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Niobium metallocenes deposited onto mesoporous silica via dry impregnation as catalysts for selective epoxidation of alkenes

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ABSTRACT

A series of niobium catalysts for the selective epoxidation was synthesised by post-synthesis modification of a commercial silica, starting from niobocene dichloride through solventless organometallic precursor dry impregnation (OM-DI) or conventional liquid-phase grafting technique. OM-DI showed to be cheaper, more versatile, less time-consuming and avoided the use of environmentally unfriendly chlorinated solvents. Nb–SiO_2 catalysts displayed an excellent performance in the epoxidation of limonene, using aqueous hydrogen peroxide as oxidant. Niobium–silica catalysts were obtained via OM-DI for the first time in this occasion. They showed conversions up to 78% and chemoselectivity to epoxide of 98%. An unexpected regioselectivity to exocyclic epoxide was also observed.

1. Introduction

Titanium-based mesoporous silica catalysts have displayed, in last decades, potentially interesting results in the selective epoxidation of alkenes with organic hydroperoxides [1–7]. This kind of oxidants is generally able to selectively epoxidise the alkenes via radical-free heterolytic oxidation mechanisms. The use of them over porous supports with large or very large pore openings (from 2 to 50 nm) has opened the way to the potential synthesis of epoxide from bulky and highly functionalised alkenes of interest for the fine and high added-value chemistry. Unfortunately, most of these catalysts suffer from rapid deactivation in the presence of water and aqueous media, and the use of hydrogen peroxide therefore leads to poor results [8–11]. The structural instability of titanium–silica systems, in fact, grows in parallel with the hydrophilicity of the surface and the defectiveness of the silica matrix [12,13]. Since mesoporous silica materials are non-crystalline solids with a high hydrophilic nature, all these intrinsic drawbacks have limited any possible exploitation of these systems on a commercial large scale so far [7]. On the contrary, the study of niobium-based silicates for liquid-phase oxidation deserves a more careful attention, even though a lower number of research teams have focused their attention on them [14,15]. The stability and the robustness of Nb–SiO_2 catalysts towards metal leaching with respect to other transition metals, such as vanadium and chromium, is an important advantage for their use with hydrogen peroxide and/or in water-containing media [16–19]. In most literature reports, niobium–silica catalysts are tested in the epoxidation of simple alkenes as probe substrates [20–26]. Only few groups focused on the epoxidation of more complex and functionalised alkenes [27,28]. The epoxidation of cyclic unsaturated terpenes is an interesting benchmark reaction as it provides a broad series of data in terms of catalyst activity as well as chemo- and regioselectivity.

For these reasons, one major target of the present report is to prepare and study a series of niobium-based catalysts and to compare their catalytic behaviour with reference titanium-based catalysts, in the liquid-phase epoxidation of a doubly unsaturated cyclic terpene, such as limonene (Scheme 1). Particular attention has been paid to the synthesis method of the solid catalysts to be used in the reaction. Single-site heterogeneous catalysts, especially obtained by post-synthesis grafting of titanocene precursors, have previously shown promising results in the epoxidation of alkenes

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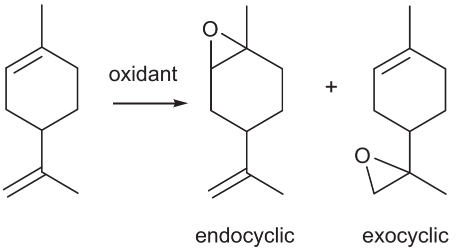

Scheme 1. Epoxidation of limonene.

[4,29–32]. Such catalytic systems are typically obtained by chemisorption of the precursor under liquid-phase conditions in chlorinated solvents. So, in order to avoid the use of hazardous and environmentally unsustainable media (in particular, the use of trichloromethane during the grafting procedure) and to simplify, whenever possible, the preparation steps, an alternative solventless synthesis method based on the dry impregnation of organometallic precursors (OM-DI) over silica has been here experimented and evaluated. Thanks to this technique, the finely ground solid OM precursor is mixed and stirred together with the oxidic support in the same vessel under reduced pressure (10^{-6} bar) at various temperatures. The OM precursor is therefore locally vaporised and deposited on the surface of the support. A comparable technique has already been applied to the preparation of transition and post-transition metal oxidic catalysts [33–35]. In particular, the absence of the solvent prevents a possible blocking of the pores, avoids the filtration step and usually allows a low level of contamination by undesired compounds eventually present in the solvent [36]. Many authors have successfully investigated the use of metal chlorides and metal alkoxides as precursors [37–39]. In this report, a series of catalysts obtained by OM-DI have been prepared starting from *bis*(cyclopentadienyl)niobium dichloride, and their features were compared to those of titanium-systems obtained from *bis*(cyclopentadienyl)titanium dichloride. In fact, despite the fact that niobocene and titanocene dichlorides have showed, at theoretical level, suitable characteristics for the application in solventless vapour-deposition techniques [40], to the best of our knowledge, their use in the synthesis of catalysts through this method has not been reported yet.

