



# The stability of niobium-silica catalysts in repeated liquid-phase epoxidation tests: A comparative evaluation of in-framework and grafted mixed oxides



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## ARTICLE INFO

### Article history:

Received 29 October 2014

Received in revised form 25 January 2015

Accepted 29 January 2015

Available online 16 February 2015

### Keywords:

Niobium

Heterogeneous catalysis

Mesoporous silica

Hydrogen peroxide

Alkene epoxidation

## ABSTRACT

Two types of niobium-containing silica catalysts, (i) in-framework mixed oxide, obtained by co-precipitation type synthesis, and (ii) grafted niobium sites on silica supports, obtained via post-synthesis deposition from niobocene dichloride, were prepared. Both solids were tested in a series of five repeated batch-wise liquid-phase epoxidation tests of limonene with 50% aqueous hydrogen peroxide.

Nb/SiO<sub>2</sub> prepared by co-precipitation synthesis kept fully its epoxidation activity during the first two recycles, with a gradual decrease in activity in the following runs. Conversely, Nb/SiO<sub>2</sub> prepared by deposition suffered from a more marked loss of activity since the first reuses. Most of the isolated Nb sites were maintained and no large Nb<sub>2</sub>O<sub>5</sub> domains were formed during the recovery and regeneration tests. The distribution, geometry and coordination state of the Nb sites was therefore preserved, especially for the Nb/SiO<sub>2</sub> sample prepared via co-precipitation. The presence of small Nb<sub>2</sub>O<sub>5</sub> domains, even formed during repeated recycles, was not detrimental for the epoxidation reaction and, in general, Nb(V) sites inserted in a silica matrix proved to be a rather robust epoxidation catalyst for alkenes in the presence of aqueous hydrogen peroxide.

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## 1. Introduction

Heterogeneous niobium-based catalytic systems, in particular mixed oxides and silicates, have recently emerged from the transition metal set, since they showed useful properties which can be exploited in several reactions [1,2], for their marked acid properties [3,4] as well as for their oxidation properties [5], such as in the oxidation of alkenes [6–12], phenols [13], alcohols [14–16] or sulfides [17,18]. The high robustness towards hydrolysis and metal leaching is one of the reasons for the major attention paid to Nb-containing silica solids in the field of heterogeneous oxidation catalysis. Such peculiar feature is ascribed by some authors to the relatively low surface mobility of niobium atoms and to the optimal geometry of Nb–O–Si bond angles [19]. These factors likely render Nb species less prone to hydrolysis/solvolytic in protic media and make them suitable to be used in aqueous media, in water-containing liquid phases and in the presence of aqueous hydrogen peroxide, as a direct oxidant.

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Hydrogen peroxide is a sought-after oxidant according to green chemistry guidelines and is also able to selectively epoxidise alkenes via radical-free heterolytic oxidation mechanisms [20]. V, Ta or Zr-containing solids have previously been proposed for alkene epoxidations, but they often suffer from metal leaching problems [21,22]. Widely-studied Ti-silica systems, which have shown, for this reaction, very good catalytic performances, often require water-free conditions and anhydrous organic hydroperoxides, as oxidants, especially when the reaction is performed over highly hydrophilic nanostructured Ti-silicate solids [23]. Therefore, the use of Nb-silicate/H<sub>2</sub>O<sub>2</sub> oxidizing catalytic systems is promising and highly desirable, although it has been only partially explored in the recent literature.

Prompted by these observations and the promising results recently achieved with the Nb–SiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> system, we focused our attention onto the following question: how can the method of preparation of a solid niobium-silica catalyst affect its performance?

Some previous studies have investigated the relationships between structural and/or morphological features and catalytic

properties of niobium oxide species on silica [24–26]. But, to our best knowledge, only one direct comparison has been reported so far, between the performances in the selective oxidation of alkenes of in-framework niobia-silica mixed oxides and the ones of grafted niobium(V)-silica catalysts obtained by post-synthesis modifications [27] and no reports are present on grafted catalysts prepared from organometallic niobium precursors. In addition, in most papers, the robustness and stability of Nb-silica catalysts were evaluated after two catalytic runs maximum (*i.e.* 1 recycle). It is, on the contrary, essential to evaluate the catalyst behavior after repeated cycles under stress conditions, as evidenced by some works on niobia-silica [10,28–30] and widely-studied titanium-silica epoxidation catalysts [17,31]. In fact, in the presence of water (both as a medium for the oxidant and as a product from hydrogen peroxide consumption), some isolated Nb(V) sites may aggregate and form NbO<sub>x</sub> domains.

In order to shed some light onto these points, we have here compared two types of niobium(V)-silica catalysts: a mixed oxide, obtained by co-precipitation type synthesis, and a grafted niobium-silica catalyst, obtained via post-synthesis deposition from a niobium organometallic precursor. The amount of Nb was in any case low (<2 wt.%) to exploit the catalytic properties typical of dispersed Nb phases and because such loading proved to be the optimal loading for the epoxidation of a large variety of alkenes [10,32]. Both systems were tested in the batch-wise liquid-phase epoxidation of limonene with aqueous hydrogen peroxide and their behavior was also studied in repeated use and recovery catalytic tests.

