



Use of titanium-containing silica catalysts prepared by rapid and straightforward method in selective oxidations[☆]

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ARTICLE INFO

Article history:

Received 26 April 2012

Received in revised form 20 July 2012

Accepted 23 July 2012

Available online 13 September 2012

Keywords:

Selective oxidation

Titanium–silica catalysts

Citratoperoxotitanate(IV) complex

Hydrogen peroxide

2,3,6-Trimethylphenol

Limonene

Cyclohexene

trans-Stilbene

ABSTRACT

A series of titanium-containing silica catalysts (Ti₄/SiO₂) with small oligomeric Ti centres is obtained by impregnation of the air-stable and water-soluble tetranuclear Ti complex (NH₄)₈[Ti₄(C₆H₄O₇)₄(O₂)₄]·8H₂O onto commercial non-ordered mesoporous silica supports. Catalyst preparation is performed under very mild conditions, with no controlled atmosphere, following a simple, cheap, safe and sustainable methodology. Ti₄/SiO₂ catalysts can be used in the presence of TBHP or aqueous hydrogen peroxide and were tested in the selective oxidation of limonene, cyclohexene, *trans*-stilbene and 2,3,6-trimethylphenol. These catalysts showed performances fully comparable to (or even better than) those obtained with titanium-silicate materials prepared *via* conventional post-synthesis grafting approaches from organometallic precursors.

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1. Introduction

The post-synthesis modification of structured porous oxidic materials is a versatile and accessible method to prepare tailored catalysts with desired properties. Thanks to this approach it is possible to select easily the support with the most suitable features (chemical nature, composition, morphology and stability) and choose the most promising catalytic centres in terms of chemical species, loading, redox ability or acid/base character [1,2]. So, active metal centres can be added to the porous support by grafting, that is by irreversible deposition of a precursor metal species and formation of covalent bonds between the metal site and the support. At the end, the metal centre possesses a different chemical surrounding with respect to the parent precursor, since the coordination shell around the metal centre is partially modified during the deposition *via* covalent bonding and, eventually, during any further thermal treatment [3].

Grafting strategy has been widely exploited for the preparation of titanium–silica catalysts. The catalyst for olefin epoxidation developed by Shell for the styrene monomer-propylene oxide

(SMPO) process is a milestone in the preparation of grafted Ti(IV)–SiO₂ systems. The catalyst is obtained in a multistep gas-phase process by deposition of the Ti precursor (TiCl₄ or an organotitanium compound), heating the obtained material, followed by steaming and silylation [4,5]. The Shell Ti(IV)/SiO₂ catalyst is effective in epoxidation using alkylhydroperoxides as oxidants because of the formation of site-isolated Ti species on the surface of the support and the increased Lewis acidity of the Ti(IV) due to electron withdrawing effect by the siloxy ligands [6]. More recently, an exponential evolution of the post-synthesis grafting strategy was observed in the synthesis of Ti(IV)–silica catalysts where TiCl₄ [7,8], Ti(OiPr)₄ [9–14], Ti(OBu)₄ [15] or Ti(OEt)₄ [16], TiF₄ [17] or Ti(triethanolamine)-isopropoxide [18], were grafted either in liquid or vapour phase onto both ordered (such as MCM-41, MCM-48 and SBA-15) and non-ordered mesoporous silicas. Such systems showed interesting results in the epoxidation of non-functionalised alkenes, dienes and allylic alcohols with *tert*-butylhydroperoxide and aqueous hydrogen peroxide as oxidant, sometimes, under mild conditions [19]. Organometallic and inorganic precursors with an increasing complexity level can also be used, when peculiar characteristics in terms of isolation, dispersion, chemical nature or nuclearity of the catalytically active metal sites are desired: e.g. Ti(η⁵-C₅H₅)₂Cl₂ [20,21], Ti[SiMe₂(η⁵-C₅H₄)₂]₂TiCl₂ [22], [Ti(OiPr)₂(OMent)]₂ and [Ti(OMent)₄] (OMent = 1*R*,2*S*,5*R*-(–)-menthoxo) [23], [(^tBuO)₂Ti{μ-O₂Si[OSi(O^tBu)₃]}₂]₂ [24] or

[☆] Contribution in honour of Prof. Pio Forzatti's 65th birthday.

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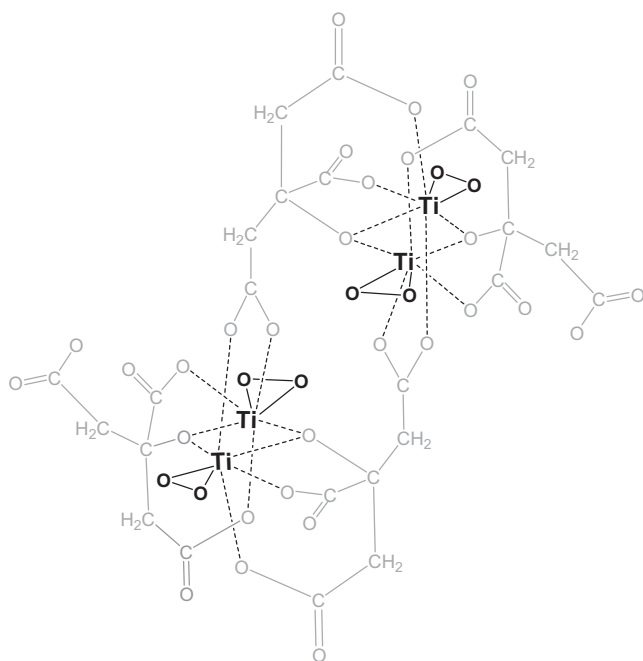


Fig. 1. Schematic structure of $(\text{NH}_4)_8[\text{Ti}_4(\text{C}_6\text{H}_4\text{O}_7)_4(\text{O}_2)_4] \cdot 8\text{H}_2\text{O}$ complex.