2. Experimental details

2.1. Catalyst preparation

All Nb/SiO_2 and Ti/SiO_2 catalysts were prepared starting from one type of commercially available Davisil silica (Grace Davison, LC60A), with 60–200 μm particle size, 605 $m^2\,g^{-1}$ specific surface area, 1.11 $mL\,g^{-1}$ total pore volume and a mean mesopore diameter broadly centred around 5.5 nm. The silica was pretreated in air at 500 °C for 1 h and at 500 °C for 1 h under dynamic vacuum (10^{-6} bar) and cooled to room temperature under vacuum.

For Nb/SiO_2 and Ti/SiO_2 catalysts obtained via OM-DI (Nb/SiO_2-DI and Ti/SiO_2-DI), the silica support was rehydrated with high purity deionised (18 MΩ cm) water (MilliQ Academic, Millipore) for 2 h and then dried at the rotary evaporator. The sample was calcined at 300 °C for 1 h in air and overnight under dynamic vacuum. Either niobium or titanium precursor, *bis*(cyclopentadienyl)niobium(IV) dichloride ($Nb(Cp)_2Cl_2$; 95% Aldrich) or *bis*(cyclopentadienyl)titanium(IV) dichloride ($Ti(Cp)_2Cl_2$; 97% Fluka), was finely milled and added under inert atmosphere in solid phase to the silica. The solid mixture was stirred overnight under static vacuum at various temperatures ($T = X$ °C in M/SiO_2-DI-X). The mixture was calcined under oxygen at 500 °C for 2 h to obtain the final catalyst.

For Nb/SiO_2 and Ti/SiO_2 catalysts obtained via liquid-phase grafting (Nb/SiO_2-liq and Ti/SiO_2-liq), $Nb(Cp)_2Cl_2$ or $Ti(Cp)_2Cl_2$, respectively, was grafted onto the surface of the silica adapting the procedure developed by Maschmeyer et al. for Ti only [29,41] and extending it to niobium precursors.

2.2. Catalyst characterisation

The Nb and Ti content of the prepared samples was determined by inductively coupled plasma optical emission spectroscopy ICP-OES (ICAP 6300 Duo, Thermo Fisher Scientific) after mineralisation of the samples in a microwave digestion apparatus (Milestone MLS 1200; maximum power 500 W) with a mixture of hydrofluoric (aq. 40 wt.%) and fuming nitric acid.

Diffuse reflectance UV–vis spectra were recorded in the range from 200 to 800 nm on pure samples using a Praying – Mantis Diffuse Reflectance Accessory (Harrick Sci) mounted in an Evolution 600 spectrophotometer (Thermo). A Spectralon® disc was used as reference material for background measurement. The spectra were recorded under air at room temperature on the samples after calcination at 500 °C in air and cooled under dynamic vacuum.

Raman spectra were recorded in the range 4000–50 cm^{-1} at 4 cm^{-1} resolution with 2000 scans, using a RFS 100 Bruker FT-Raman spectrometer with a 1064 nm wavelength excitation laser. Laser power was set at 100 mW. The Raman spectra were elaborated by using OPUS 5.0 software realised by Bruker Optics Company.

X-ray diffractograms (XRD) were collected on unoriented ground powders with a Thermo ARL 'XTRA-048 diffractometer with a Cu Kα ($\lambda = 1.54$ Å) radiation. Diffractograms were recorded at room temperature between 2° and 70° 2θ degrees with a step size of 0.02°, and a rate of 1° $2\theta\,min^{-1}$. Pure Nb_2O_5 (Aldrich, 99.99%) was used for comparison.

2.3. Catalytic tests

All catalysts were pretreated in air at 500 °C and cooled to room temperature under vacuum prior to use. The epoxidation tests on (*R*)-(+)-limonene (97% Aldrich; 98% *e.e.*) were carried out in a round-bottom glass batch reactor in an oil bath at 90 °C with magnetic stirring (ca. 800 rpm) under inert atmosphere. Acetonitrile (Aldrich, HPLC grade) was used as solvent. Aqueous hydrogen peroxide (H_2O_2; 50% Aldrich) or *tert*-butyl hydroperoxide (TBHP; 5.5 M in decane; Aldrich) was used as solvent, with an oxidant to substrate molar ratio of 2: 1 and 1.1: 1, for H_2O_2 and TBHP, respectively. The total volume of the mixture was 5 mL. Samples were taken after reaction times of 1, 2, 3, 6 and 24 h and analysed on GC chromatograms (Agilent 6890 Series; HP-5 column, 30 m × 0.25 mm; FID detector), with mesitylene (Fluka, puriss. ⩾99%) as internal standard. GC-peaks were identified by comparison with peaks of genuine samples of reference standards and by means of GC–MS. Peaks of regioisomers of the epoxides (endocyclic and exocyclic limonene epoxide; Scheme 1) were confirmed and quantified by ^1H NMR signals in the range 3.5–2.5 ppm. Data of catalytic performance (in Tables 2 and 3) are an average of at least three measurements. A standard deviation of ±2%, ±4% and ±2 h^{-1} has to be considered on average for the conversion, selectivity and specific activity values, respectively. In the case of some promising catalytic systems (Nb/SiO_2-DI-RT), fully comparable results were obtained over different batches of catalyst, prepared in multiple times. Neither significant auto oxidation nor support-catalysed contributions to epoxidation were recorded with niobium- and titanium-free siliceous supports, limonene conversion being about 10–12% with no remarkable epoxide formation. The formation of peroxyimidic acid, due to the concomitant presence of acetonitrile and hydrogen peroxide, can be excluded under these conditions. After all tests, the presence of residual hydrogen peroxide or TBHP was checked and confirmed by iodometric assays and titrations.

