested in *tert*-butanol as solvent. Hydrogen peroxide was added dropwise over 3 h (4.17 mmol H$_2$O$_2$ h^{-1} g$_{cat}$$^{-1}$). In all tests, remarkable amounts of oxidised products were always detected (Table 2). On the contrary, when H$_2$O$_2$ was added in only one aliquot at the beginning of the reaction, negligible amounts of oxidised products were detected (maximum yield 5% after 24 h) and a plethora of unidentified by-products in tiny amounts was observed. It is therefore evident that the dropwise addition is crucial to have an active and effective catalyst in epoxidation.[15] This is a noteworthy result, since no titanocene-grafted silica catalysts have proved to be active in epoxidation with H$_2$O$_2$ so far.[14]

The main products observed are: cyclohexene epoxide (EPOX), cyclohexane-1,2-diol (DIOL) and 2-*tert*-butoxycyclohexanol (HETH) (Scheme 1). The latter two compounds are diagnostic of acid-catalysed epoxide ring opening by water and *tert*-butanol, respectively. In particular, the formation of significant amounts of HETH, barely observed in previous reports under similar conditions,[15,20,22] suggests a marked acidic character. Such acidity is attributed to the introduction of titanium centres on the silica matrix by grafting.[7,23] One possible

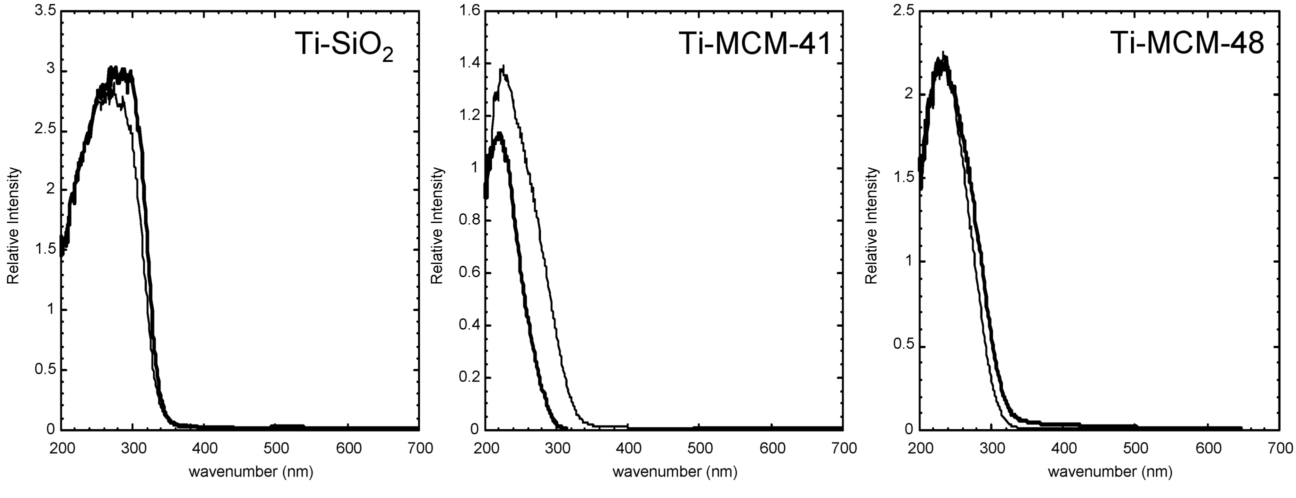

Fig. 2 DR-UV-Vis spectra of calcined Ti-SiO$_2$ (left), Ti-MCM-41 (middle) and Ti-MCM-48 (right) before (thick line) and after one-run of catalysis (thin line) in the presence of aqueous H$_2$O$_2$.

explanation for such enhanced acidity might come from the geometrical constraints of the tripodal titanium centres obtained by the combination of mesostructured solid supports and calcination. A similar increase in Lewis acidity was observed in the case of Al-supported Lewis acids.[24] Interestingly, only the non-ordered silica-supported catalysts are able to promote the epoxide opening with water, whereas mesostructured supports are selective towards the opening with *tert*-butanol. The hydrophilic/hydrophobic balance and the more probable presence of different titanium species (mono-, di-, and tripodal) on silica may account for those results. In any case, the total amount of oxidation products (EPOX + DIOL + HETH) is similar with all the catalysts, even slightly higher with Ti/SiO_2. Conversely, the absence (yield < 3%) of allylic oxidation products, such as cyclohex-2-enol or cyclohex-2-enone, is indicative of the minor role of the homolytic pathway under these conditions, in contrast with solids prepared by grafting of $Ti(O^iPr)_4$.[20,22]

