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Grafted non-ordered niobium-silica materials: Versatile catalysts for the selective epoxidation of various unsaturated fine chemicals

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ABSTRACT

Two kinds of niobium(V)-silica catalysts for the selective epoxidation were synthesised by post-synthesis modification of non-ordered mesoporous silica supports, starting from niobocene dichloride via solventless organometallic precursor dry impregnation or conventional liquid-phase grafting technique. Grafted Nb/SiO_2 solids were used as catalysts, in the presence of aqueous H_2O_2, for the epoxidation of unsaturated cyclic and terpenic compounds of interest for fine and specialty chemistry, in particular: cyclohexene, 1-methylcyclohexene, limonene, carveol, α-terpineol, isopulegol, carvotanacetol, carvone, as well as squalene and isopulegyl acetate. These catalysts showed high yields (up to 73%) and excellent chemoselectivities to the desired epoxides (up to 98%), also in short reaction times (down to 1 h).

1. Introduction

Starting from the first syntheses of transition metal-containing mesoporous silicates in the early 1990s, many research teams have directed their efforts in developing innovative catalysts for liquid-phase oxidation reactions and have tested these solids in the selective epoxidation of bulky intermediates of interest for the fine chemical industry [1]. In fact, the optimal performance of the titanium silicalite-1 (TS-1) zeotype, obtained by incorporation of Ti centres within the structure of a MFI zeolite [2], is still currently unbeaten in terms of activity, selectivity, robustness and recyclability [3–5]. The remarkable efficiency of TS-1 for selective oxidation with aqueous hydrogen peroxide is attributed to: 1) the isolation of titanium sites, preventing the undesired and useless decomposition of H_2O_2, and 2) the hydrophobic character of the lattice, enabling the preferential adsorption of the hydrophobic substrates within the micropores, even in the presence of water [6]. However, the main drawback of such microporous zeotypes is due to the limited dimensions of their channels (typically *ca.* 0.5 nm × 0.6 nm maximum). So, only simple and less bulky reactants, whose kinetic diameter is smaller than 0.55 nm, can be easily epoxidised in their porous network [7].

Several authors have proposed the strategy of heterogenisation via covalent anchoring of homogeneous catalytic systems with a proven activity and selectivity (such as organometallic species, metal-Schiff base complexes or metal silsesquioxanes), in order to obtain effective heterogeneous catalysts for the epoxidation of heavy and bulky substrates [8–12]. However, such approach is not always easily feasible and requires a delicate know-how of surface-chemistry modifications [13].

Mesoporous metal-containing silicates were expected to overcome these problems, opening the way to the agile oxidation of sterically demanding (and high added-value) substrates. Unfortunately, these materials showed intrinsically poorer activity than TS-1 when used with aqueous H_2O_2, because of the presence, on their surface and mesopores, of a large number of silanols, which promote the preferential adsorption of water at the expenses of non-polar alkene substrates [14]. On these systems, organic hydroperoxides, such as cumyl hydroperoxide (CHP) or *tert*-butylhydroperoxide (TBHP), are the most suitable oxidants, since they can be used under anhydrous conditions, hence avoiding (or reducing) the problems linked to the hydrolysis and the leaching of surface Ti species [15–17]. Nevertheless, it is worth highlighting that hydrogen peroxide was used successfully for the epoxidation of bulky olefins over Ti-silicates in few notable examples. This was possible thanks to the peculiar morphology and/or robustness of the porous material, as in the epoxidation of cyclododecene over Ti-MCM-48 [18] and of caryophyllene over Ti-MMM-2 [19], or by

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applying a drop-wise addition of H_2O_2 to minimise the detrimental effects of water on the mesoporous catalyst, as in the epoxidation of cyclohexene and methyl oleate over Ti-MCM-41 [20–22].

In the search for mesoporous silicates containing metals other than Ti, that are active and truly heterogeneous, the metals of Group 4, *i.e.* Zr and Hf, showed scarce performances [23], whereas promising results were obtained by using metals of Group 5. Vanadium silicates suffer from extensive leaching, mainly due to extra-framework hexa-coordinated V(V) species that are readily hydrolysed in the presence of protic solvents [24–26]. Very few reports about tantalum-containing mesoporous silica materials show interesting data, but a deeper investigation has not been carried out so far [27,28].

The study of niobium-containing silica catalysts for liquid-phase oxidation is, on the contrary, a field in restless expansion [29–31]. These solids have shown promising catalytic performances in water-containing liquid-phase oxidation reactions and a higher stability and robustness towards metal leaching and hydrolysis, with respect to Ti-silica ones. Mesoporous niobium-silica materials are effective systems for the epoxidation of cycloalkenes and their catalytic activity is found to be influenced by the dispersion of niobium in SiO_2 matrix and by the synthesis conditions [32]. Mesoporous materials, in which niobium centres are homogeneously dispersed into the silicate matrix, catalysed efficiently the epoxidation of unsaturated terpenes and alkenes of interest for the industry of the intermediates [33–38]. On such Nb-SiO_2 based systems, aqueous H_2O_2 can be used as a direct oxidant, added in one aliquot since the beginning of the reaction and no slow drop-wise addition of the oxidant is therefore needed.

