

# Catalytic properties of silica supported titanium, vanadium and niobium oxide nanoparticles towards the oxidation of saturated and unsaturated hydrocarbons

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## Abstract

The catalytic properties of silica supported titanium, vanadium and niobium oxide nanoparticles towards the oxidation of different organic substrates (cyclohexane, cyclohexene, 1-hexene) using tertbutylhydroperoxide (TBHP) and molecular oxygen as the oxidizing agents was studied. Titanium (1.9 nm), vanadium (2.3 nm) and niobium (1.6 nm) oxide nanoparticles stabilized on silica were synthesized by the reduction of  $\text{TiCl}_4 \cdot 2\text{THF}$ ,  $\text{VCl}_3 \cdot 3\text{THF}$  and  $\text{NbCl}_5 \cdot 2\text{THF}$  with  $\text{K}[\text{BEt}_3\text{H}]$ . These materials were characterized by inductive coupled plasma-optical emission spectroscopy (ICP-OES), Fourier transformed infrared spectroscopy (FTIR), high resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) analyses. The solids obtained were employed as heterogeneous catalysts. For 1-hexene and cyclohexene, the titanium oxide nanostructured material showed 100% selectivity towards the epoxidation product, with conversions above 50%. In the case of cyclohexane, the titanium oxide nanoparticles are 100% selective towards the desired oxidation products (cyclohexanol and cyclohexanone). The highest oxidation activity was achieved with the vanadium oxide nanoparticles for the three substrates studied: cyclohexane, cyclohexene and 1-hexene, TN 562, 878 and 1190 mol of product/mol of metal, respectively, after 6 h of reaction time at 80 °C. Nevertheless, with this metal the selectivity is different to the one obtained for with the titanium oxide nanostructured system. The niobium catalyst was less active than the titanium and vanadium oxide catalysts, although it proved to be more selective towards the formation of alcohols.

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## 1. Introduction

The oxidation of organic substrates represents one of the most important industrial chemical reactions [1], explaining the significant effort invested in the research and development of new heterogeneous catalysts with increased activities and selectivities in these types of reactions. In particular, alkene epoxidation

is one of the main aims in this area [2,3]. The oxidation of cyclohexane and cyclohexene to cyclohexanol and cyclohexanone is the key reaction in the synthesis of adipic acid, which is an essential precursor in the production of nylon 6 and nylon 66 [4].

It is well known that amongst the most active homogeneous and heterogeneous catalysts for alkene and alkane oxidation, are those based on transition metals of groups 4 (Ti), 5 (V and Nb) and 6 (Mo) [5–10]. In the case of heterogeneous catalysts, it has been proved that a proper selection of preparation conditions is essential to obtain a homogeneous metal dispersion on the support, which in turn, generates highly active and selective catalysts towards oxidation reactions [9–14].

Over the last decade, the research and development of transition metal nanoparticles has received a lot of attention in many

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areas of science. This interest is because nanosized particles show different physical and chemical properties to those of the same materials in the bulk [15,16]. The main reasons for these differences originate in the electronic properties and in the very high ratio between superficial atoms and total number of atoms in the particles found in these nanomaterials. Both properties mentioned above, are of interest from the catalytic point of view, since they can aid in raising the activity and selectivity of a reaction and, in some cases, induce new reactivities and selectivities never observed with classical catalysts [15–17].

This work presents a catalytic study of the oxidation of saturated and unsaturated hydrocarbons with titanium, vanadium and niobium oxide nanoparticle systems supported on silica.

## 2. Experimental

### 2.1. Materials

All the syntheses were carried out under an argon atmosphere (99.99% pure) using Schlenk techniques for the manipulation of air sensitive compounds [18].

The metal precursors  $\text{TiCl}_4 \cdot 2\text{THF}$  (Aldrich),  $\text{VCl}_3 \cdot 3\text{THF}$  (Strem)  $\text{NbCl}_4 \cdot 2\text{THF}$  (Strem) were used as supplied.