In all cases, the global yield in oxidised products was the highest just at the end of the addition period (3 h). For longer reaction times, in fact, no further formation of products was detected and a decrease in global yield was observed, due to the partial deposition of organic by-products on the surface of the solid catalysts (confirmed by the increasing carbon content with time, as observed by thermogravimetric analysis), thus causing a loss of activity of the catalyst. The ^{13}C-CP-MAS-NMR spectra of the recovered solids show, over all catalysts, three signals at 76, 32, and 23 ppm, in excellent agreement with the presence of adsorbed diol (Fig. 2-SI).† In addition, the determination of hydrogen peroxide by iodometric titration revealed that minimal amounts (max. 5%) of oxidising agent are present at the end of the dropwise addition, showing that any evolution of the reaction mixture is not due to oxidation processes, but to non-oxidative side reactions. Fig. 3 shows how cyclohexene epoxide is rapidly and partly converted into secondary products over Ti/SiO_2 in the two hours following the slow H_2O_2 addition. For these reasons, all catalytic data have been evaluated at 3 h, just at the end of the dropwise addition of H_2O_2.

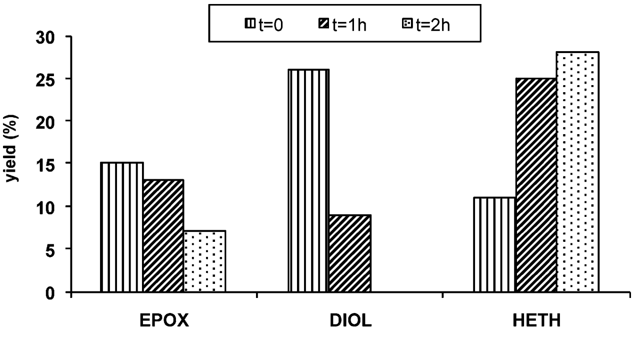

Fig. 3 Distribution of the detected products during the epoxidation of cyclohexene over Ti/SiO_2 in *tert*-butanol. Samples are taken at time *t* after the end of the dropwise addition of H_2O_2.

Table 3 Yield (*Y*) and selectivity (*S*) in cyclohexene epoxidation over titanocene-grafted silica catalysts in acetonitrile[a]

Catalyst	Aq. H_2O_2 concentration (wt%)	EPOX		Other products
		Y^b	S^c	
Ti/SiO_2	30	25	> 98	n.d.[d]
Ti/MCM-41	30	34	> 98	n.d.
Ti/MCM-48	30	44	> 98	n.d.
$Ti\text{-}d/SiO_2$	30	35	> 98	n.d.
$Ti\text{-}d/SiO_2$	30[e]	2	< 5	large number
Ti/MCM-41	50	41	93	ENOL, ENONE
Ti/MCM-48	50	63	90	ENOL, ENONE
$Ti\text{-}d/SiO_2$	50	39	91	ENOL, ENONE

[a] Catalyst (200 mg) pre-treated under vacuum at 140 °C for 12 h; cyclohexene : H_2O_2 = 5 : 1; cyclohexene : decane = 2.43 : 1; 5 mL MeCN; 85 °C; batch reactor; H_2O_2 addition over 3 h; 4.17 mmol H_2O_2 h^{-1} g_{cat}^{-1}. EPOX: cyclohexene epoxide; ENOL: cyclohexane-2-en-1-ol; ENONE: cyclohexane-2-enone. [b] Yield at the end of the H_2O_2 addition (3 h). [c] Selectivity at the end of the H_2O_2 addition (3 h). [d] Not detected. [e] One-aliquot H_2O_2 addition (*Y* and *S* after 24 h).

In order to minimise the occurrence of acid-catalysed secondary products, acetonitrile was chosen as a solvent. Thanks to its slightly basic nature, it has already been shown to allow an increase of the formation of epoxides and to hinder the formation of undesired side products.[7,25] Specific tests and spectroscopic analyses excluded, however, the formation of peroxyimidic acid in the reaction mixture under these conditions, as could be expected from the simultaneous presence of acetonitrile and H_2O_2, but only under basic conditions.[26] The role of the nitrile solvent as an active component in the *in situ* formation of the oxidising agent can be hence excluded.