The main goal of the present work is to describe the use of grafted niobium non-ordered mesoporous silica materials as water-tolerant catalysts for the epoxidation of a broad series of unsaturated substrates. Actually, promising results have already obtained by applying these catalysts for the epoxidation of cyclohexene, limonene and some fatty acid methyl esters (FAMEs) [39–41]. Here, this kind of grafted Nb-SiO_2 catalysts are applied to a wide series of cyclic alkenes, terpenes and terpenoids in order to study the influence of C=C double bond position and of additional functional groups (*e.g.*, alcoholic –OH moiety) on the catalytic performance. The catalysts were prepared according to a post-synthesis approach following two routes: (i) liquid-phase grafting and (ii) an alternative solventless synthesis method based on dry impregnation of niobocene dichloride (organometal dry impregnation; OM-DI), that proved to be versatile, cheap, environmentally convenient and straightforward.

2. Experimental details

2.1. Catalyst preparation

Niobium-silica catalysts were all prepared by grafting *bis*(cyclopentadienyl)niobium(IV) dichloride ($Nb(Cp)_2Cl_2$; 95% Aldrich) onto Grace Davison, Davisil SiO_2 LC60A, 60–200 μm, as described previously in detail [40]. All supports were pre-treated in dry air at 500 °C for 1 h, then left for 1 h at 500 °C under vacuum and finally cooled to room temperature under vacuum.

For the catalyst obtained via dry impregnation (Nb/SiO_2-DI), the silica support was hydrated with high purity deionised water (MilliQ Academic, Millipore, 18 MΩ cm) for 2 h, dried at rotary evaporator and then pre-treated in air at 300 °C for 1 h and under vacuum overnight at 300 °C. $Nb(Cp)_2Cl_2$ was finely ground and mixed, under inert atmosphere in solid phase, to the silica. The so-obtained samples were stirred overnight under steady vacuum at room temperature (20 °C). The resulting light brown mixtures were calcined under dry oxygen at 500 °C for 2 h to obtain the final Nb(V)-silica catalysts.

Conversely, Nb/SiO_2-liq was prepared via liquid-phase grafting on the same support. In this case, $Nb(Cp)_2Cl_2$ was grafted onto the surface of the silica support by adapting and applying the grafting protocol developed by Maschmeyer et al. [42] and modified by some of us [43].

2.2. Catalyst characterisation

The Nb elemental content of the prepared samples was determined by inductively coupled plasma optical emission spectroscopy (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%) and fuming nitric acid.

X-ray diffractograms (XRD) were collected on unoriented ground powders with a Thermo ARL 'XTRA-048 diffractometer using Cu Kα ($\lambda = 1.54$ Å) radiation. Diffractograms were recorded at room temperature with a step size of 0.02° and a rate of $1^\circ\ 2\theta\ \text{min}^{-1}$.

N_2 physisorption measurements were carried out at 77 K in the relative pressure range from 1×10^{-6} to 1 P/P_0 by using a Quantachrome Autosorb 1MP/TCD instrument. Prior to analysis, the samples were outgassed at 100 °C for 3 h (residual pressure lower than 10^{-6} Torr). Apparent surface areas were determined by using Brunauer–Emmett–Teller equation (BET), in the relative pressure range from 0.01 to 0.1 P/P_0. Pore size distributions were obtained by applying the BJH (Barret–Joyer–Halenda) approach to the desorption branch.

Diffuse reflectance UV–vis (DR UV–vis) spectra were recorded at room temperature using a PerkinElmer Lambda 900 spectrometer equipped with an integrating sphere accessory, and using a custom-made quartz cell. Before the analysis, the samples were dispersed in anhydrous $BaSO_4$ (5 wt.%).

Thermogravimetric analysis (TGA) was performed on a Setaram SETSYS Evolution instrument, under dry air flow in the temperature range 25–800 °C.

2.3. Catalytic tests

All catalysts were pre-treated under dry air at 500 °C and cooled to room temperature under vacuum prior to use. The epoxidation tests on the alkenes, namely, cyclohexene (Aldrich 99%), 1-methyl-1-cyclohexene (Aldrich 97%), *R*-(+)-limonene (Aldrich 97%), (−)-carveol (Aldrich 97%), α-terpineol (Aldrich 90%), isopulegol (Aldrich techn.), carvotanacetol (prepared by selective hydrogenation of carveol, as previously described [44,45]), *R*-(−)-carvone (Aldrich 98%), isopulegyl acetate (Aldrich 96%) and squalene (Aldrich ≥98%) were carried out in a round-bottom glass batch reactor in an oil bath at 90 °C equipped with magnetic stirring (*ca.* 800 rpm) under inert atmosphere. The substrate (1.0 mmol) was dissolved in acetonitrile (Aldrich, HPLC grade; 5.0 mL) and aqueous hydrogen peroxide (H_2O_2; aq. 50% Aldrich; 2.0 mmol) was used as oxidant. The samples were taken after reaction times of 1, 2 and 4 h and analysed by gas-chromatography (Agilent 6890 Series; HP-5 column, 30 m × 0.25 mm; FID detector). Mesitylene (Fluka, puriss. ≥99%) was used as internal standard. GC-peaks were identified by comparison with peaks of genuine samples of reference standards and/or by means of GC-MS analysis. In the tests of squalene epoxidation, the reaction was followed by ^1H and ^{13}C NMR analysis at room temperature (Bruker UXNMR, 400 MHz) [46,47]. After all tests, the presence of residual hydrogen peroxide was checked and confirmed by iodometric assays and titrations. In none of the cases hydrogen peroxide was the limiting reagent. Specific activity, SA, of the catalyst is defined as the amount (moles) of

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converted alkene per amount (moles) of total Nb in the unit of time (1 h).