In order to check the leaching of niobium or titanium species, the solid catalyst was removed from the liquid mixture by centrifugation, and the resulting solution was tested for further reaction. In the tests for the recovery of the catalyst, the solid was separated by filtration and thoroughly washed with fresh acetonitrile and then with methanol (Fluka, HPLC grade). The filtered solid was dried at 100 °C, weighed, activated again at 500 °C in dry air and then reused in a new test as described above.

3. Results and discussion

3.1. Catalyst preparation

The first goal of this work is to prepare niobium-containing silica catalysts (and some reference titanium catalysts) via a versatile solventless deposition of metallocene dichloride precursors under controlled reduced pressure (10^{-6} bar).

For this aim, a dry impregnation approach was chosen. A cheap commercially available non-ordered mesoporous silica was chosen as support. Its specific surface area is high (ca. 600 $m^2\,g^{-1}$), thus providing a broad surface for the deposition of the organometallic precursor. Niobocene dichloride has been preferred as a precursor to the more common niobium alkoxides, since the former is less reactive, less moisture-sensitive and more easy-to-handle than the latter.

The silica support was previously calcined at 500 °C to clean the surface and remove completely any organic impurity eventually present as a contaminant. However, such treatment may lead to a marked condensation of the silanol groups and reduce excessively the number of free –OH moieties available for chemisorption of the metallocene precursor. So, the support was first rehydrated with water and then treated at a milder temperature (300 °C) [42]. During the deposition process, the temperature at which the dry impregnation occurred was varied as the only parameter. In the case of Nb/SiO_2-DI systems, a large set of temperatures was tested, spanning from 170 °C down to 25 °C (room temperature), and a broad series of Nb/SiO_2-DI catalysts was therefore obtained (Table 1). For Ti/SiO_2-DI systems, 120 °C was chosen as optimal deposition temperature [40].

During the dry impregnation process, the higher the temperature, the faster was the colouring of the white support due to the deposition and (partial) decomposition of the metal precursor onto the silica.[2] At the end, in all cases, the freshly prepared catalysts (before calcination) showed a uniform colour (brown-greenish for niobium systems or brown-red for titanium ones) in all parts, suggesting an even deposition of the metal species. The mapping for Nb element by SEM-EDS analysis on Nb/SiO_2-DI samples shows, at micrometric level, a uniform concentration of metal species on the support (Supplementary Information; Fig. S1).

By means of a final calcination in oxygen, the organic cyclopentadienyl ligands and the partially decomposed carbonaceous moieties (eventually formed during the deposition step) were burnt away, and the active Ti(IV) and Nb(V) centres on silica were obtained. Some investigations on the mechanism of the grafting via dry impregnation technique and on the nature of the intermediate species are still in progress and will be discussed in a further study.

Table 1
Synthesis details and metal content of the series of Ti/SiO_2 and Nb/SiO_2 catalysts.

Catalyst	Synthesis method	Synthesis temperature (°C)	Metal loading (wt.%)[a]
Ti/SiO_2-DI-120	Dry impregnation	120	1.66
Ti/SiO_2-liq	Liquid-phase grafting	Room temperature	1.75
Nb/SiO_2-DI-170	Dry impregnation	170	1.96
Nb/SiO_2-DI-150	Dry impregnation	150	1.71
Nb/SiO_2-DI-80	Dry impregnation	80	1.49
Nb/SiO_2-DI-RT	Dry impregnation	Room temperature	1.75
Nb/SiO_2-liq	Liquid-phase grafting	Room temperature	1.30

[a] Determined by digestion and ICP-OES analysis.

In all catalysts, the desired expected metal loading was 2 wt.%, according to the amount of metallocene precursor added in the dry impregnation mixture. In fact, 2 wt.% is generally, for Ti and Nb, the optimal loading for the epoxidation of a large variety of alkenes [27,31,41,43]. Nevertheless, the actual metal content showed that only a part of the expected metal was present (Table 1). A fraction of the precursor was lost, likely deposited on the walls of the glass vessel where the dry impregnation process was carried out or taken by the pump during the evacuation procedure. Also, in this case, however, the elemental analysis of different aliquots of powder sampled randomly on the same batch of catalyst showed a uniform dispersion of the metal species on silica support.

