



Liquid phase cyclohexene oxidation over vanadia based catalysts with tert-butyl hydroperoxide: Epoxidation versus allylic oxidation



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ABSTRACT

VO₂-SiO₂ based catalysts with V contents between 5 and 20 wt.% were prepared from inorganic precursors via the sol-gel process and subsequently dried, calcined and reduced at 673 K. Structural characterization of these materials was carried out with X-rays diffraction (XRD), ICP, N₂ adsorption-desorption at 77 K, UV-vis diffused reflectance spectroscopy (DR UV-vis), FTIR and pyridine adsorption followed by FTIR. Their catalytic activities in the cyclohexene epoxidation with TBHP as oxidant and heptane as solvent were also examined. Results of XRD and DR UV-visible spectroscopy revealed that VO₂ species are well dispersed on silica. BET analysis showed that the surface area decreases from 390 to 22 m² g⁻¹ with V content. The results of pyridine adsorption followed by FTIR indicated that the 5 wt.% VO₂-SiO₂ catalyst displays low acid densities. Experimental results pointed out that the 5 wt.% VO₂-SiO₂ catalysts offer excellent activity. The obtained cyclohexene conversion and selectivity toward epoxide are 21% and 84% respectively. A reaction mechanism explaining clearly epoxidation versus allylic oxidation is proposed.

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1. Introduction

During the last fifteen years, fine-chemical industry has pointed out that olefin epoxidation is one of the most important reactions in industrial organic synthesis [1]. Among olefins, cyclohexene is one of the most studied compounds. Cyclohexene oxide (epoxy-cyclohexane) is a useful monomer in polymerization and coating industries. It is used in the synthesis of alicyclic target materials including pesticides, pharmaceuticals, perfumery and dye stuffs [2,3]. However, in the epoxidation of alkenes, several side reactions can take place, i.e. oxidation in the allylic positions, ring-opening of the epoxide by hydrolysis or solvolysis, epoxide rearrangement or even total breakdown of the C=C double bond. Cyclohexene is one of the most difficult cases, as the first two situations, namely allylic oxidation and epoxide ring-opening, can occur extensively [4].

It is well known that among the most active homogeneous and heterogeneous catalysts for alkenes and alkanes oxidation, are those based on transition metals of groups 4 (Ti), 5 (V and Nb) and

6 (Mo) [5]. In the case of heterogeneous catalysts, the preparation conditions play a crucial role in obtaining high metal dispersion on the support, which in turn, generates highly active and selective catalysts toward oxidation reactions [6–9].

Among the supported metals used in cyclohexene oxidation, titanium is probably the most widely used. The couple TiO₂-SiO₂ has been known for a long time as an efficient catalyst in liquid-phase oxidation reactions, when using hydrogen peroxide or alkylhydroperoxides as oxygen donors [10–19]. Besides titanium, vanadium has been used in homogeneous [20–22] and heterogeneous [23–30] oxidation reactions of cyclohexene. Most heterogeneous vanadium catalysts are supported catalysts prepared by impregnation. Thereafter, the sol-gel method has been used for the preparation of vanadia-silica catalysts which have been tested in reactions such as selective catalytic reduction of nitric oxide with ammonia [31], epoxidation of allyl alcohol [32], and oxidation of alkenes [33].

Many spectroscopic techniques have been employed to study supported vanadia catalysts in order to establish the effect of the support on vanadia dispersion and the type of vanadium species present [34–37]. Wachs et al. [35,37] and Weckhuysen and Keller [38] described the possible structures of supported vanadium species and their effects on the catalytic activity. Different species may be present on SiO₂ and Al₂O₃ supports: isolated VO₄ species,

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polymeric VO₄ species, crystalline V₂O₅ and mixed oxide with support [38].

As noted above, the epoxidation of cyclohexene [39–44] is rivaled by allylic oxidation that forms mainly cyclohexene-2-one and cyclohexene-2-ol [45–48].

In the present work, we report the sol–gel synthesis of X wt.% VO₂–SiO₂ catalysts with V contents from 5 to 20 wt.%, calcined and reduced at 673 K. The prepared catalysts are characterized by physico-chemical techniques, such as, ICP, infrared spectral analysis using pyridine as a probe molecule, X-rays diffraction (XRD), specific surface area determination (BET) and UV–Vis DR Spectroscopy, to understand their behavior, and their performances as solid catalysts for epoxidation of cyclohexene, using tert-butyl hydroperoxyde (TBHP) as oxidant. The results of this work and those already published [49] are focused on the evidence of active sites and the comprehension of the mechanism of epoxidation versus allylic oxidation.

2. Experimental

2.1. Synthesis

2.1.1. Starting materials

The following chemicals were employed for the preparation of X wt.% VO₂–SiO₂ materials: tetraethylorthosilicate (C₈H₂₀O₄Si, Aldrich 98%), ammonium metavanadate (NH₄VO₃, Strem chemicals 99%), chloridric acid (Aldrich 37%), ethanol (Aldrich 98%).

2.1.2. Synthesis of SiO₂

The preparation was carried out in a 100 mL beaker. 16.22 mL (0.091 mol) of tetraethylorthosilicate was dissolved in 13 mL of ethanol. The mixture was stirred for 24 h, and then 4.5 mL of HCl was added to this solution. The resulting gel was then stirred for 24 h. This gel was first dried at 333 K for one night, next at 393 K for another night and then calcined in air at 673 K for 4 h.