In order to check the possible leaching of Nb species, the solid catalyst was rapidly removed from the liquid mixture by centrifugation and the resulting solution was tested for further reaction [48,49]. 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 gently at 110 °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 and characterisation

Niobocene(IV) dichloride species were deposited on the silica support either by base-induced liquid-phase covalent grafting or by solvent-less deposition under reduced pressure onto the activated silica surface. In all catalysts, the desired expected Nb loading was 2 wt.%, according to the amount of metallocene precursor added at the beginning of the dry impregnation or grafting procedure. Indeed, 2 wt.% is the optimal loading for the epoxidation of a large variety of alkenes [36,39]. Nevertheless, the measured Nb content showed that only a part of the expected metal was present (Table 1). In particular, via liquid-phase grafting, a remarkable part of the precursor was not deposited onto the silica surface, thus resulting in a sample with a low final Nb content (0.76 wt.%). In this case, in fact, Nb was deposited on the silica surface by chemisorption only and the loosely physisorbed niobocene dichloride precursor was removed by washing with fresh chloroform. At this step, part of the initial expected niobium loading was lost.

The samples underwent physico-chemical characterisation in order to investigate the surface properties of the catalysts and the nature and dispersion of the niobium sites on the support.

The textural properties of Davisil SiO_2 and derived catalysts, prepared by both dry impregnation (Nb/SiO_2-DI) and liquid-phase grafting (Nb/SiO_2-liq), were studied by N_2 physisorption analysis at 77 K. An isotherm of type IV with an H2 hysteresis loop, typical for solids with disordered structural pore size distribution, was observed for all the samples (Table 1). The presence of Nb metal centres led to a reduction of the specific surface area (estimated by BET method, S_{BET}), passing from 580, for pure SiO_2, to 435 and 444 $m^2\,g^{-1}$ for Nb/SiO_2-liq and Nb/SiO_2-DI samples, respectively. The pores size distribution resulted broad for all samples, covering a wide range of values from 4.0 to 10.0 nm. Finally, the pores volume of SiO_2 samples decreased as a consequence of Nb introduction, passing from 0.97 $cm^3\,g^{-1}$ for SiO_2 to 0.78 and 0.79 $cm^3\,g^{-1}$ for Nb/SiO_2-DI and Nb/SiO_2-liq samples, respectively. The coordination geometry and the chemical environment of the Nb sites dispersed on the silica surface were evaluated by using DR UV–vis spectroscopy (Fig. 1).

As a general feature, both the UV–vis spectra of Nb/SiO_2-liq and Nb/SiO_2-DI samples show a main absorption with maximum centred at *ca.* 245 nm, tentatively assigned to $O^{2-} \rightarrow Nb^{5+}$ charge-transfer bands of isolated Nb(V) centres (Fig. 1) [50]. In addition, especially for Nb/SiO_2-DI sample, the band at 245 nm appears asymmetric and slightly broadened towards low frequency side as a consequence of the expansion of the Nb coordination sphere (from tetrahedral to octahedral) promoted by the presence of coordinated water molecules.

No absorption bands were detected above 400 nm, indicating that no large Nb_2O_5 domains are present on both catalysts surface (Fig. 1) [51]. Nevertheless, the spectrum of the sample prepared by dry impregnation shows a shoulder centred at *ca.* 340 nm, ascribed to the presence of Nb_2O_5-like nano-aggregates formed during the dry impregnation process (Fig. 1b) [41].

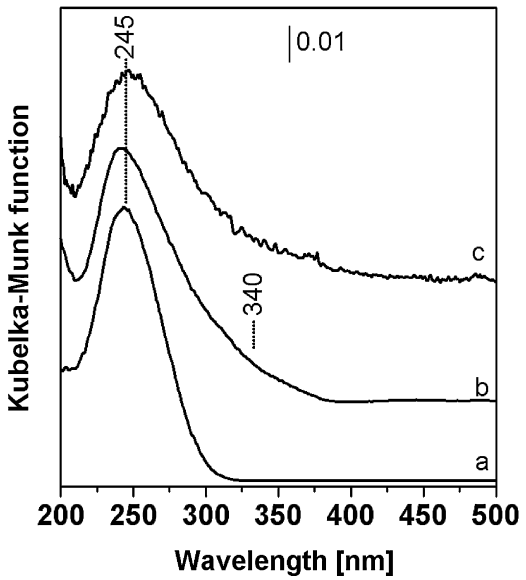

Fig. 1. DR UV–vis spectra of Nb/SiO_2-liq (a) and Nb/SiO_2-DI (b) and Nb/SiO_2-DI, after five catalytic cycles (c).

The presence and the nature of these aggregates was confirmed by XRD analysis. In fact, the diffractogram of Nb/SiO_2 prepared by dry impregnation approach showed, in addition to the broad signal typical of the amorphous silica observed in the 15–35° 2θ range, three weak and wide reflections at *ca.* 23°, 29° and 37° 2θ, typical of nanometre-sized crystalline Nb_2O_5 aggregates (data not shown for the sake of brevity), which were not present in the XRD pattern of Nb/SiO_2-liq sample [41]. These results confirm that the dry impregnation methodology led to the formation of nano-sized Nb_2O_5 aggregates on the surface of the support, whereas the liquid-phase grafting approach led to a uniformly dispersed sample, with a very large amount of surface single-site Nb atoms on the silica.