In a parallel way, two Nb/SiO_2-liq and Ti/SiO_2-liq catalysts were prepared via metallocene grafting in liquid phase and were used as comparison for OM-DI systems. It is worth noting that Ti/SiO_2 prepared by grafting titanocene in liquid phase is a widely studied system in literature [4,29–31], whereas the Nb/SiO_2 analogue has been prepared, to our best knowledge, for the first time in this work. From a merely synthetic point of view, the dry impregnation approach is simpler and cheaper, as it does not require the use of a hazardous and environmentally unfriendly solvent (in particular, chloroform to dissolve properly metallocene dichlorides) or of a base (triethylamine), to trigger the chemisorption of (cyclopentadienyl)metal moieties onto the surface silanols. In addition, the poor solubility of $Nb(Cp)_2Cl_2$ in chloroform (lower than $Ti(Cp)_2Cl_2$) causes a less efficient use of the organometallic precursor, and an amount lower than expected of Nb was therefore grafted onto the final solid (1.30 wt.% *vs.* expected 2 wt.%).

3.2. Catalyst characterisation

The pristine silica support (SiO_2) and the catalysts prepared by both dry impregnation (DI) and liquid-phase grafting (liq) (after calcination) showed type IV isotherms with an H2 hysteresis loop typical of solids with disordered structural pore size distribution. The pores size distribution in the support and in the derived catalysts covered a wide range of values from 2.0 to 8.0 nm. The deposition of niobium on the SiO_2 surface led to a reduction in the specific surface area, from 605 $m^2\,g^{-1}$, for the support, to 481 and 447 $m^2\,g^{-1}$ for Nb/SiO_2-liq and Nb/SiO_2-DI samples, respectively, and a reduction in the pores volume, from 1.11 $cm^3\,g^{-1}$, for the support, to 0.87 and 0.85 $cm^3\,g^{-1}$ for Nb/SiO_2-liq and Nb/SiO_2-DI, respectively. These values indicate that, in both cases, the deposition of the active species occurred mainly onto the internal surface of the porous solids, causing a moderate shrinkage of the non-ordered porosity.

The calcined samples underwent DR UV–vis spectroscopic analysis in order to have an evaluation on the site isolation and the coordination geometry of the metal sites, by monitoring the ligand-to-metal charge-transfer bands of Nb(V) and Ti(IV) (Fig. 1).

For all Nb/SiO_2 and Ti/SiO_2 systems, no absorption bands were detected above 400 nm. No large domains of Nb_2O_5 or TiO_2 were

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[2] The colouring of the support was extremely rapid for Nb/SiO_2-DI-170 and it turned light brown in few minutes, while the dry impregnation at room temperature led to a pale green material in few hours.

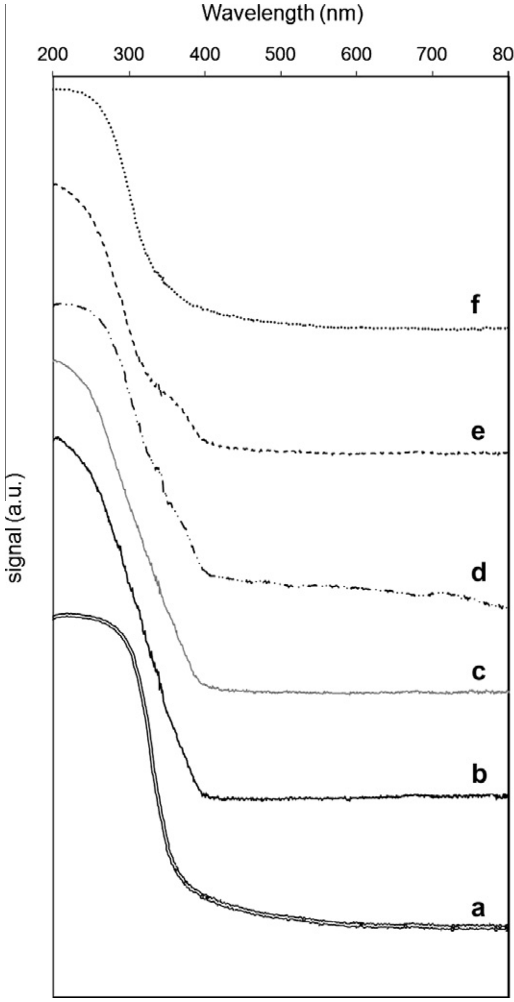

Fig. 1. DR UV–vis spectra of dry Ti/SiO_2-DI-120 (a), Nb/SiO_2-DI-RT (b), Nb/SiO_2-DI-80 (c), Nb/SiO_2-DI-150 (d), Nb/SiO_2-DI-170 (e) and Nb/SiO_2-liq (f) after calcination (before catalytic test).

therefore present on the catalysts [44,45]. As a general feature, all samples showed an absorption maximum in the range 210–250 nm that is assigned to the charge-transfer transition between oxygen atoms and the metal centres (Nb(V) and Ti(IV)) in tetrahedral coordination (Fig. 1) [23,46,47]. This indicates that the metal centres are isolated, and both synthetic methods are suitable to obtain the deposition of evenly dispersed Nb(V) and Ti(IV) sites.