2.1.3. Synthesis of the system X wt.% VO₂–SiO₂

Typical procedure for the preparation of 5 wt.% VO₂–SiO₂: the mixed oxide was prepared by an acidic-catalyzed sol–gel process [6]. A quantity of 0.46 g of ammonium metavanadate (NH₄VO₃) was dissolved in the mixture of 16.22 mL of tetraethylorthosilicate and 13 mL of ethanol. The mixture was stirred for 24 h, and then 4.5 mL of HCl was added to this solution. The resulting gel was then stirred for 24 h. This gel was first dried at 333 K for one night, next at 393 K for another night and then calcined in air at 673 K for 4 h, and finally reduced, under hydrogen flow, at 673 K for 4 h. The materials obtained have a green color which indicates the presence of reduced vanadium (IV) species [33].

2.2. Materials characterization

The chemical composition of the samples was determined by inductively coupled plasma emission spectroscopy (ICP) using a Varian ICP OES.

The BET surface area was determined from N₂ adsorption isotherms at 77 K using a Quantachrom NOVA 1000 instrument. Prior to adsorption measurements, the sample was outgases at 673 K for 3 h.

The UV–visible spectra (200–800 nm) of these samples were collected on an UV/Vis spectrometer Perkin Elmer with integration sphere. The baseline was recorded using MgO as a reference.

The FTIR spectra of the solid samples were recorded using an Agilent Technologies Cary 60 series FTIR spectrometer, with ATR accessories, and a measuring range of 4000–400 cm⁻¹.

FTIR analysis of pyridine adsorption was carried out on a NEXUS-Nicolet spectrometer with a 4 cm⁻¹ resolution and a

4000–400 cm⁻¹ scanning range. The spectrometer was equipped with MCT detector cooled by liquid nitrogen. 18–20 mg of the catalyst sample was pressed into a self-supported wafer of approximately 2 cm in diameter, then evacuated at 623 K for 4 h, and finally cooled down to 293 K. A known amount of pyridine was then introduced in the cell at room temperature and the wafer was degassed at 423 K for 15 min to remove the physisorbed fraction. Finally pyridine adsorbed was followed by evacuation for 15 min at different temperature. The IR spectrum thus obtained was used to calculate the amount of acid sites on the sample by measuring the peak area of pyridine adsorbed.

2.3. Catalytic experiments

The catalytic epoxidation of cyclohexene with tertibutylhydroperoxyde TBHP (Aldrich, 70 wt.% in H₂O) as an oxidant was carried out in a two neck glass round-bottom flask equipped with a magnetic stirrer and a reflux condenser. First, TBHP was stirred with heptane as solvent in order to perform a phase transfer from water to organic phase. Typically, 25 mL of heptane and 38.45 mmol (5.5 mL) of oxidant (TBHP) were mixed in a closed Erlenmeyer flask and magnetically stirred for 24 h. The organic phase was then separated from the aqueous phase. To control the phase transfer, the concentration of the remaining TBHP in the aqueous phase was determined by iodometric titration. Less than 10% of the initial TBHP remained in the aqueous phase. Then, 29 mmol (3 mL) of cyclohexene, 0.1 g of catalyst and the TBHP–heptane mixture were mixed in the magnetic stirrer-glass reactor at 338 K during 6 h. The reaction products were identified by comparison with authentic products and the course of reactions was followed by gas chromatography (GC), using a SCHIMADZU 14-B gas chromatograph equipped with Agilent HP-FFAP capillary column. A flame ionization detector (FID) was used and 0.5 μL of the sample was analyzed. Before the GC analysis, the remaining TBHP was decomposed by introducing an excess of triphenylphosphine (Aldrich). On the other hand, to control the remaining TBHP, an iodometric titration was performed at the end of the reaction (after 6 h) by analyzing the organic phase.

$$\text{Conversion(\%)} = 100 \times \frac{[\text{C}_6\text{H}_{10}]_0 - [\text{C}_6\text{H}_{10}]_t}{[\text{C}_6\text{H}_{10}]_0}$$

$$\text{Selectivity(\%)} = 100 \times \frac{\text{moles of individual product}}{\text{moles of total products}}$$

3. Results and discussion

3.1. Catalyst characterization

Table 1 shows that experimental vanadium loadings, measured by ICP for two samples, 5 and 15 wt.% VO₂, are very close to the theoretical values.

Nitrogen adsorption–desorption revealed a type-I adsorption isotherm (cf. ESI; Fig. S1) corresponding to a microporous structure according to the IUPAC [52]. The corresponding textural parameters are also presented in Table 1. The X wt.% VO₂–SiO₂ mixed oxides surface area decreases from 390 to 22 m² g⁻¹ when the VO₂ content rises from 5 to 20 wt.%. The decrease in surface area, average pore diameter and pore volume with an increasing vanadium loading is attributed to the blocking of micro-pores (covering effect) [2,50].

The XRD analysis (cf. ESI; Fig. S2†) showed that all catalysts based on silica have amorphous nature of silica and the peak of VO₂ phase does not appear. This implies that either VO₂ is well dispersed on silica with a crystal size below the detection limit of the method

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