3.2. Catalytic tests

The two catalysts, Nb/SiO_2-liq and Nb/SiO_2-DI, were tested in the selective epoxidation, under heterogeneous conditions, of a broad range of alkenes of interest for fine and flavours and fragrances (F&F) chemistry: cyclohexene **1**, 1-methylcyclohexene **2**, limonene **3**, carveol **4**, α-terpineol **5**, isopulegol **6**, carvotanacetol **7**, carvone **8**, isopulegyl acetate **9** and squalene **10**.

All catalysts were active in the presence of hydrogen peroxide as oxidant and no detectable leaching of metal species in solution was recorded. Tests on cyclohexene and limonene either with Nb-free silica or without catalyst showed that there was no significant auto-oxidation or support-catalysed contribution to epoxidation: the epoxide amount resulted under the chromatographic detection limit. This confirms that niobium is the active site over which oxidation takes place.

3.2.1. Performance in the epoxidation of cyclic alkenes

Cyclohexene **1** and 1-methylcyclohexene **2** were readily epoxidised to epoxycyclohexane and 1,2-epoxy-methylcyclohexane, respectively, in 1 h, with a very high selectivity (Table 2). Nb/SiO_2-liq, in particular, showed a remarkably higher activity than Nb/SiO_2-DI, if one considers that the former contains only 43% of Nb with respect to the latter (Fig. 2). Such behaviour is consistent with the one observed on other epoxidation catalysts [52–55] and is attributed to a high fraction of evenly dispersed sites on the surface

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Table 1
Textural features of SiO_2 support and Nb-silica catalysts.

Sample	Metal loading (wt.%)[a]	S_{BET}[b] ($m^2 g^{-1}$)	PV[c] ($cm^3 g^{-1}$)	PD[d] (nm)
SiO_2	–	580	0.97	4.0–10.0
Nb/SiO_2-DI	1.75	444	0.78	4.0–10.0
Nb/SiO_2-liq	0.76	435	0.79	4.0–10.0

[a] Nb content measured by ICP–MS.
[b] BET specific surface area.
[c] Specific pore volume.
[d] Mean pore diameter.

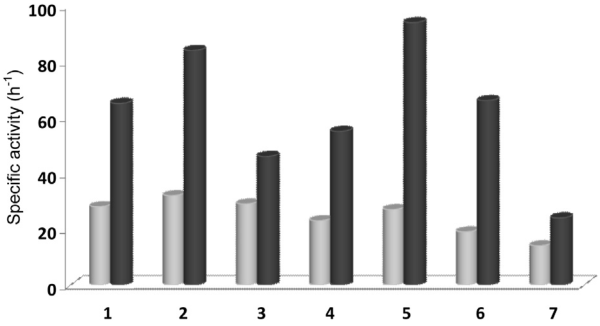

Fig. 2. Specific activity (h^{-1}) after 1 h of Nb/SiO_2-DI (grey) and Nb/SiO_2-liq (black) in the epoxidation of alkenes **1**–**7**.

and, hence, to a better availability of Nb(V) centres in the catalysts prepared via liquid-phase grafting [40]. In fact, in the sample Nb/SiO_2-DI, in which some niobia-like aggregates were detected by spectroscopic investigation (*v. supra* and [41]), a fraction of Nb sites can be buried within the aggregate and thus inaccessible, or less accessible, for the reactant. However, a partial contribution by the small domains of niobia to the epoxidation reaction cannot be *a priori* excluded, since hydrogen peroxide can interact cooperatively with crystalline niobia to generate oxidising species [30,56]. Therefore, the presence of such niobia aggregates cannot be considered fully detrimental.

In terms of reactivity of the two cyclohexenes, 1-methylcyclohexene was more readily epoxidised than unsubstituted cyclohexene. The trisubstituted alkene showed indeed a higher nucleophilic character with respect to cyclohexene, thus favouring the electrophilic transfer of the oxygen from hydrogen peroxide to the alkene [36,57,58].

In all cases, the selectivity to the desired epoxide was very high, with a good oxidant efficiency due to a limited useless decomposition of H_2O_2 (oxidant efficiency in all tests was around 35–40 mol%). At longer reaction times (4 h), the selectivity decreased, as part of the epoxide underwent acid-catalysed rearrangement or ring-opening. Nb(V) centres on the silica surface, indeed, possess intrinsic acidic character [51], leading to the formation of secondary products obtained by subsequent acid-catalysed transformations (cyclohexanone and methylcyclohexanone, cyclohexanediol and methylcyclohexanediol, derived from cyclohexene oxide and methylcyclohexene oxide, respectively). No appreciable yield of allylic oxidation products, such as cyclohexenol or methylcyclohexenol, was detected. This means that the oxidation reaction follows mainly a heterolytic pathway, since the presence of Nb sites is able to address the reaction towards a non-radical mechanism [59].

3.2.2. Performance in the epoxidation of cyclic unsaturated terpenes

Both catalysts were also active in the epoxidation of a broad series of cyclic unsaturated terpenes with a menthane-like skeleton (Table 2). In particular, such screening aims at studying the influence of the C=C double bond position and the presence of an alcoholic moiety (if any) on the catalytic performances.

With all cyclic terpenes (limonene **3**, carveol **4**, α-terpineol **5**, isopulegol **6**, carvotanacetol **7**; Scheme 1) Nb/SiO_2-liq showed higher conversion and higher specific activity values than Nb/SiO_2-DI, as observed above with simpler cyclic alkenes (Fig. 2). The good and uniform dispersion of the Nb(V) sites obtained by liquid-phase grafting is an advantage on these substrates too.