$[\text{Ti}_6(\mu_3\text{-O})_6(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{OPh})_6(\text{OEt})_6]$ [25]. In the preparation of these systems, a non-negligible skill is necessary, as most of these inorganic or organometallic precursors require controlled and specific handling conditions (anhydrous conditions, inert atmosphere, absence of protic solvents, use of unfriendly solvents, etc.). For these reasons, in the present work, titanium-based catalysts supported on silica were prepared using a very easy, robust, rapid and safe post synthetic method. $(\text{NH}_4)_8[\text{Ti}_4(\text{C}_6\text{H}_4\text{O}_7)_4(\text{O}_2)_4] \cdot 8\text{H}_2\text{O}$ was used as titanium precursor. It is an air-stable and water-soluble tetranuclear Ti complex prepared by inexpensive and convenient synthesis [26,27] and it is suitable to be considered as a potential easy-to-handle precursor for the preparation of porous grafted titanium-silicate catalysts for the selective oxidation of a series of substrates with different characteristics.

2. Experimental details

2.1. Catalyst preparation

Commercial amorphous Davisil silica and Nippon-Kasei silica were received from the suppliers (Grace Davison; LC60A and Nippon-Kasei). Davisil silica was washed in 1 M aqueous HNO_3 , thoroughly rinsed and dried in oven prior to use. Nippon-Kasei silica was used without any further pre-treatment. MCM-41 mesoporous materials were prepared by hydrothermal synthesis [28], calcined, to remove the templating agent and used as such.

The aqueous solution of tetranuclear ammonium citratoperoxotitanate(IV) complex, $(\text{NH}_4)_8[\text{Ti}_4(\text{C}_6\text{H}_4\text{O}_7)_4(\text{O}_2)_4] \cdot 8\text{H}_2\text{O}$ (Fig. 1) was synthesized according to the literature protocol [26]. In a typical synthesis 0.20 g of Ti powder (Fluka; 99.7%) was stirred in a cold aqueous (ultrapure deionized water; Millipore MilliQ) solution containing 16 mL of 30% aqueous hydrogen peroxide (Aldrich) and 4 mL of 30% aqueous ammonia solution (Carlo Erba reagents) to yield a yellowish transparent solution. Then, an equimolar amount of citric acid (0.80 g; Carlo Erba; p.a.) was added and stirred until complete dissolution to give a yellow brilliant solution. The solution is used as such, without any further treatment (Ti content ca. 5 g L^{-1}).

$\text{Ti}_4/\text{SiO}_2\text{-D}$ and $\text{Ti}_4/\text{SiO}_2\text{-N}$ catalysts were prepared by impregnation at the rotary evaporator at room temperature of an aliquot of the aqueous solution, described above, of the complex $(\text{NH}_4)_8[\text{Ti}_4(\text{C}_6\text{H}_4\text{O}_7)_4(\text{O}_2)_4] \cdot 8\text{H}_2\text{O}$ (mixed to ultrapure deionized water to obtain the desired final Ti loading on the solid) onto Davisil silica and Nippon-Kasei silica, respectively. The impregnated samples were calcined at 550°C for 3 h under oxygen flow (20 mL min^{-1}). $\text{Ti}/\text{SiO}_2\text{-D}$ and $\text{Ti}/\text{MCM-41}$ catalysts were used as reference catalysts and were prepared by grafting $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2$ as described in previous literature [20,21].

2.2. Catalyst characterization

Titanium content in the catalysts was determined by ICP-AOS spectroscopy (Intrepid Iris, Thermo Elemental), after dissolution of the solid matrix with a HF-HNO_3 digestion mixture.

BET specific surface area, pore size distribution and total pore volume were obtained by nitrogen adsorption-desorption isotherms at 77 K, using a Micromeritics ASAP 2010 analyser or ASAP 2400 instrument. Before the adsorption, the solids were pre-heated under high vacuum in three steps: 1 h at 423 K, 1 h at 513 K, and finally 4 h at 623 K. Diffuse reflectance (DR) UV-vis spectra were recorded on a Shimadzu 2501PC spectrophotometer.

2.3. Catalytic tests

All the catalysts were dried and calcined at 500°C under dry air flow for 1 h prior to use. In all cases, samples of the reaction mixture were taken at periodic intervals and the catalytic performance was determined by GC analysis (HP6890; HP-5 30m-column; FID and GC "Tsvet 500"; $30 \text{ m} \times 0.25 \text{ mm}$ Supelco MDN-5S column; FID). GC-MS analyses were performed using a gas chromatograph Agilent 6890 (quartz capillary column $30 \text{ m} \times 0.25 \text{ mm}/\text{HP-5 ms}$) equipped with a quadrupole mass-selective detector Agilent MSD 5973. ^1H NMR spectra were recorded on an MSL-400 Bruker spectrometer.

The epoxidation tests on (*R*)-(+)-limonene (1 mmol; 97% Aldrich; 98% e.e.) were carried out in a glass batch reactor at 85°C using ethyl acetate (Carlo Erba, RPE) as solvent (5 mL; previously dried over 3A zeolites), in the presence of the catalyst (50 mg, that is ca. 0.02 mmol Ti), anhydrous *tert*-butylhydroperoxide as oxidant (TBHP; Aldrich, 5 M solution in decane; oxidant to limonene molar ratio = 1.1) and mesitylene as internal standard.

