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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

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by 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 $1° 2\theta \min^{-1}$.

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