## 2. Experimental

### 2.1. Materials

Niobium-silica catalysts were prepared by co-precipitation using ammonium niobate(V) oxalate hydrate complex, ANBO (Sigma Aldrich, 99.99%), as niobium precursor, and tetraethylorthosilicate, TEOS (Sigma Aldrich, purity >99.0%), as silica source, and by grafting bis(cyclopentadienyl)niobium(IV) dichloride (Nb(Cp)<sub>2</sub>Cl<sub>2</sub>; 95%, Aldrich) onto Grace Davison, Dav SiO<sub>2</sub>, (Davasil SiO<sub>2</sub> LC60A, 60–200 μm). Dav silica is commercially available from the manufacturer.

The Nb-silica catalyst obtained via co-precipitation (Nb/SiO<sub>2</sub>-CP) was prepared as described in Ref. [26]. Briefly, the Si-font (TEOS) was hydrolyzed in acid-aqueous solution and then ANBO was added. Then, pH was increased by ammonia solution that caused the precipitation of the unripe solid. The Nb-silica catalyst obtained via dry impregnation (Nb/SiO<sub>2</sub>-DI) was prepared as described in detail previously [34]. Briefly, the silica support was first hydrated with high purity deionized water (MilliQ Academic, Millipore, 18 MΩ cm) for 2 h, dried in a rotary evaporator then heated in air at 300 °C for 1 h and under vacuum overnight at 300 °C. Nb(Cp)<sub>2</sub>Cl<sub>2</sub> was finely ground and mixed, under an inert atmosphere in the solid phase, with the silica. The mixture was stirred overnight under vacuum at room temperature. The resulting light brown solid were calcined in dry oxygen at 500 °C for 2 h to obtain the final white Nb/SiO<sub>2</sub>-DI catalyst.

Bulk hexagonal-phase Nb<sub>2</sub>O<sub>5</sub> (Aldrich, 99.99%) was used as such, for comparison.

### 2.2. Characterization

The content of Nb in the prepared samples was determined by inductively coupled plasma optical emission spectroscopy ICP-OES (ICAP 6300 Duo, Thermo Fisher Scientific) after mineralization 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 (DR UV-Vis) spectra were measured by using a Perkin Elmer Lambda 900 spectrometer equipped with an integrating sphere accessory and using a hand-made quartz cell that allows analysis both under vacuum conditions (residual pressure 10<sup>-5</sup> mbar) and under controlled gas atmosphere. Prior to the analysis, the samples were dispersed in anhydrous BaSO<sub>4</sub> (10 wt%). DR-UV-Vis spectra were collected in air atmosphere. Spectra were measured in absorbance mode and converted in Kubelka-Munk function in the 500–200 nm range.

N<sub>2</sub> physisorption measurements were carried out at –196 °C in the relative pressure range from 1 × 10<sup>-6</sup> P/P<sub>0</sub> to 1 using a Quantachrome Autosorb 1MP/TCD instrument. Prior to the analysis, the samples were outgassed at 100 °C for 3 h (residual pressure 10<sup>-6</sup> mbar). Specific surface area values were determined using the Brunauer-Emmett-Teller (BET) equation. Pore size distributions were obtained by applying the NLDFT method.

Thermogravimetric analysis (TGA) was performed on a high-temperature thermal balance (Perkin Elmer; 7HT – Pyris Manager) in the temperature range between 50 and 1000 °C, under dry air with a temperature rate of 5 °C min<sup>-1</sup>.

### 2.3. Catalytic tests

All catalysts were pretreated under dry air at 500 °C and cooled down to room temperature under vacuum prior to use. The epoxidation tests on (*R*)-(+)-limonene (97% Aldrich; 98% e.e.) were performed 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) and aqueous hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>; Aldrich, 50%) were used as solvent and oxidant, respectively, with an oxidant to substrate molar ratio of 2:1. The total volume of the mixture was 5 mL. Samples were taken at regular intervals and analyzed on GC chromatogram (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. A standard deviation of ±2%, ±4% and ±2 h<sup>-1</sup> has to be considered on average for the conversion, selectivity and specific activity values, respectively. The distribution of stereoisomers in the reaction samples was determined by <sup>1</sup>H NMR spectroscopy (Bruker, 300 MHz), evaluating the diagnostic peak ratios. The formation of peroxyimide 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 was checked and confirmed by iodometric assays. Through the quantification of residual hydrogen peroxide, it was possible to evaluate the average oxidant efficiency, that is the global amount of oxidized products obtained per amount of consumed oxidant.

In order to check the leaching of niobium species, the solid catalyst was removed from the liquid mixture by centrifugation at the temperature of the reaction (“hot filtration” test) and the resulting solution was tested for further reaction [33]. In the tests for the recovery and reuse of the catalyst, the solid was separated by filtration at room temperature 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 up to five times in a new test as described above.

## 3. Results and discussion

### 3.1. Preparation of the catalysts

Two types of Nb/SiO<sub>2</sub> catalysts were prepared following two different synthesis strategies. Nb/SiO<sub>2</sub>-CP was obtained by co-pre-

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