The epoxidation tests on *trans*-stilbene (1 mmol; Aldrich, 96%) were carried out in a glass batch reactor at 90°C using acetonitrile (Sigma-Aldrich; for HPLC) as solvent (5 mL; previously dried over 3A zeolites) in the presence of the catalyst (100 mg, that is ca. 0.04 mmol Ti), anhydrous TBHP (oxidant to stilbene molar ratio = 1.2) and mesitylene as internal standard.

The epoxidation tests on cyclohexene (2.5 mmol; Aldrich, 99%) were carried out in a glass batch reactor at 90°C using acetonitrile as solvent (5 mL) in the presence of the catalyst (100 mg, corresponding to ca. 0.04 mmol Ti) and mesitylene as internal standard. A solution of H_2O_2 (30% aqueous solution; Riedel-de-Haen) in acetonitrile (1 mmol H_2O_2 in 1.8 mL of solution) was added dropwise (0.01 mL min^{-1} over 3 h, corresponding to $3.33 \text{ mmol H}_2\text{O}_2 \text{ h}^{-1} \text{ g}_{\text{cat}}^{-1}$) with an automatic dosimetric apparatus. At the end of the addition, the initial cyclohexene to oxidant molar ratio was 2.5. Yields were computed according to the relation (oxidant as limiting agent):

$$Y_{\text{epox}} = \left[\frac{\text{mol}(\text{obtained epoxide})}{\text{mol}(\text{added H}_2\text{O}_2)} \right] \times 100$$

using pure standards to evaluate the GC response factors.

The oxidation tests on 2,3,6-trimethylphenol (TMP; Fluka 98%) were performed under vigorous stirring (500 rpm) in thermostated

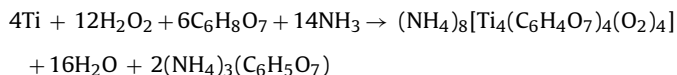
glass vessels at 80 °C for 20–30 min. Typically, the reactions started by adding 0.35 mmol H₂O₂ (30 wt.% in water; determined iodometrically) to a mixture containing 0.1 mmol of TMP, the catalyst (0.006 mmol of Ti), the internal standard (biphenyl; Aldrich 99%) and 1 mL of acetonitrile.

In the tables displaying the catalytic performance, a standard deviation of ±2%, ±4% and ±4% has to be considered on average for the conversion, selectivity and yield values, respectively. The presence of H₂O₂ in the final reaction mixture and the oxidant efficiency was checked by iodometric tests and titrations on the final solutions.

3. Results and discussion

3.1. Catalyst preparation

The aqueous solution containing the tetranuclear citratoperoxotitanate(IV) complex having the chemical formula (NH₄)₈[Ti₄(C₆H₄O₇)₄(O₂)₄]·8H₂O was easily obtained starting directly from metallic titanium dispersed in water in the presence of hydrogen peroxide and citric acid according to the following reaction [26]:



The limpid yellow solution was directly employed as an impregnation solution to deposit the tetranuclear Ti(IV) complex onto the desired silica support by means of a rotary evaporator to get a uniformly coloured light yellow powder. The use of the impregnation solution within the 24 h after the preparation was of crucial importance, since this titanium(IV) peroxocomplex is unstable (the mother solution turns into a yellowish milky suspension after 1 day) and slowly hydrolyses to produce polymers of titanium oxide hydrates, that might lead to uneven large TiO₂ agglomerates during the grafting [27]. The final Ti(IV)-silica catalyst was obtained by a calcination treatment under oxygen in order to remove the organic citrate moieties and the ammonium-containing species, as confirmed by C,H,N elemental analysis (total carbon and nitrogen below detection limit, respectively, in all cases after calcination).

It is worth highlighting the straightforwardness of the catalyst preparation, as the whole procedure was performed under very mild conditions, by using basic laboratory equipment (magnetic stirrer and standard rotary evaporator) with no controlled atmosphere, no heating devices (during grafting) and no use of organic solvents. In addition, the supports here used are commercially available silica materials. Such preparation approach was somehow envisaged in a previous literature work where the tetranuclear Ti(IV)-peroxocomplex was deposited onto a low-surface area silica [29]. Nevertheless, the present methodology, starting directly from metallic Ti, represents a clear advantage, since it is less time-consuming and more environmentally friendly with respect to several other approaches for the synthesis of Ti-containing grafted mesoporous silica catalysts reported in literature so far.

Two series of Ti-SiO₂ catalysts were prepared in various batches, by varying the Ti content in the impregnation solution and aiming at obtaining a final Ti loading of ca. 1 wt.% and 2 wt.%. The samples were named Ti-SiO₂-X-1 and Ti-SiO₂-X-2, respectively.

For the sake of simplicity, catalysts prepared from tetranuclear citratoperoxotitanate(IV) complex *via* grafting are named Ti₄-SiO₂-X catalysts. However, this does not necessarily mean that the tetranuclear Ti₄ core of the original cluster was kept after the grafting and the following calcination (v. Section 3.2).

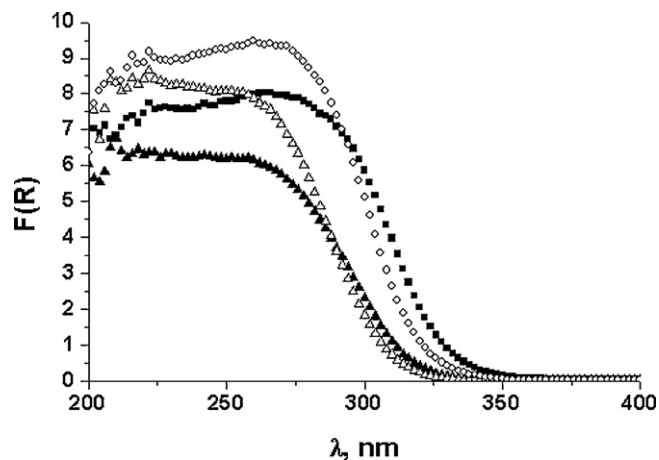


Fig. 2. DR UV-vis spectra of Ti₄/SiO₂-D-1 (Δ), Ti₄/SiO₂-D-2 (◇), Ti₄/SiO₂-N-1 (▲) and Ti₄/SiO₂-N-2 (■). All samples were calcined prior to measurements.