Nevertheless, Nb/SiO_2 samples prepared by dry impregnation showed a shoulder centred at 350 nm due to the presence of Nb_2O_5-like nano-aggregates formed during the dry impregnation process. It is important to note that this shoulder increased in intensity passing from Nb/SiO_2 sample prepared at room temperature to samples obtained at higher temperatures (Nb/SiO_2-DI-80, Nb/SiO_2-DI-150 and Nb/SiO_2-DI-170). This feature suggests that some Nb_2O_5-like aggregates with nanometre size were formed during the dry impregnation procedure carried out at higher temperatures due to a higher extent of decomposition under those conditions [45,48,49]. So, in these cases, when the deposition of the metallocenic precursor was extremely rapid, it led to a less controlled and irregular formation of relatively large oxidic niobium domains.

Finally, Nb/SiO_2-DI and Ti/SiO_2-DI catalysts displayed rather comparable spectroscopic patterns to their Nb/SiO_2-liq and Ti/SiO_2-liq analogues obtained via liquid-phase grafting techniques, especially when they were prepared at room temperature.

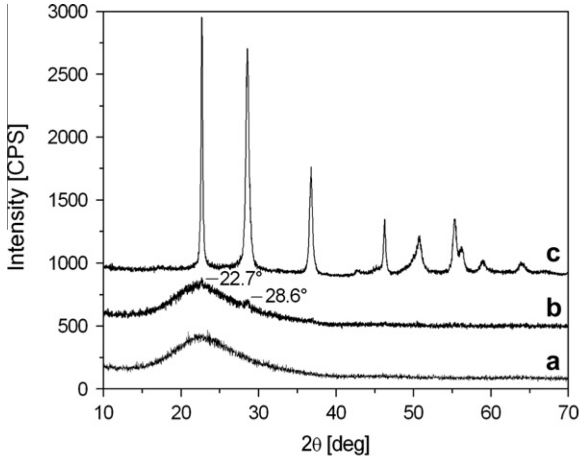

Fig. 2. X-ray patterns of Nb/SiO_2-liq (a), Nb/SiO_2-DI-80 (b) and bulk Nb_2O_5 (c) samples.

The chemical nature of the aggregates, responsible of the UV band observed at higher wavelengths (at ca. 350 nm), was confirmed by collecting XRD pattern and Raman spectrum of the Nb/SiO_2-DI sample prepared at higher temperatures (80 °C). X-ray diffractogram of Nb/SiO_2-DI-80 in comparison with that of Nb/SiO_2-liq solid is reported in Fig. 2.

Nb/SiO_2 sample prepared via liquid-phase grafting showed an X-ray profile characterised by the presence of a wide band centred at 22° 2θ, typical of amorphous silica (Fig. 2). No peaks attributed to the presence of Nb_2O_5 crystalline aggregates were clearly detectable in this sample, suggesting that the Nb centres were homogeneously distributed on the silica surface, in agreement with the spectroscopic results. Different features were observed for the sample prepared by dry impregnation at 80 °C (Fig. 2). In this specific case, along with the presence of the band typical of the amorphous silica (band at 22° 2θ), two weak X-ray peaks at 22.7° and 28.6° θ were clearly visible. By comparing the diffractogram of Nb/SiO_2-DI-80 with the one of a commercial Nb_2O_5 with orthorhombic structure [50], it was possible to observe that these two peaks can be ascribed to the presence of Nb_2O_5 nanometre size aggregates on the silica surface, in agreement with DR UV–vis data.

Raman spectroscopy is a powerful method to identify the surface metal oxide species on oxide supports, providing information at molecular level. On the light of these considerations, Nb/SiO_2-DI-80 sample was submitted to Raman spectroscopy characterisation in order to identify the nature of Nb_2O_5 species present on the silica surface and to support the X-ray diffraction results described above.

Fig. 3 shows the Raman spectra of bulk Nb_2O_5 sample in comparison with Nb/SiO_2-DI-80 and Nb/SiO_2-liq solids.