Most of the epoxidation activity took place within the first hour of reaction. For longer reaction times, the rate of advancement of the reaction decreased due to the gradual formation of oxidised side products on the surface of the catalyst, leading to a gradual deactivation of Nb sites [32] (with the notable unexpected exception of Nb/SiO_2-liq in the presence of carvotanacetol **7**).

Taking into account the effect of a hydroxyl moiety in allylic, homoallylic or bishomoallylic position (for carvotanacetol, isopulegol and α-terpineol, respectively), the presence and the proximity of the OH-group did not favour necessarily the epoxidation step and no neat trend in reactivity can be described: carvotanacetol was less easily epoxidised than α-terpineol; limonene and carveol showed fully similar conversion values. Such behaviour differs from the trend observed in the epoxidation of the same series of terpenes over Ti(IV)-silica catalysts with *tert*-butylhydroperoxide (TBHP), where the reactivity trend followed the clear order: allylic > homoallylic > bishomoallylic [58].

Nevertheless, by comparing the reactivity of isopulegol **6** and isopulegyl acetate **9** (*i.e.* the same molecule backbone, bearing either an OH- or an acetyl-group; Scheme 2), some promotion effect by the hydroxyl moiety was evident and conversion values on the terpenic alcohol resulted twice as higher as its acetylated derivative (Fig. 3).

From these results, there is not a sharp evidence of the role of the OH-group in enhancing epoxidation rate, as it has been observed, conversely, on several titanium-containing homogeneous or heterogeneous epoxidation catalysts [45,58,60]. For sure, in some examples, the presence of an alcoholic function on the alkene molecule is an advantage for epoxide formation, but such enhancement is largely substrate-dependent and is not valid on a general basis. This feature is therefore a remarkable difference in the epoxidation behaviour of Nb-based systems with respect to Ti-based ones.

Interestingly, a direct comparison between the performances obtained with carveol **4** and carvone **8**, showed that Nb-SiO_2 catalysts are active in the epoxidation of α,β-unsaturated ketones too (Fig. 4). Carvone was indeed less easily epoxidised with H_2O_2 than carveol (36% *vs.* 51% of conversion after 1 h, respectively) and such behaviour was reasonably expected, taking into account the poorer nucleophilic character of the C=C bond in α,β-unsaturated ketones than in allylic systems. However, carvone showed surprisingly better performances than carvotanacetol **7** (in Fig. 4 for the sake of comparison) and this is a remarkable result. In fact, electron-deficient α,β-unsaturated ketones usually need a completely different approach to be epoxidised in the presence of H_2O_2 with good yields in epoxide, such as heterogeneous catalysts with a neat basic character [61]. So, this is a further noteworthy

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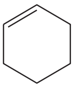
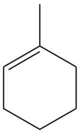
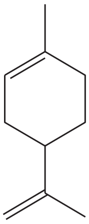
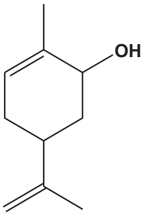
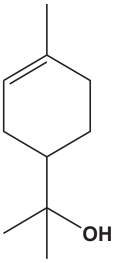
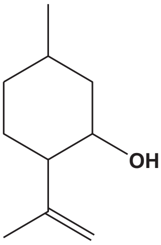
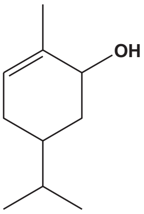
Table 2
Performance of Nb/SiO_2-liq and Nb/SiO_2-DI in the catalytic epoxidation of cyclic alkenes and unsaturated terpenes.

Alkene		Catalyst	C[a] 1 h (%)	S[b] 1 h (%)	C[a] 4 h (%)	S[b] 4 h (%)
	Cyclohexene **1**	Nb/SiO_2-DI	53	94	82	87
		Nb/SiO_2-liq	53	90	65	74
	1-Methylcyclohexene **2**	Nb/SiO_2-DI	59	85	99	53
		Nb/SiO_2-liq	71	94	86	56
	Limonene **3**	Nb/SiO_2-DI	58	98[c]	62[d]	97[c,d]
		Nb/SiO_2-liq	64	>98[c]	74[d]	>98[c,d]
	Carveol **4**	Nb/SiO_2-DI	51	73[c]	65	60[c]
		Nb/SiO_2-liq	78	46[c]	80[d]	57[c,d]
	α-Terpineol **5**	Nb/SiO_2-DI	52	51	66	44
		Nb/SiO_2-liq	77	89	83	48
	Isopulegol **6**	Nb/SiO_2-DI	42	84	58	86
		Nb/SiO_2-liq	71	89	76	74
	Carvotanacetol **7**	Nb/SiO_2-DI	23	66	37	63
		Nb/SiO_2-liq	26	59	61	57

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

[a] Conversion of alkene.

[b] Selectivity to alkene monoepoxide.

[c] Selectivity to monoepoxide (sum of exocyclic + endocyclic isomers).

[d] Values after 3 h of reaction.