3.2. Catalyst characterization

The textural data of the mesoporous silica supports and of some representative grafted Ti-silica catalysts are summarised in Table 1. The elemental analysis data for the catalysts are also reported there. All the silica starting materials had a medium-high or high specific surface area and this favoured a good dispersion of the Ti species on the support. In general, the specific surface area, pore volume and mean mesopore diameter values showed a slight decrease after the grafting procedure. This is due to the deposition of homogeneous thin layers of titanium-containing species onto the inner surface of mesopores, as already described in previous reports [25,30]. Nevertheless, in none case a dramatic drop of pore volume was observed. This is an evidence that no mesopores have been blocked or plugged after the deposition of the titanium(IV) peroxocomplex precursor.

DR UV-vis spectra of the grafted catalysts obtained from citratoperoxotitanate(IV) complex with ca. 1 and 2 wt.% Ti content over Davisil (D) and Nippon-Kasei (N) silica supports are shown in Fig. 2. Even for the low Ti content samples (1 wt.%), along with small adsorption at ca. 210–220 nm, which is characteristic of site isolated Ti(IV), the spectra show a broad absorption band centred around 260 nm, suggesting the presence of titanium oxidic aggregates with a dimeric or oligomeric nature [31,32]. The tetranuclear titanium core of the pristine complex was likely destroyed during the calcination treatment. Nevertheless, spectroscopic data suggest that no complete dissociation of the polynuclear Ti(IV) precursor occurred to produce isolated Ti species during the grafting and calcination procedure. The DRS UV-vis band shifted to longer wavelengths with increasing Ti loading in the samples, indicating a further condensation of Ti species on the silica surface. However, no anatase microcrystallites, which are manifested by a characteristic absorption at 330–340 nm, were identified. These results are therefore consistent with a final structure consisting of a few Ti atoms bonded through bridging oxygen atoms, similar to that observed by EXAFS on analogous systems used for gas-phase epoxidation reactions [29].

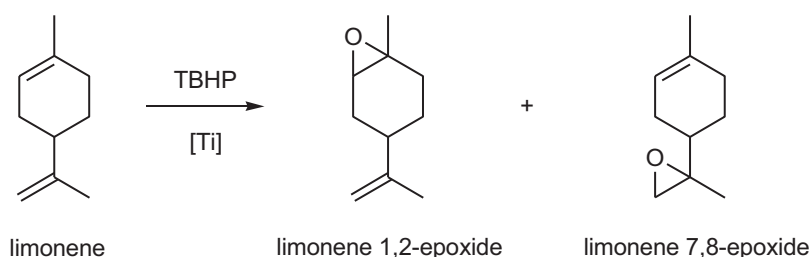
3.3. Evaluation of the catalytic performance

3.3.1. Limonene epoxidation

The epoxidation of limonene is considered a suitable reaction to evaluate the oxidation properties of the prepared catalysts on a model unsaturated terpene (Scheme 1). In addition, limonene epoxide is an important building block for the synthesis of several products from renewable sources and, in particular, of a new biodegradable polymer, such as polylimonene carbonate [33]. The

Table 1
Textural properties of the catalysts.

Support/catalyst	Ti content (wt.%)	BET surface area, S ($\text{m}^2 \text{g}^{-1}$)	Pore volume, V ($\text{cm}^3 \text{g}^{-1}$)	Mean pore diameter, D (nm)
SiO ₂ -D	–	529	0.88	5.4
SiO ₂ -N	–	679	0.66	3.8
MCM-41	–	972	0.65	2.6
Ti ₄ /SiO ₂ -D-1	1.26	493	0.83	5.3
Ti ₄ /SiO ₂ -D-2	2.35	488	0.82	5.3
Ti ₄ /SiO ₂ -N-1	1.19	650	0.52	3.6
Ti ₄ /SiO ₂ -N-2	1.89	602	0.49	3.2
Ti/SiO ₂ -D	1.75	499	0.85	5.2
Ti/MCM-41	1.88	861	0.53	2.4

**Scheme 1.**

results for the catalytic limonene epoxidation with anhydrous TBHP in the presence of Ti₄/SiO₂ catalysts and of two reference grafted catalysts, Ti/SiO₂-D and Ti/MCM-41 are shown in Table 2.

As expected, limonene 1,2-epoxide was more abundant than limonene 7,8-epoxide over all the catalysts, since the endocyclic C=C bond is richer in electronic density than the exocyclic one. Titanium(IV) peroxocomplex-derived catalysts (Ti₄/SiO₂-D and Ti₄/SiO₂-N) showed better (or, at least, comparable) conversion values, during the reaction (24 h), than conventionally grafted catalysts taken as references. However, taking into account the initial specific activity (TOF values after 1 h; Table 2), all the Ti₄/SiO₂ catalysts showed a comparable behaviour, that is slightly lower to the one of reference grafted catalysts. Then, if one considers the turnover number (TON) at the end of the tests, Ti₄/SiO₂ samples with a lower Ti loading (*ca.* 1 wt.%) were more active than 2 wt.% ones (49 and 52 TON vs. 29 and 29 TON, respectively). These results are consistent with the observation that, when the precursor is evenly dispersed on silica, thanks to the high specific surface area of the support, the presence of some oligomeric octahedral Ti species (as evidenced by DRS UV-vis spectra too) is not detrimental to the epoxidation mechanism, at least under these conditions [11,34]. With regard to the selectivity to limonene epoxide, Ti₄/SiO₂ catalysts displayed better results than reference Ti-silica samples. In fact, a lower amount of acid-catalysed rearrangement by-products (such as carvone) occurred and selectivity values higher than 80% were obtained. This behaviour suggests that the acidic character of

Ti₄/SiO₂ systems was less marked than the one of Ti/SiO₂ [6,35]. Iodometric measurements on the final mixtures revealed that in none of the tests TBHP had been the limiting agent of the reaction and the oxidant efficiency (the amount of oxidised products obtained per amount of consumed oxidant) was in all cases very high (always higher than 90%).