Under these optimised conditions (slow H_2O_2 addition and acetonitrile as solvent), no products other than cyclohexene epoxide (EPOX) were detected (Table 3). This is the first example of highly selective epoxidation catalysts using aqueous H_2O_2 as oxidizing agent. The selectivity in epoxide reaches, therefore, the unprecedented value of >98%. The yield to EPOX spanned from 44% to 25% according to the order Ti/MCM-48 > Ti/MCM-41 > Ti/SiO_2. The better behaviour of the ordered mesoporous catalyst with respect to non-ordered ones (with similar weight Ti loading) is likely attributed to the better isolation and dispersion of Ti(IV) sites on high surface-area MCM-48 and MCM-41 silicas, as confirmed by the position of the band maxima of UV-Vis DRS (Fig. 2). The use of $Ti\text{-}d/SiO_2$ with a comparable Ti surface concentration as ordered mesoporous catalysts (*ca.* 0.2 Ti nm^{-2}) leads to a notable increase in EPOX yield from 25% to 35%, respectively. Such behaviour shows that well-dispersed tetrahedral Ti centres, notwithstanding their total amount, are the optimal sites for this reaction. No significant differences between MCM-41 and amorphous silica were observed under these conditions, in agreement with previous results.[27] An additional point is the lower yield of oxidation products obtained in acetonitrile than in *tert*-butanol, 44% *vs.* 52% with Ti/MCM-48 or 35% *vs.* 65% with $Ti\text{-}d/SiO_2$. This result is in excellent agreement with the role of Ti centres as Lewis acids, demonstrated by the activity *vs.* acidity correlations in theoretical and experimental studies with modified Ti centres on silica.[28]

The crucial role of the method of H_2O_2 addition was confirmed by comparing the results obtained over the most active catalyst (Ti/MCM-48) with the addition of the same amount of oxidant according two different ways: when H_2O_2 was added dropwise over 3 hours, 44% yield was achieved, whereas, when H_2O_2 was added suddenly, in one shot, the yield of EPOX was almost zero and a wide range of minor compounds was detected (Table 3). The slow H_2O_2 addition to the reaction mixture is therefore crucial to have an effective and highly selective epoxidation catalyst. Under these conditions, the oxidant efficiency proved to be high (max. 75%, min. 50% of the consumed H_2O_2). On the contrary, when H_2O_2 was added in only one aliquot, a sudden loss of activity was recorded, as also confirmed by previous DRS-UV-Vis evaluation.[14] The slow dropwise addition minimizes the local concentration of H_2O_2 in the surroundings of grafted Ti sites, suppresses the unproductive disproportionation of H_2O_2 into O_2 and H_2O and favours the heterolytic pathways instead of the homolytic ones (leading to the formation of allylic oxidation side products). In addition, the negative effect of water in the reaction medium was confirmed by some tests where more concentrated H_2O_2 (50% aqueous solution) was employed and added dropwise. Under these conditions, yields as high as 63% and 41% can be achieved over Ti/MCM-48 and Ti/MCM-41, respectively (*vs.* 44% and 34% with 30% aq. H_2O_2; Table 3). The presence of water in the reaction medium could, in fact, enhance the hydrolytic cleavage of Ti–O–Si bonds of the grafted moieties and thus the rapid aggregation of Ti isolated sites into less active (or totally inactive) large TiO_2-like clusters. Nevertheless, with 50% aq. H_2O_2 solution, the relatively higher instant concentration of H_2O_2 in the reaction mixture leads to an increase of the side production of allylic oxidation compounds (cyclohex-2-en-1-ol: ENOL and cyclohex-2-enone: ENONE; Scheme 1) and hence to a slight decrease in selectivity to epoxide.

Also, in acetonitrile, longer reaction times after the 3 h of addition did not increase the yield to EPOX. A further dropwise addition of a second aliquot of H_2O_2 did not increase markedly the yield of EPOX (calculated with respect to the added H_2O_2), confirming that a fraction of H_2O_2, although small, remains unproductive.

The four titanocene-derived catalysts were easily recovered by filtration, washed, calcined and reused in a second catalytic run (Table 4 and Fig. 4). The calcination step at 500 °C is necessary to remove the organic by-products (*ca.* 2–5 wt%, as shown by TGA analysis) that lead to an irreversible deactivation of the Ti centres and to regenerate the environment of the catalytic sites. Interestingly, all the catalysts kept their epoxidation activity and very high selectivity to epoxide. In particular, Ti/SiO_2 and Ti/MCM-41 showed fully comparable or even better epoxide yields with respect to the first run over the fresh catalyst.