Raman spectrum of bulk diniobium pentoxide was characterised by a strong band centred at 700 cm^{-1}, associated with the stretching modes of different niobia polyhedra in orthorhombic phase, in agreement with X-ray results and as reported in the literature [50]. This peak was completely absent in the Raman spectrum of Nb/SiO_2-liq sample, but it is clearly visible (yet with a lower intensity with respect to pure Nb_2O_5 solid) in the Raman profile of niobium-containing silica prepared by dry impregnation at 80 °C. Such result confirms that the dry impregnation methodology, when it was carried out at higher temperatures, led to the formation of a small amount of nanometric Nb_2O_5 aggregates with orthorhombic structure on the surface of the siliceous support. Such relatively larger aggregates were due to the fact that, at

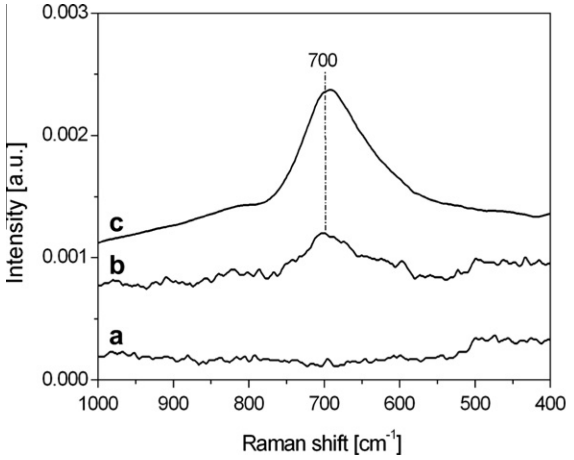

Fig. 3. Raman spectra of Nb/SiO_2-liq (a), Nb/SiO_2-DI-80 (b) and bulk Nb_2O_5 (c) samples.

higher temperatures, the particles of the organometallic precursor may, at some extent, undergo decomposition before they can sublimate and deposit onto the activated silica support surface. Nevertheless, in order to obtain catalysts where the metal centres are as disperse as possible, milder dry impregnation temperatures, thus lower deposition rates, appeared to be the ideal ones.

3.3. Catalytic performance

The catalysts were tested and compared in the liquid-phase epoxidation of limonene. By studying this reaction, it is possible to evaluate not only the activity and chemoselectivity of the catalysts, but also their regioselectivity (with respect to the formation of the endocyclic or exocyclic epoxide; Scheme 1). In addition, two oxidants were used and compared: hydrogen peroxide, one of the most promising reagents for environmentally sustainable oxidation processes and *tert*-butyl hydroperoxide (TBHP), an oxidant that is particularly suitable for use under anhydrous conditions [51,52].

From the direct comparison of niobium- and titanium-based silica catalysts (Table 2), Nb/SiO_2 systems displayed the best performance with hydrogen peroxide as oxidant, whereas Ti/SiO_2 systems showed good results in the presence of TBHP only. The better results in epoxidation achieved over mesoporous titanium–silica catalysts in the presence of TBHP rather than with H_2O_2 are widely described in previous literature [7,10] and references therein and are generally ascribed to the poor robustness of Ti–O–Si bonds in mesoporous titanium–silica systems against hydrolysis and to their aggregation in the presence of water [47]. Indeed, some low initial formation of epoxide (ca. 7% yield) was detected in the first hour of reaction, but then, it rapidly disappeared, as it transformed into a wide range of secondary products. Conversely, niobium–silica materials did withstand the presence of aqueous H_2O_2 and showed a remarkable epoxidation activity even after 1 h of reaction. In particular, in all the tests, aqueous H_2O_2 was added in one aliquot at the beginning of the reaction, and no slow dropwise addition of the oxidant was adopted. In fact, such peculiar protocol of oxidant addition has been successful in the epoxidation of various alkenes over Ti–silica catalysts, as it minimises the unproductive decomposition of hydrogen peroxide and keeps the local water concentration as low as possible [53–55]. This was not the case when Nb/SiO_2 solids were used as catalysts, and no dropwise oxidant addition protocol was thus necessary.

In terms of specific activity of the catalysts (moles of limonene converted per mole of metal present in the catalyst in the unit of time), Nb/SiO_2 catalysts showed better performances than Ti/SiO_2 ones. Actually, the limonene conversion on Nb/SiO_2 reached high values during the first hour of reaction, and then, it attained its maximum within the fourth hour, without any noteworthy improvement in the following 24 h (Supplementary Information; Fig. S2). The loss in activity after the forth hour of reaction can be ascribed to the gradual formation of oxidised side products on the surface of the catalyst, leading to a gradual deactivation of niobium sites [23]. The amount of organic by-products on the surface of the spent catalyst was relatively moderate (C, H, N elemental analysis showed some 3–4% of carbon on the washed, used catalyst), but such deposits could be removed completely only by calcination at high temperature (above 400 °C) in air.

Iodometric assays on the final mixtures revealed that in none of the tests, hydrogen peroxide had been the limiting agent of the reaction, and the oxidant efficiency (the amount of oxidised products obtained per amount of consumed oxidant) was, on average, rather good with hydrogen peroxide (above 60%). For this reason, the loss in catalyst activity described above cannot be ascribed to the complete consumption (via unproductive disproportionation) of hydrogen peroxide, since, at the end of all tests, a non-negligible amount of oxidant was always detected.