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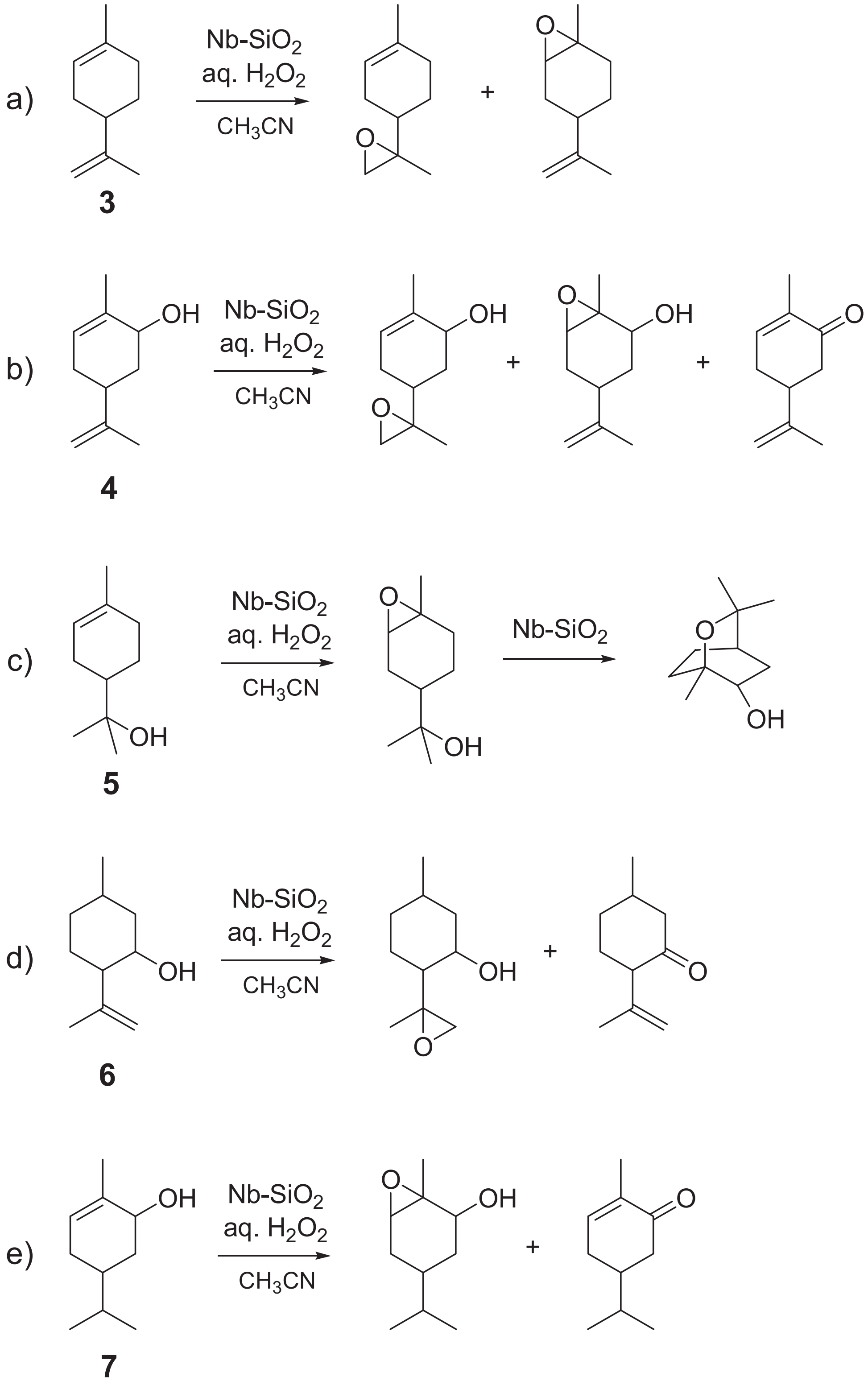

Scheme 1. Epoxidation of cyclic unsaturated terpenes **3**–**7**.

difference in the epoxidation behaviour of Nb-based systems with respect to Ti-based ones.

In terms of selectivity to desired epoxides, values spanned from >98% with limonene epoxide to less than 50% with α-terpineol epoxide. Such variability in chemoselectivity values is largely affected by the reactivity of the terpenic substrates: the higher the number of possible side products (ketones, by-products from epoxide rearrangement, *etc.*), the lower is the selectivity to the target molecule (Scheme 1). So, limonene was epoxidised with excellent selectivity (limonene epoxide was practically the only product) and no side products, due to parallel oxidation pathways (*e.g.*, allylic oxidation or hydroperoxidation) were formed. Carveol, carvotanacetol and isopulegol, on the contrary, suffered from the concurrent oxidation of the OH-group and *ca.*

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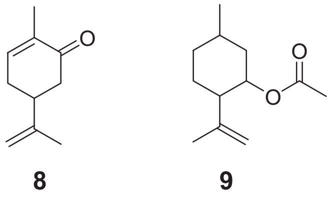


Scheme 2. Carvone **8** and isopulegyl acetate **9**.

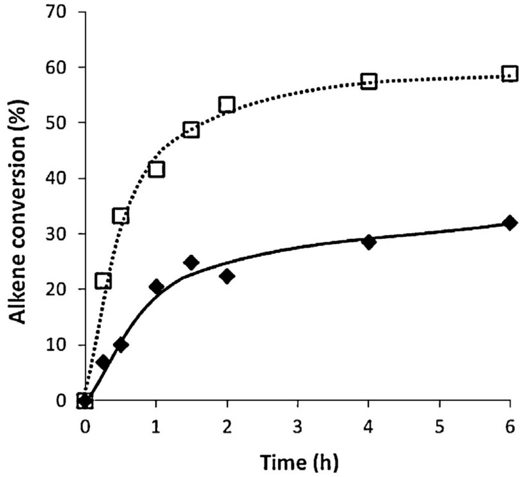


Fig. 3. Conversion profile *vs.* time for isopulegol **6** (□) and isopulegyl acetate **9** (♦) over Nb/SiO$_2$-DI.