So, for limonene epoxidation, Ti₄/SiO₂ catalysts can represent an interesting alternative to reference grafted titanosilicate solids prepared *via* conventional Ti(η^5 -C₅H₅)₂Cl₂ grafting.

3.3.2. Stilbene epoxidation

The catalysts were also tested in the epoxidation of *trans*-stilbene in the presence of TBHP (Scheme 2). *trans*-Stilbene is a further model substrate for epoxidation over mesoporous redox-active catalysts, as it is bulky (it cannot be converted on conventional TS-1), it does not possess allylic positions to be oxidised and the possible formation of *cis*-epoxides (from the alkene in *trans* configuration) reveals the occurrence of free-radical epoxidation mechanisms [20,36].

The results of stilbene epoxidation with anhydrous TBHP over of Ti₄/SiO₂ catalysts and reference grafted catalysts are reported in Table 3. In terms of initial conversion and activity (within the first hour of reaction), the catalysts prepared from supports with higher specific surface area showed higher conversion values (namely, Ti₄/SiO₂-N-1, Ti₄/SiO₂-N-2 and Ti/MCM-41). Then, for longer reaction times, catalysts of the Ti₄/SiO₂-N series gave the

Table 2
Catalytic performance of Ti-containing catalysts in limonene epoxidation.

Catalyst	Ti content (wt.%)	Conversion 1 h (%)	Conversion 24 h (%)	TOF ^a 1 h (h^{-1})	TON ^b 24 h	epox Sel ^c 24 h (%)
Ti ₄ /SiO ₂ -D-1	1.26	18	65	14	49	85
Ti ₄ /SiO ₂ -D-2	2.35	40	72	16	29	81
Ti ₄ /SiO ₂ -N-1	1.19	20	65	16	52	82
Ti ₄ /SiO ₂ -N-2	1.89	26	57	13	29	83
Ti/SiO ₂ -D	1.75	33	61	18	32	74
Ti/MCM-41	1.88	42	68	21	33	62

Reaction conditions: 5 mL ethylacetate solvent, 50 mg catalyst, TBHP:limonene molar ratio = 1.1, 85 °C, 24 h.

^a TOF: turnover frequency after 1 h ($[\text{mol converted limonene}]/([\text{mol Ti}][\text{time}])$).

^b TON: turnover number after 24 h ($[\text{mol converted limonene}]/[\text{mol Ti}]$).

^c Selectivity to endocyclic 1,2-monoepoxide.

Table 4
Catalytic performance of Ti-containing catalysts in cyclohexene epoxidation.

Catalyst	Ti content (wt.%)	epox yield ^a 3 h (%)	epox Sel ^b 3 h (%)	TON ^c 3 h
Ti ₄ /SiO ₂ -D-1	1.26	26	>98	10
Ti ₄ /SiO ₂ -D-2	2.35	24	90	5
Ti ₄ /SiO ₂ -N-1	1.19	35	95	13
Ti ₄ /SiO ₂ -N-2	1.89	30	96	8
Ti/SiO ₂ -D	1.75	28	>98	8
Ti/MCM-41	1.88	34	>98	9

Reaction conditions: 5 mL acetonitrile solvent, 100 mg catalyst, cyclohexene:H₂O₂ molar ratio = 2.5, oxidant addition = 3.33 mmol H₂O₂ h⁻¹ g_{cat}⁻¹, 90 °C, 3 h.

^a Yield of cyclohexene epoxide after 3 h.

^b Selectivity to cyclohexene epoxide after 3 h.

^c TON: turnover number after 3 h ([mol converted cyclohexene]/[mol Ti]).

acid, according to a potential alternative route where cyclohexene epoxide replaces cyclohexanone [38].

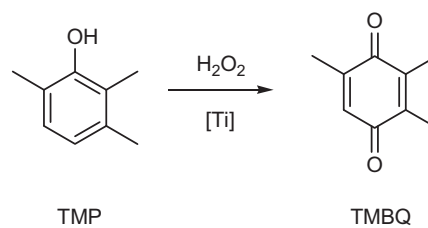
The data of cyclohexene epoxidation in the presence of aqueous hydrogen peroxide over Ti₄/SiO₂ catalysts and two reference Ti/SiO₂-D and Ti/MCM-41 catalysts are shown in Table 4. In all tests, hydrogen peroxide was added dropwise, following a strictly controlled addition rate (3.33 mmol H₂O₂ h⁻¹ g_{cat}⁻¹). A minimal local H₂O₂ concentration in the surroundings of Ti sites is indeed crucial to avoid a fast deactivation of the catalyst and the formation of large amounts of free-radical species leading to undesired side products [39]. In addition, the dropwise addition of the oxidant minimized the unproductive decomposition of hydrogen peroxide and, under these conditions, the oxidant efficiency proved to be rather good, with values spanning from ca. 60% to 75%.