On titanium, on the contrary, the initial reaction rate was lower, and longer reaction times (as long as 24 h) were necessary to attain with Ti/SiO_2 + TBHP systems the same results as those obtained with Nb/SiO_2 + H_2O_2 in only 3 h. For this reason, reaction times of 1 and 3 h were chosen as the most significant one for a direct comparison of the catalytic properties. The oxidant efficiency was always very high (higher than 90%) with TBHP. Thanks to this, it was possible to use a lower excess of oxidant with TBHP (1.1:1

Table 2
Catalytic performance of Ti/SiO_2 and Nb/SiO_2 catalysts in the liquid-phase epoxidation of limonene.

Catalyst	Oxidant	C^a 1 h (%)	S^b 1 h (%)	*Endo/exo*^{c} 1 h	C^a 3 h (%)	S^b 3 h (%)	Act^d 1 h (h^{-1})
Nb/SiO_2-DI-RT	H_2O_2	58	98	27:73	62	97	29
Nb/SiO_2-DI-RT	TBHP	7	n.d.	n.d.	14	71	4
Nb/SiO_2-liq	H_2O_2	64	>98	24:76	74	>98	46
Nb/SiO_2-liq	TBHP	29	80	76:24	30	80	20
Ti/SiO_2-DI-120	H_2O_2	10	40	n.d.	13	10	3
Ti/SiO_2-DI-120	TBHP	45	96	98:02	55	>98	13
Ti/SiO_2-liq	H_2O_2	12	62	91:09	18	20	3
Ti/SiO_2-liq	TBHP	52	93	92:08	77	81	14

Conditions: dry CH_3CN solvent; 100 mg cat; 1.0 mmol limonene; 2.0 mmol aq. H_2O_2 or 1.1 mmol dry TBHP; reflux temperature; batch reactor.
[a] Limonene conversion.
[b] Selectivity to limonene epoxide.
[c] Endocyclic/exocyclic epoxide ratio.
[d] Specific activity ($[\text{mol}_{\text{converted limonene}}]$ $[\text{mol}_{\text{Nb}}\ \text{h}]^{-1}$) after 1 h.

Table 3
Catalytic performance of the series of Nb/SiO_2 catalysts (obtained under different synthesis conditions) in the liquid-phase epoxidation of limonene with hydrogen peroxide.

Catalyst	C^a 1 h (%)	S^b 1 h (%)	C^a 24 h (%)	S^b 24 h (%)	Act^c 1 h (h^{-1})
Nb/SiO_2-DI-170	43	96	61	95	20
Nb/SiO_2-DI-150	47	>98	63	92	25
Nb/SiO_2-DI-80	57	>98	73	91	35
Nb/SiO_2-DI-RT	58	98	66	90	29
Nb/SiO_2-liq	64	>98	80	77	46

Conditions: dry CH_3CN solvent; 100 mg cat; 1.0 mmol limonene; 2.0 mmol aq. H_2O_2; reflux temperature; batch reactor.

[a] Limonene conversion.

[b] Selectivity to limonene epoxide.

[c] Specific activity ($[mol_{converted\ limonene}]\ [mol_{Nb}\ h]^{-1}$) after 1 h.

oxidant to limonene molar ratio) than with hydrogen peroxide (2:1 molar ratio). Over Ti/SiO_2 systems too, TBHP was not the limiting reagent, under these conditions.

The comparison of the two series of niobium catalysts, namely prepared via dry impregnation or via liquid-phase grafting, shows that the dispersion of the metal sites is an important factor in terms of catalytic-specific activity. Nb/SiO_2-liq, in fact, proved to be the most active catalyst, and this is consistent with the good site isolation of Nb centres observed by DR UV–vis spectroscopy (Fig. 1). However, Nb/SiO_2-DI catalysts obtained at lower temperatures (RT or 80 °C) showed interesting performances too, in terms of alkene conversion after 1 h (57% and 58%, respectively), thanks to their good level of Nb site dispersion, notwithstanding the presence of a small fraction of nanosized Nb_2O_5-like aggregates formed during the dry impregnation process (see Section 3.2). In this case and under these conditions, the presence of a limited fraction of niobia nanodomains is not fully detrimental, as it happens when TiO_2 aggregates are present on titanium–silica catalysts, leading to the undesired decomposition of the oxidant [7,56]. Nb_2O_5-like aggregates can, on the contrary, show some epoxidation activity themselves [57] and do not lead to complete disproportionation of hydrogen peroxide (H_2O_2 was not the limiting agent under these conditions; see above).

With regard to the selectivity to epoxides, the reaction preferentially led to the chemoselective formation of limonene epoxides (both endo and exocyclic ones), except in the case of $Ti/SiO_2 + H_2O_2$ systems, in which the poor selectivity values were due to the extended formation of undesired side products via free-radical homolytic oxidation processes [58]. In these cases, important amounts of allylic oxidation products (i.e. carveol and isomeric compounds) were detected. Conversely, Nb/SiO_2-liq, the most active system, led to the formation of acid-catalysed secondary products over long reaction times (24 h) and, hence, to lower epoxide selectivity values (77%; Table 3).