The silica gel (Gomasil G-200) used as inorganic support is 98.8%  $\text{SiO}_2$  and 0.69%  $\text{Na}_2\text{SO}_4$  content, with a mean grain size of 0.5  $\mu\text{m}$ . The silica gel was activated at 250 °C under vacuum during 72 h, and then kept under an argon atmosphere before its use. After activation, the  $\text{SiO}_2$  showed a BET specific surface area of 169  $\text{m}^2/\text{g}$ . Rhodia Silices de Venezuela C.A. donated this material.

### 2.2. Synthesis of the silica supported metal oxide nanoparticles

To obtain the metal oxide nanoparticles supported on silica, firstly the metallic nanoparticles of titanium, vanadium and niobium were synthesized following the method established by Bönemann [19], then stabilized on silica and finally oxidized under 1 atm of molecular oxygen.

As an example, here follows the procedure for the synthesis of niobium oxide nanoparticles. A solution of  $\text{K}[\text{BEt}_3\text{H}]$  (1 M, 80 ml, 80 mmol) in tetrahydrofuran (THF) was added dropwise to a suspension of  $\text{NbCl}_4 \cdot 2\text{THF}$  (10.24 g, 20 mmol) in THF at room temperature during 2 h. After 2 h of constant stirring at room temperature, a dark brown solution was obtained. The KCl formed during the reaction was removed by filtration and the solvent was eliminated under vacuum. A dark solid was obtained which later was redissolved in fresh THF and added to a silica/THF suspension. This suspension was stirred for at least 8 h, and then dried under vacuum during 24 h resulting in a light brown solid. All three silica supported nanoparticles (titanium, vanadium and niobium) are extremely sensitive to air.

Finally, the nanometric metal oxides supported on silica are obtained by the exposure of the previously synthesized systems to 1 atm of molecular oxygen.

### 2.3. Characterization of the silica supported metal oxide nanoparticles

Routine FTIR was performed on a Perkin-Elmer 1760-X spectrometer using CsI disks. The elemental analyses were carried out by atomic emission with coupled inductive plasma on a Thermo Jarrel ASH model IRIS H12. The high resolution transmission electron microscopy (HRTEM) was carried out in a CM30 Phillips Microscope with a 0.19 nm resolution. Samples were prepared using carbon-coated copper grids. One drop of a THF suspension of  $[\text{M}_x\text{O}_y/\text{SiO}_2]$  was placed on the carbon-coated grid using a microsyringe. Different samples of each nanostructured materials were prepared; these samples were subject to scanning in entire the area verifying the homogeneity of the nanoparticles dispersion. The size and size distribution of the nanoparticles was determined through manual analysis enhancing the contrast of the digital micrographs, which are the output of the HRTEM, at least 100 particles per sample were measured. This analysis was corroborated employing Image Pro Plus 5.0 as a digital processing program.

The X-ray photoelectron spectroscopy, XPS, was carried out in a Escalab 220i-XL equipped with a monochromatic source  $\text{Mg K}\alpha$  ( $h\nu = 1253.6 \text{ eV}$ ). The deconvolutions of the XPS spectra were carried out using a XPS Peak Fitting program version 4.1.

Gas chromatography (GC) analyses were performed on a Perkin-Elmer Autosystem XL with a flame ionization detector (FID), equipped with a PE-Alumina capillary column (30 m). Gas chromatography coupled with mass spectroscopy (GC-MS) was performed on a HP6890 equipped with a Mass Selective Detector 5973.

### 2.4. Catalytic activity

The catalytic studies of the solids obtained, were carried out in Fischer–Porter bottles. Metal supported catalyst (100 mg) was introduced in the Fischer–Porter bottle along with 2 ml of organic substrate (cyclohexane, cyclohexene and 1-hexene) and 0.5 ml of TBHP as the oxidizing agent. The reactions were carried out under 1 atm of argon or 3 atm of molecular oxygen and at 80 °C. This study was done in order to determine the influence of molecular oxygen in the catalytic activity of the solid towards oxidation reaction. All reactions were studied with different reaction times.

The TBHP percentage was determined through iodometric analysis, before and after catalytic oxidation reaction [20].

## 3. Results and discussions

### 3.1. Synthesis and characterization of nanostructured systems

The titanium, vanadium and niobium oxide nanoparticles were synthesized firstly following the method established by Bönemann [19] for the preparation of metallic nanoparticles, then stabilized on silica and finally oxidized under 1 atm of molecular oxygen.

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