In all tests, a high selectivity (>90%) in cyclohexene epoxide was obtained at the end of the slow H₂O₂ after 3 h. Nevertheless, some cyclohex-2-enol, cyclohex-2-enol and cyclohexane-1,2-diol has been detected with Ti₄/SiO₂-D-2, Ti₄/SiO₂-N-1 and Ti₄/SiO₂-N-2. This behaviour confirms that well dispersed, virtually isolated Ti(IV) sites (as those obtained by grafting Ti(η⁵-C₅H₅)₂Cl₂) are the optimal loci for this kind of epoxidation reaction [39,40]. With regard to cyclohexene epoxide yield, the Ti₄/SiO₂ systems are, on average, comparable to reference Ti/SiO₂ catalysts. However, Ti₄/SiO₂-N catalysts gave rise to sensibly higher epoxide yields than Ti₄/SiO₂-D and this can be due to the larger specific surface area of SiO₂-N support and hence to the better dispersion of Ti centres in the former systems than the latter ones. In fact, Ti₄/SiO₂-N-1, with the highest specific surface area (Table 1), but with the lowest Ti content as well (1.19 wt.%), showed the highest epoxide yield (35%) and the highest activity over 3 h, which is even better than the performance obtained on Ti/MCM-41.

So, for this reaction and under these conditions, Ti₄/SiO₂ catalysts display a catalytic performance that is, on average, comparable or superior to the one achieved on reference systems.

3.3.4. 2,3,6-Trimethylphenol oxidation

Some of us have recently investigated in detail the oxidation reaction of 2,3,6-trimethylphenol (TMP) into 2,3,5-trimethyl-1,4-benzoquinone (TMBQ, a key intermediate of vitamin E) (Scheme 4), using as catalysts mesoporous titanium-silica materials obtained by hydrothermal synthesis [41,42] or prepared by grafting titanocene dichloride onto the surface of commercial silica [43,44]. Very high selectivity for the main product TMBQ (up to 100%, in the best cases) at complete conversion of TMP was achieved in the presence of titanium-grafted catalysts (Ti/SiO₂). A strong dependence of the product selectivity on the surface concentration of titanium active centres was revealed and, for this peculiar reaction, the advantages of titanium cluster-site catalysts over titanium single-site catalysts in hydrogen peroxide based selective oxidation reaction was highlighted [44,45].



Scheme 4.

The results of the catalytic TMP oxidation with 30% aqueous H₂O₂ in the presence of Ti₄/SiO₂ catalysts are summarized in Table 5. The results acquired using conventionally grafted catalysts, Ti/SiO₂-N and Ti/MCM-41 (with different Ti surface concentrations), are appended for comparison. In this case, aqueous hydrogen peroxide was introduced in a single aliquot with no need of dropwise addition of the oxidant (slow oxidant addition was necessary for cyclohexene epoxidation; v. Section 3.3.3, but it is detrimental for the TMP oxidation [41]). The oxidant efficiency was rather high in these experiments, with values around 75%, fully in line with other previous measurements [44].

The TMP conversion was very close to 100% for all catalysts after 30 min. In terms of turn-over frequency (TOF), the differences were more marked: conventional Ti/MCM-41 showed higher activity (TOF = 2.7 min⁻¹) than Ti₄/SiO₂ materials (TOF = 1.6–2.2 min⁻¹). This might be explained either by some gradual reduction of the number of accessible Ti sites in the supported cluster species or by changes in the nature of the active site (e.g., altering coordination number of Ti(IV) from 4 in a single site to 5 in a dinuclear centre), hence affecting the oxidising capacity of the Ti site in the oxidation of the coordinated substrate molecule [44]. However, in terms of selectivity to TMBQ, the performance over Ti₄/SiO₂ catalysts was far better than over reference conventional Ti/SiO₂ systems that comprise site-isolated Ti centres. In fact, the quinone was practically the only product when the titanium(IV) peroxocomplex was used as precursor, whereas larger amounts of side products (mostly, 2,2',3,3',5,5'-hexamethyl-4,4'-biphenol and 2,3,6-trimethyl-4-(2,3,6-trimethyl)phenoxyphenol, originated from C–C and C–O coupling of intermediate phenoxy radicals [46]) were detected over Ti/SiO₂-N and Ti/MCM-41 with comparable Ti loading, in the range from 1 to 2 wt.%. This is therefore a confirmation that clustered polynuclear Ti sites (such as those obtained from tetranuclear Ti peroxocitrate complex) show, at least in this particular reaction, superior performance with respect to isolated Ti single sites [44]. In fact, while for Ti/silica catalysts prepared using mononuclear Ti precursor (Ti/SiO₂-N and Ti/MCM-41) the selectivity to TMBQ increased with increasing Ti surface concentration, the use of the polynuclear Ti peroxocomplex precursor gave excellent selectivities even at rather low Ti loadings and, hence, at low Ti surface concentrations. The close proximity of Ti sites with one another is therefore an important prerequisite to obtain TMBQ in nearly quantitative yields.

3.4. Evaluation of the heterogeneous nature and recyclability of the catalysts

The heterogeneous nature of the citratoperoxotitanate(IV)-derived silica catalysts was verified under the conditions used in the reaction described above. Hot filtration tests followed by separation of the solid catalyst were performed and the resulting solution was tested in catalysis to evaluate any leaching of active homogeneous Ti species. In no case, homogeneous and catalytically active Ti species were formed in the presence of aqueous hydrogen peroxide or dry TBHP.

Table 5
Catalytic performance of Ti-containing catalysts in TMP oxidation.