20–30% of the products were due to the formation of carvone, carvotanacetone and isopulegone, respectively, in the reaction mixture.

Finally, α-terpineol **5** was converted into the epoxide, which underwent rapidly acid-catalysed intermolecular ring closure, leading to 2-hydroxy-1,8-cineol [58,62]. After 4 h of reaction, in fact, the selectivity to α-terpineol epoxide dropped down to 44–48%, the rest being mainly composed by the bicyclic cineol (Scheme 1).

Finally, in terms of regioselectivity, when doubly unsaturated terpenes were studied (limonene **3** and carveol **4**), the formation of the monoepoxide occurred with unexpected regioselectivity towards the exocyclic isomer. In fact, exocyclic 7,8-limonene epoxide and 7,8-carveol epoxide were formed preferentially from limonene and carveol over both catalysts, with exocyclic/endocyclic ratios of *ca.* 75:25 and *ca.* 60:40, respectively. In this particular case, the expected preferential epoxidation of the endocyclic unsaturation (more nucleophilic than the exocylic one [55]) did not occur and the terminal exocyclic epoxide is the major product.

Such peculiar behaviour, however, is to be attributed mainly to steric factors and this statement can be confirmed by a set of specific tests. In fact, by using TBHP as oxidant, instead of hydrogen peroxide, the epoxidation of limonene was slower, but, in particular, exocyclic/endocyclic ratio was the opposite (*i.e.*, 24:76 with Nb/SiO$_2$-liq, at 29% conversion after 1 h).

Then, by using hydrogen peroxide as oxidant and a non-porous Nb-SiO$_2$ catalyst, prepared by grafting Nb(V) centres onto a pyrogenic nanosized (Aerosil380) silica [39], the unusual regioselectivity towards exocyclic limonene epoxide was no longer observed.

Finally, some efforts were devoted to exploit such particular regioselectivity towards terminal unsaturations for the epoxidation of squalene **10** (Scheme 3). The regiospecific preparation of terminal squalene epoxides would be extremely useful as a precursor for the synthesis of a variety of polycylic steroidic derivatives with relevant biological activity [46,47]. Unfortunately, no marked regioselectivity was observed on this substrate and the formation of the more stable internal epoxides was regularly observed over both catalysts at various reaction times (Fig. 5).

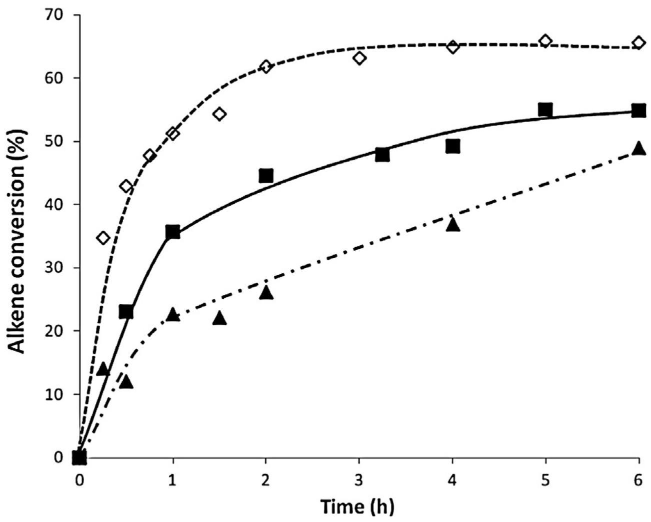
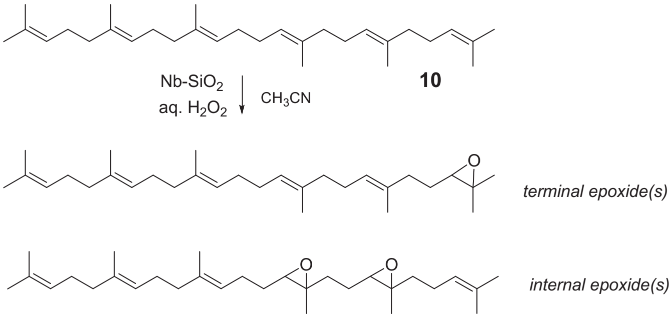


Fig. 4. Conversion profile *vs.* time for carveol **4** (◇), carvone **8** (■) and carvotanacetol **7** (▲) over Nb/SiO$_2$-DI.



Scheme 3. Epoxidation of squalene **10**.

All these evidences confirm that the regioselective behaviour recorded on limonene and carveol was not due to intrinsic electronic reasons, but, rather, to some special interactions among this kind of substrates, the heterogeneous catalyst and the oxidant.

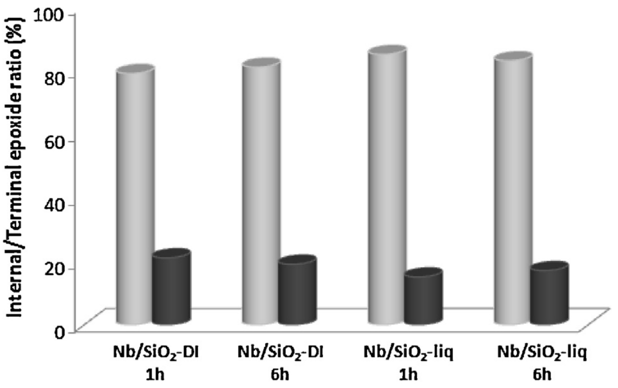


Fig. 5. Internal (grey) to terminal (black) epoxide ratio, at different reaction times, in the epoxidation of squalene **10**.