Finally, in terms of regioselectivity, a surprising preferential regioselective epoxidation of the exocyclic C=C bond was observed with Nb/SiO_2-DI and Nb/SiO_2-liq catalysts in the presence of H_2O_2 only. In the other cases, with Nb/SiO_2 + TBHP and with all Ti–silica systems, a fully expected preference towards endocyclic C=C bond was obtained. Actually, the electrophilic oxygen from the activated oxidant species (H_2O_2 or TBHP) should always attack preferentially the trisubstituted endocyclic unsaturation [27], but over $Nb/SiO_2 + H_2O_2$, the opposite is true. The reasons causing such inversion in regioselectivity are not fully elucidated. Preliminary investigations, however, seem to suggest that sterical factors have a stronger influence on the regioselectivity than electronic ones. Experimental work is in progress to explicate this unusual result.

As a last point, the influence of the temperature at which dry impregnation is performed was studied with respect to the catalytic behaviour (Table 3). Particular attention was paid to niobium-containing silica catalysts, as they showed the most promising features in epoxidation. The four catalysts, Nb/SiO_2-DI-170, 150, 80 and RT, displayed an inverse trend of the activity as a function of the dry impregnation temperature. Roughly, the milder the temperature, the higher was the specific activity of the catalyst and, hence, the higher the limonene conversion value. In fact, the most active niobium catalysts resulted to be the Nb/SiO_2-DI-80 and the Nb/SiO_2-DI-RT systems. Then, a moderate (but non-negligible) diminution of the specific activity was recorded, and on Nb/SiO_2-DI-170, it was 40% or 30% less than the one obtained on Nb/SiO_2-DI-80 or Nb/SiO_2-DI-RT, respectively. Such observation is in good agreement with DR UV–vis and Raman spectroscopic data, according to which the milder the dry impregnation temperature, the better was the dispersion of the niobium sites and the lower the occurrence of Nb_2O_5-like aggregates. These relatively larger Nb_2O_5-like aggregates, indeed, even though they had not a detrimental effect *per se* on the catalytic performance, likely led to a lower catalyst activity, as they caused the diminution of the amount of available active tetrahedral Nb(V) on the catalyst surface [26,45]. Nevertheless, taking into account the values of yield to the desired epoxide (in terms of conversion × selectivity), then, DI-derived catalysts showed interesting performances as well.

The four Nb/SiO_2-DI catalysts showed, on the contrary, fully comparable results in terms of chemoselectivity and regioselectivity (ca. 75:25 endocyclic/exocyclic epoxide ratio, over all the catalysts in Table 3). Such behaviour is a clue that the niobium active sites were obtained with a different dispersion and accessibility, by varying the temperature of the dry impregnation process, but they did not change in chemical nature.

All the catalysts (both niobium- and titanium-based ones) were easily recovered by filtration, washed, calcined and reused in a second catalytic run. They kept their epoxidation activity and very high selectivity to epoxide. The conventional tests to prove the heterogeneous nature of the catalytic reaction confirmed no homogeneous and catalytically active niobium or titanium species were formed in the presence of aqueous H_2O_2 or anhydrous TBHP. The good stability not only of $Ti–SiO_2$, but also of $Nb–SiO_2$ catalysts has been already reported in previous works [27,29,48]. It is worth highlighting, however, that Nb/SiO_2-DI-RT and Ti/SiO_2-DI-RT showed fully comparable performance with the results recorded over fresh catalysts (see also DRS UV–vis spectra after one catalytic test; Supplementary Information, Fig. S3).

4. Conclusions

An alternative solventless post-synthesis protocol has been successfully proposed and optimised for the preparation of mesoporous silica epoxidation catalysts containing titanium and niobium sites. The synthesis method, based on an organometallic dry impregnation (OM-DI) approach of metallocenic precursors, was particularly convenient with respect to previously described (and widely studied) liquid-phase grafting techniques, as it is cheaper, more versatile, less time-consuming and avoids the use of environmentally unfriendly chlorinated solvents and of amine additives. It led to reasonably even dispersions of Nb(V) or Ti(IV) sites on the mesoporous silica surface. OM-DI-derived catalysts were active in the selective epoxidation of limonene and were nearly comparable to the catalysts obtained via liquid-phase grafting methodology.

Ti/SiO_2-DI catalysts showed good results in the epoxidation with anhydrous TBHP. Nb/SiO_2-DI catalysts, on the contrary, displayed an excellent performance in the presence of aqueous hydrogen peroxide. High conversions (up to 78%) and a complete chemoselectivity to the desired epoxide (>98%) were obtained over Nb/SiO_2-DI-RT catalyst in short reaction times (1 h). Additionally, Nb/SiO_2 systems showed an unexpected peculiar regioselectivity towards the epoxidation of the less electron-rich exocyclic C=C double bond of limonene.

For these reasons, niobium-containing mesoporous silica catalysts obtained by post-synthesis methods deserve a deeper attention. They can indeed find several potential applications in the selective oxidation of various richly functionalised substrates, for which their particular selectivity properties can be exploited at best.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2012.11.015.

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