Catalyst	Ti content (wt.%)	Ti surface concentration ^a (Ti atom nm ⁻²)	TMP conversion (%)	TMBQ selectivity (%)	TOF _{TMP} ^b (min ⁻¹)
Ti ₄ /SiO ₂ -D-1	1.26	0.30	99	96	2.0
Ti ₄ /SiO ₂ -D-2	2.18	0.52	97	100	2.2
Ti ₄ /SiO ₂ -N-1	1.19	0.22	96	99	1.6
Ti/SiO ₂ -N	2.09	0.38	97	91	1.4
Ti/MCM-41	2.00	0.26	98	77	2.7
Ti/MCM-41	0.95	0.12	97	47	2.7

Reaction conditions: 0.1 M TMP, 0.35 H₂O₂, 0.006 mmol Ti catalyst, 1 mL acetonitrile solvent, 80 °C, 30 min.

^a Estimation based on BET surface area of the support and Ti content.

^b (moles of TMP consumed)/(moles of Ti × time), determined from the initial rates of TMP consumption.

Ti₄/SiO₂ catalysts were easily recovered by filtration, washed, calcined and reused, at least, in a second catalytic run. The calcination step at 500 °C was necessary to remove the organic by-products (ca. 2–5 wt.%, as shown by TGA analysis) that lead to deactivation of the Ti centres and to regenerate the chemical environment of the catalytic sites. The recycled catalysts kept their oxidation ability. In particular, reused Ti₄/SiO₂ systems showed a small loss (ca. 8–10%) of activity for limonene and *trans*-stilbene with respect to fresh catalyst. For cyclohexene epoxidation, fully comparable or even slightly better activity with respect to the first run was recorded. For TMP oxidation, the catalysts were reused in several consecutive catalytic runs and solids with a higher Ti concentration showed to be more stable to deactivation than the catalysts with a lower Ti loading.

In general, no remarkable changes in selectivity to desired products were observed over the reused catalysts with respect to the values obtained on fresh systems.

4. Conclusions

The impregnation in aqueous solution of tetranuclear citratoperoxotitanate(IV) complex over commercial non-ordered mesoporous silica proved to be a simple, cheap and sustainable method to synthesize active catalysts for the selective oxidation of different classes of organic substrates. Such kind of Ti(IV)-containing catalysts can be prepared in a straightforward, safe and reproducible way over a broad variety of supports (either commercial or custom-made), since no rigorously controlled reaction conditions, no special handling and no uncommon reagents are required.

Ti₄/SiO₂ catalysts can be used in the presence of TBHP or aqueous hydrogen peroxide and they showed, in general, catalytic performances fully comparable to or, in some peculiar cases, even better than those obtained with titanium-silicate materials prepared via conventional post-synthesis grafting approaches from organometallic precursors. In particular, Ti₄/SiO₂ are suitable oxidation catalysts for those application in which a strict Ti(IV) site isolation is not mandatory and where, on the contrary, the presence of oligomeric TiO_x species is beneficial.

For these reasons, citratoperoxotitanate(IV)-derived silica catalysts can be considered a valid alternative to costly ordered mesoporous titanosilicates as catalysts for the selective oxidation of a broad range of substrates with different characteristics.

Acknowledgements

C.P., M.G., V.D.S. and R.P. acknowledge financial support from EC 7th Framework Programme through the Marie Curie Initial Training Network NANO-HOST (Grant Agreement No. 215193) and of the Italian Ministry of Education, University and Research through the Project "ItalNanoNet" (Rete Nazionale di Ricerca sulle Nanoscienze; Prot. No. RBPR05JH2P).