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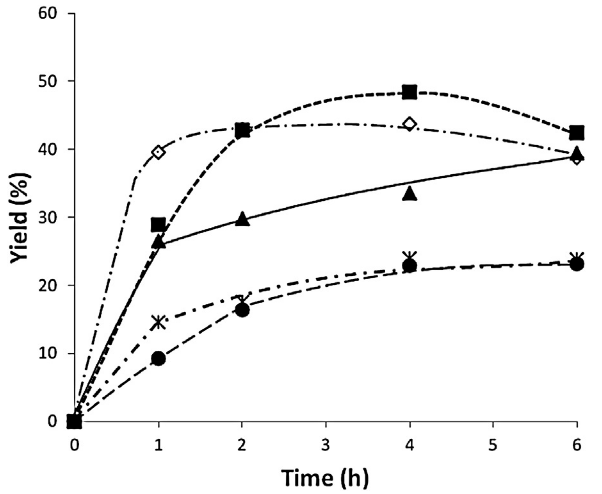

Fig. 6. Conversion profile *vs.* time for limonene **3** epoxidation over Nb/SiO$_2$-DI (◊) 1st run, (■) 2nd run, (▲) 3rd run, (□) 4th run, (●) 5th run.

3.3. *Recover and recycling*

The catalysts were easily recovered by filtration, washed, calcined and reused in subsequent catalytic runs. In order to recover the pristine activity, the organic deposits on the catalyst surface had to be removed only by thorough calcination of the spent catalyst. Such treatment converted back the yellowish colour of the spent catalyst to the pure white of the fresh one.

Detailed recovery and reuse tests were performed for limonene epoxidation. The recycled Nb-SiO$_2$-DI catalyst underwent five catalytic runs overall (Fig. 6). By thermogravimetric analysis (TGA), it was possible to quantify the amount of carbonaceous products adsorbed on the silica surface after the catalytic tests. After the fifth run, for Nb/SiO$_2$-DI, the carbonaceous deposits resulted to be 3.2 wt.%. The catalyst kept its epoxidation activity during the first reuse. Then, it decreased gradually to about one fourth of the initial activity at the fifth run. The selectivity to limonene epoxide, on the contrary, was very high in all cases until the fourth run and only in the last run some decrease in selectivity was observed. The promising stability of Nb-silica catalysts has been already reported in previous works [36,63], but it is important to evaluate the catalyst behaviour over repeated runs, if some further exploitation at larger scale is envisaged.

The dispersion of Nb sites was evaluated by DR UV–visible spectroscopy at the end of the recovery and reuse tests too. Prior to the analysis, the deactivated sample was calcined at 500 °C for 3 h in air in order to remove the by-products formed during the catalytic runs. The spent Nb/SiO$_2$-DI catalyst showed a main band at *ca.* 250 nm, assigned to $O^{2-} \rightarrow Nb^{5+}$ charge-transfer transitions, typical of isolated Nb(V) centres with tetrahedral and octahedral geometry (Fig. 1c). Moreover, a shoulder centred at *ca.* 340 nm, assigned to Nb_2O_5-like nano-aggregates, was also observed. Similar absorptions appeared in the spectrum of the fresh Nb/SiO$_2$-DI catalyst too (Fig. 1b). No absorption bands above 400 nm were detected, indicating that no large Nb_2O_5 domains were formed during the recovery and regeneration tests.

It can be concluded that, in this example, the distribution, geometry and coordination state of the Nb sites was preserved. This happened despite the fact that the catalyst has been regenerated several times and that Nb sites were obtained via a post-synthesis deposition method (which, in principle, gives rise to metal centres more prone to leaching than in-framework synthesis approaches).

4. Conclusions

Mesoporous non-ordered niobium-silica solids proved to be versatile, rather robust and efficient catalysts for the epoxidation, in the presence of aqueous hydrogen peroxide, of a broad series of unsaturated cyclic and terpenic compounds of interest for fine and specialty chemistry. These heterogeneous catalysts can be prepared via liquid-phase grafting of niobocene dichloride or via an organometallic dry-impregnation approach from the same precursor. High yields (up to 73%) and excellent chemoselectivity to the desired epoxides (up to 98%) were obtained in short reaction times (1 h). It is evident, however, that these performances can be further optimised by tuning carefully the experimental conditions, adapting them to the target substrate of interest. Interestingly, Nb/SiO$_2$ systems showed an unexpected peculiar regioselectivity towards the epoxidation of the less electron-rich exocyclic C═C double bond of limonene **3** and carveol **4**. In addition, carvone **8**, an α,β-unsaturated ketone, was efficiently epoxidised on the same catalysts as well.

Finally, niobium-silica systems showed some advantages, in terms of catalytic performance, with respect to widely-used and deeply-studied titanium-silica solids. In particular, they did not suffer, under reaction conditions here tested, from severe rapid deactivation by water and non-anhydrous reagents can thus be employed. They can lose, on the contrary, some catalytic activity whenever they are reused and recycled extensively in several catalytic runs. For these reasons, mesoporous niobium(V)-silica materials can deserve a deeper study as heterogeneous catalysts to be applied in the selective epoxidation of bulky and richly functionalised unsaturated molecules for high added-value applications.

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