Table 4 Yield (Y) and selectivity (S) in cyclohexene epoxidation over titanocene-grafted silica catalysts in acetonitrile (second run over recovered catalyst)

		EPOX		
Catalyst	Aq. H_2O_2 concentration (wt%)	Y^a	S^b	Other products
Ti/SiO_2-rec	30	29	> 98	n.d.[c]
Ti-d/SiO_2-rec	30	33	> 98	n.d.
Ti/MCM-41-rec	30	40	> 98	n.d.
Ti/MCM-48-rec	30	34	> 98	n.d.

Catalyst (200 mg) recovered, washed and calcined in air 500 °C for 1 h; cyclohexene : H_2O_2 = 5 : 1; cyclohexene : decane = 2.43 : 1; 5 mL MeCN; 85 °C; batch reactor; H_2O_2 addition over 3 h; 4.17 mmol H_2O_2 h^{-1} g_{cat}^{-1}. EPOX: cyclohexene epoxide.[a] Yield at the end of the H_2O_2 addition (3 h). [b] Selectivity at the end of the H_2O_2 addition (3 h). [c] Not detected.

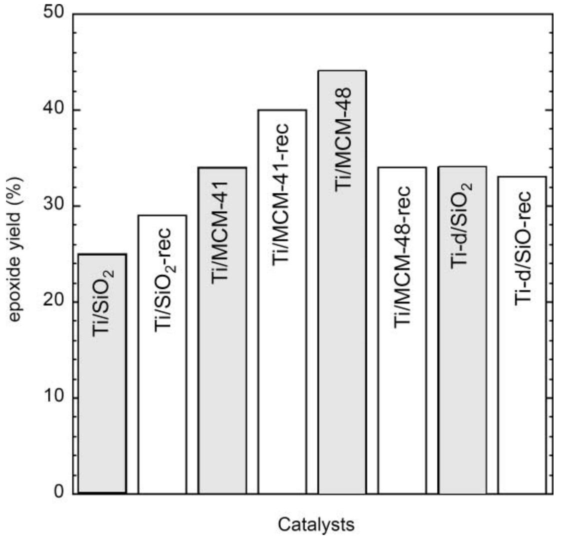

Fig. 4 Epoxide yields over four Ti-catalysts (grey) showing >98% selectivity in epoxide of cyclohexene using aqueous 30% H_2O_2: Ti/SiO_2, Ti/MCM-41, Ti/MCM-48 and Ti-d/SiO_2. Epoxide yields on reuse catalysts are reported in white bars.

Surprisingly, Ti/MCM-48 underwent some deactivation from 44% to 34%, although its Ti dispersion was unchanged after one-run recycling as evidenced in UV-Vis (Fig. 2). Conversely, from UV-Vis spectroscopic evaluation, Ti/SiO_2 and Ti/MCM-41 displayed some aggregation of the Ti centres after the first run (Fig. 2), whereas their activity increased (from 25% to 29% and from 34% to 40% in epoxide yield, respectively).

Isolated Ti sites under tetrahedral or octahedral coordination (with absorption bands between 200 and 300 nm) are therefore suitable for epoxidation reaction in the presence of aqueous H_2O_2. A surface density of 0.2 Ti nm^{-2} seems to be appropriate to obtain high activity silica-based titanium catalysts for epoxidation. Analogously, the high specific surface area of the support (such as in MCM-48) together with the low local water concentration, thanks to the slow addition technique, may play a relevant role in minimizing the aggregation of Ti species on the surface of the catalyst during the reaction time.

Conclusions

Titanocene-grafted mesostructured silica catalysts proved, for the first time, to be sustainable and efficient catalysts in the liquid-phase epoxidation of alkenes with aqueous hydrogen peroxide. Thanks to the application of the dropwise addition of the oxidant solution during the reaction, the side production of allylic oxidation compounds (cyclohexenol and cyclohexenone) is negligible and the selectivity to the desired epoxide is very high. The role of the slow addition of H_2O_2 addition is crucial to avoid, or at least minimise, the useless decomposition of the oxidant and to keep the local water concentration as low as possible. The catalysts can be recovered, reused and the catalytic as well as the spectroscopic properties are almost unchanged (or, sometimes, improved) after one-run recycling.

These results open the way to the exploitation of titanocene-derived systems in highly selective oxidations of other richly functionalised molecules of interest in the synthesis of fine chemicals.