References

- [1] V. Dal Santo, M. Guidotti, R. Psaro, L. Marchese, F. Carniato, C. Bisio, Proceedings of the Royal Society A 468 (2012) 1904.
- [2] V. Dal Santo, F. Liguori, C. Pirovano, M. Guidotti, *Molecules* 15 (6) (2010) 3829.
- [3] C. Louis, M. Che, Anchoring and grafting of coordination metal complexes onto oxide supports, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), *Preparation of Solid Catalysts*, Wiley-VCH, Weinheim, 1999, p. 341.
- [4] R.A. Sheldon, M.C.A. van Vliet, in: R.A. Sheldon, H. van Bekkum (Eds.), *Fine Chemicals through Heterogeneous Catalysis*, Wiley-VCH, Weinheim, 2001, p. 473.
- [5] J.F.K. Buijink, J.J.M. VanVlaanderen, M. Crocker, F.G.M. Niele, *Catalysis Today* 93–95 (2004) 199.
- [6] R.A. Sheldon, J. Dakka, *Catalysis Today* 19 (1994) 215.
- [7] F. Chiker, F. Launay, J.P. Nogier, J.L. Bonardet, *Green Chemistry* 5 (2003) 318.
- [8] K.T. Li, C.C. Lin, P.H. Lin, Propylene epoxidation with ethylbenzene hydroperoxide over Ti-containing catalysts prepared by chemical vapor deposition, in: S.T. Oyama (Ed.), *Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis*, Elsevier, Amsterdam, 2008, p. 373.
- [9] S. Srinivasan, A.K. Datye, M.H. Smith, C.H.F. Peden, *Journal of Catalysis* 145 (1994) 565.
- [10] C. Cativiela, J.M. Fraile, J.I. Garcia, J.A. Mayoral, *Journal of Molecular Catalysis A* 112 (1996) 259.
- [11] A.O. Bouh, G.L. Rice, S.L. Scott, *Journal of the American Chemical Society* 121 (1999) 7201.
- [12] M.S. Morey, S. O'Brien, S. Schwarz, G.D. Stucky, *Chemistry of Materials* 12 (2000) 898.
- [13] N.V. Maksimchuk, M.S. Melgunov, J. Mrowiec-Białoń, A.B. Jarzębski, O.A. Khold-eeva, *Journal of Catalysis* 235 (2005) 175.
- [14] M.C. Capel-Sanchez, J.M. Campos-Martin, J.L.G. Fierro, *Journal of Catalysis* 234 (2005) 488.
- [15] W.S. Ahn, D.H. Lee, J.H. Kim, G. Seo, R. Ryoo, *Applied Catalysis A: General* 181 (1999) 39.
- [16] Q. Yuan, A. Hagen, F. Roessner, *Applied Catalysis A: General* 303 (2006) 81.
- [17] E. Jorda, A. Tuel, R. Teisser, J. Kervennal, *Journal of Catalysis* 175 (1998) 93.
- [18] L. Barrio, J.M. Campos-Martin, M.P. de Frutos-Escrig, J.L.G. Fierro, *Microporous and Mesoporous Materials* 113 (2008) 542.
- [19] J.M. Fraile, J.I. Garcia, J.A. Mayoral, E. Vispe, *Applied Catalysis A: General* 245 (2003) 363.
- [20] R.D. Oldroyd, J.M. Thomas, T. Maschmeyer, P.A. MacFaul, D.W. Snelgrove, K.U. Ingold, D.D.M. Wayner, *Angewandte Chemie International Edition* 35 (1996) 2787.
- [21] M. Guidotti, N. Ravasio, R. Psaro, G. Ferraris, G. Moretti, *Journal of Catalysis* 214 (2003) 242.
- [22] P. Ferreira, I.S. Goncalves, F.E. Kühn, M. Pillinger, J. Rocha, A.M. Santos, A. Thursfield, *European Journal of Inorganic Chemistry* (2000) 551.
- [23] Y. Perez, D.P. Quintanilla, M. Fajardo, I. Sierra, I. del Hierro, *Journal of Molecular Catalysis A: Chemical* 271 (2007) 227.
- [24] R.L. Brutchey, B.V. Mork, D.J. Sirbully, P. Yang, T. Don Tilley, *Journal of Molecular Catalysis A: Chemical* 238 (2005) 1.
- [25] A. Tuel, L.G. Hubert-Pfalzgraf, *Journal of Catalysis* 217 (2003) 343.
- [26] M. Kakihana, M. Tada, M. Shiro, V. Petrykin, M. Osada, Y. Nakamura, *Inorganic Chemistry* 40 (2001) 891.
- [27] M. Kakihana, M. Kobayashi, K. Tomita, V. Petrykin, *Bulletin of the Chemical Society of Japan* 83 (11) (2010) 1285.
- [28] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, *Journal of the American Chemical Society* 114 (1992) 10834.
- [29] N. Mimura, S. Tsubota, K. Murata, K.K. Bando, J.J. Bravo-Suárez, M. Haruta, S.T. Oyama, *Catalysis Letters* 110 (2006) 47.
- [30] M. Guidotti, L. Conti, A. Fusi, N. Ravasio, R. Psaro, *Journal of Molecular Catalysis A* 182–183 (2002) 151.
- [31] P. Ratnasamy, D. Srinivas, H. Knozinger, *Advances in Catalysis* 48 (2004) 1.
- [32] L. Marchese, T. Maschmeyer, E. Gianotti, S. Coluccia, J.M. Thomas, *Journal of Physical Chemistry B* 101 (1997) 8836.
- [33] C.M. Byrne, S.D. Allen, E.B. Lobkovsky, G.W. Coates, *Journal of the American Chemical Society* 126 (2004) 11404.

- [34] A. Lundin, I. Panas, E. Ahlberg, *Journal of Physical Chemistry A* 113 (2009) 282.
- [35] A. Bhaumik, T. Tatsumi, *Journal of Catalysis* 182 (1999) 349.
- [36] M. Selvaraj, K.S. Seshadri, A. Pandurangan, T.G. Lee, *Microporous and Mesoporous Materials* 79 (2005) 261.
- [37] K. Smith, G.A. El-Hiti, M. Al-Shamali, *Catalysis Letters* 109 (2006) 77.
- [38] K. Sato, M. Aoki, R. Noyori, *Science* 281 (1998) 1646.
- [39] M. Guidotti, C. Pirovano, N. Ravasio, B. Lázaro, J.M. Fraile, J.A. Mayoral, B. Coq, A. Galarneau, *Green Chemistry* 11 (2009) 1421.
- [40] M.C. Capel-Sanchez, J.M. Campos-Martin, J.L.G. Fierro, M.P. de Frutos, A. Padilla Polo, *Chemical Communications* (2000) 855.
- [41] N.N. Trukhan, V.N. Romannikov, E.A. Paukshtis, A.N. Shmakov, O.A. Kholdeeva, *Journal of Catalysis* 202 (2001) 110.
- [42] O.A. Kholdeeva, M.S. Melgunov, A.N. Shmakov, N.N. Trukhan, V.V. Kriventsov, V.I. Zaikovskii, M.E. Malyshev, V.N. Romannikov, *Catalysis Today* 91–92 (2004) 205.
- [43] O.A. Kholdeeva, I.D. Ivanchikova, M. Guidotti, N. Ravasio, *Green Chemistry* 9 (2007) 731.
- [44] O.A. Kholdeeva, I.D. Ivanchikova, M. Guidotti, C. Pirovano, N. Ravasio, M.V. Barmatova, Y.A. Chesalov, *Advanced Synthesis and Catalysis* 351 (2009) 1877.
- [45] O.A. Kholdeeva, I.D. Ivanchikova, M. Guidotti, N. Ravasio, M. Sgobba, M. Barmatova, *Catalysis Today* 141 (2009) 330.
- [46] O.V. Zalomaeva, N.N. Trukhan, I.D. Ivanchikova, A.A. Panchenko, E. Roduner, E.P. Talsi, A.B. Sorokin, V.A. Rogov, O.A. Kholdeeva, *Journal of Molecular Catalysis A: Chemical* 277 (2007) 185.