Experimental

Catalysts and materials

Titanocene-grafted catalysts were prepared by grafting titanocene dichloride onto the surface of the mesoporous silica materials as reported previously.[4,7] $Ti(Cp)_2Cl_2$ was dissolved in chloroform and allowed to diffuse into silica. The solid was then exposed *in situ* to triethylamine to activate the nucleophilic substitution of surface silanols onto titanocene. After filtering, Ti(IV) active centres were obtained after calcination under dry oxygen at 550 °C for 3 h.

Three silica materials were used as supports for grafting: SiO_2, a commercial mesoporous non-ordered silica purchased from Davison Grace (Davisil). MCM-41 and MCM-48 were prepared using Aerosil 200 (Degussa) as silica source and cetyltrimethyl ammonium bromide (CTAB) as surfactant. For MCM-41 the mixture molar ratio was: 1 SiO_2/0.1 CTAB, 0.25 NaOH, 20 H_2O. The slurry was maintained at 115 °C for 24 h before being filtered, washed, dried at 80 °C and calcined at 550 °C for 8 h. MCM-48 was prepared as reported previously.[29] For MCM-48 the mixture molar ratio was: 1 SiO_2, 0.175 CTAB, 0.38 NaOH, 120 H_2O. The slurry was maintained at 150 °C for 4 h. The solid precipitate was filtered and subjected to two successive post-synthesis treatments in water at 130 °C for 2 h. The as-synthesized MCM-48 was then filtered, washed, dried at 80 °C and calcined at 550 °C for 8 h. Textural properties of starting SiO_2, calcined MCM-41 and MCM-48, as well as their titanocene-grafted equivalents and their calcined forms named Ti/SiO_2, Ti/MCM-41 and Ti/MCM-48, respectively, are summarised in Table 1. Textural properties of titanium-containing catalysts after one run as catalyst are also reported in Table 1.

Powder X-ray diffraction (XRD) data of materials were obtained on a Bruker AXS D8 diffractometer using Cu Kα radiation and Ni filter.

Nitrogen adsorption/desorption isotherms of materials were measured using a Micromeritics ASAP 2010 instrument. The calcined samples were outgassed at 250 °C, or 120 °C for titanocene-containing samples, until a stable static vacuum of 3×10^{-3} Torr was reached. Mesopore diameters were calculated from the desorption branch of the nitrogen isotherms by the Broekhoff and de Boer (BdB) method,[30] which has been shown to provide reliable results for MCM-41 materials.[31]

UV-Vis diffuse reflectance spectra were obtained in a Varian Cary 05 E UV-Vis-NIR spectrophotometer using $BaSO_4$ as background standard. Ti content was determined by ICP-AES on an Intrepid Iris instrument (Thermo Elemental). The content of organic compounds after catalytic tests was evaluated by thermogravimetric analysis (TGA; Pyris 7HT Perkin Elmer).

Catalytic experiments

All the catalysts were dried at 140 °C under vacuum for 12 h prior to use. The catalyst (200 mg) was added to a solution of cyclohexene (12.5 mmol; Aldrich) in 5 mL of anhydrous solvent (*tert*-butanol or acetonitrile; dried over 3A zeolites). The reaction mixture was heated and stirred at 85 °C in a closed glass reactor, and a solution of H_2O_2 (30% aqueous solution; Riedel-de-Haen) in anhydrous solvent (2.5 mmol H_2O_2 in 1.8 mL of solution) was added dropwise (0.01 mL min^{-1} over 3 h corresponding to 4.17 mmol H_2O_2 h^{-1} g$_{cat}{}^{-1}$) with an automatic dosimetric apparatus. Decane with *tert*-butanol or mesitylene for acetonitrile was added as internal standard. Yields were computed according to the relation:

$$Y\ \mathrm{epox} = [\mathrm{mol\ (obtained\ epoxide)/mol\ (H_2O_2)}] \times 100$$

using pure standards to evaluate the GC response factors. Over the three systems, routine heterogeneity tests were performed (hot filtration and separation of the solid catalysts) to ascertain the heterogeneous character of the catalysts.

During recycling tests, the catalyst was filtered off, washed with fresh solvent, calcined at 500 °C for 1 h under dry air, cooled under vacuum and reused under the same conditions. Catalytic performance was determined on GC analysis (HP6890; HP-5 30m-column; FID detector). The final conversion of H_2O_2 and oxidant efficiency was confirmed by iodometric titration of the final solution.

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