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Highlights

- We have epoxidation in the presence of redox and monomeric vanadium sites.
- Allylic oxidation was obtained with acidic and/or polymeric vanadium sites.
- This reaction is heterogeneous and vanadium leaching is not observed.
- The results indicate that this material is stable for 4 cycles of the reaction.

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

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#### Abstract

VO<sub>2</sub>–SiO<sub>2</sub> based catalysts with V contents between 5 and 20wt.% 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, N<sub>2</sub> 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 VO<sub>2</sub> species are well dispersed on silica. BET analysis showed that the surface area decreases from 390 to 22 m<sup>2</sup> g<sup>-1</sup> with V content. The results of pyridine adsorption followed by FTIR indicated that the 5wt.%VO<sub>2</sub>-SiO<sub>2</sub> catalyst displays low acid densities. Experimental results pointed out that the 5wt.%VO<sub>2</sub>-SiO<sub>2</sub> catalysts offers excellent activity. The obtained cyclohexene conversion and selectivity towards epoxide are 21 % and 84 % respectively. A reaction mechanism explaining clearly epoxidation versus allylic oxidation is proposed.

Keywords: VO<sub>x</sub>-SiO<sub>2</sub>, Cyclohexene, Epoxidation versus allylic oxidation, Leaching.

#### 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 (epoxycyclohexane) is a useful monomer in polymerisation 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 towards oxidation reactions [6 - 9].

Among the supported metals used in cyclohexene oxidation, titanium is probably the most widely used. The couple  $TiO_2$ -SiO\_2 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 SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> supports: isolated VO<sub>4</sub> species, polymeric VO<sub>4</sub> species, crystalline V<sub>2</sub>O<sub>5</sub> and mixed oxide with support [38].

As noted above, the epoxidation of cyclohexene [39 - 44] is rivaled by allylic oxidation that forms mainly cyclohexene2-one and cyclohexene2-ol [45-48].

In the present work, we report the sol–gel synthesis of X wt.%VO<sub>2</sub>–SiO<sub>2</sub> 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.%VO<sub>2</sub>-SiO<sub>2</sub> materials: Tetraethylorthosilicate ( $C_8H_{20}O_4Si$ , Aldrich 98 %), ammonium metavanadate ( $NH_4VO_3$ , Strem chemicals 99 %), chloridric acid (Aldrich 37 %), ethanol (Aldrich 98 %).

#### 2.1.2. Synthesis of SiO<sub>2</sub>

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.%VO<sub>2</sub>-SiO<sub>2</sub>

Typical procedure for the preparation of 5wt.%VO<sub>2</sub>-SiO<sub>2</sub>: the mixed oxide was prepared by an acidic-catalyzed sol-gel process [6]. A quantity of 0.46 g of ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>) 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  $N_2$  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<sup>-1</sup>.

FTIR analysis of pyridine adsorption was carried out on a NEXUS- Nicolet spectrometer with a 4 cm<sup>-1</sup> resolution and a 4000–400 cm<sup>-1</sup> 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 tertiobutylhydroperoxyde TBHP (Aldrich, 70 wt. % in H<sub>2</sub>O) 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 Agile HP-FFAP capillary column. A flame ionization detector (FID) was used and 0.5  $\mu$ L 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.

Conversion (%) = 100 × 
$$\frac{[C_6H_{10}]_0 - [C_6H_{10}]_c}{[C_6H_{10}]_0}$$

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

#### 3. Results and discussion

#### 3.1. Catalyst characterization

Table1 shows that experimental vanadium loadings, measured by ICP for two samples, 5 and 15 wt.%VO<sub>2</sub>, are very close to the theoretical values.

Nitrogen adsorption–desorption revealed a type-I adsorption isotherm (cf. ESI; Fig. S1<sup>†</sup>) corresponding to a microporous structure according to the IUPAC [52]. The corresponding textural parameters are also presented in Table 1. The X wt.%VO<sub>2</sub>-SiO<sub>2</sub> mixed oxides surface area decreases from 390 to 22 m<sup>2</sup> g<sup>-1</sup> when the VO<sub>2</sub> 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<sup>†</sup>) showed that all catalysts based on silica have amorphous nature of silica and the peak of VO<sub>2</sub> phase does not appear. This implies that either VO<sub>2</sub> is well dispersed on silica with a crystal size below the detection limit of the method [50] or a completely amorphous phase was formed on the sample [51].

Matarial	wt.% of V	S <sub>BET</sub>	Pore volume	Pore size
Material	measured by ICP	$/m^2 g^{-1}$	$/cm^3g^{-1}$	/Å
5%VO <sub>2</sub> -SiO <sub>2</sub>	4.83	390	0.19	20
10%VO <sub>2</sub> -SiO <sub>2</sub>	1	177	0.10	18
15%VO <sub>2</sub> . SiO <sub>2</sub>	14.80	77	0.02	13
20%VO <sub>2</sub> - SiO <sub>2</sub>		22	0.03	25

Table 1 Vanadium weight percentage determined by ICP and BET surface area results

The UV-Vis spectra of the samples are shown in Fig. 1. All samples present two bands located at around 260 and 380 nm. The first UV-Vis band of vanadium species in the range 240-280 nm should be assigned to charge transfer transitions, involving oxygen and vanadium (IV) in tetrahedral coordination, present in isolated species [53, 54]. The band at 380 nm is attributed to octahedral  $V^{4+}$  species [53]. However, the band in the absorption range of 500-850 nm, attributed to d-d transition of  $V^{4+}$  [55], is not observed at low vanadium loadings. According to Luan et al. [56], Dutoit et al. [57] and also Golińska et al. [58], the intensity of d-d transitions of  $V^{4+}$  recorded in the range of 500–850 nm is generally 10 to 30 times lower than that of CT transitions. This may explain the lack of UV–vis bands, characteristic of  $V^{4+}$  species, whereas the intensity of the last band increases with increasing vanadium content (Fig. 1) [59]. The samples 15 and 20 wt.%VO<sub>2</sub>-SiO<sub>2</sub> show even the presence of new

polymeric species such as those in tetrahedral environment (~320 nm) [60] and in octahedral environment (~480 nm) [53, 60]. In conclusion, increasing the vanadium content leads to the formation of polymeric species that coexist with isolated vanadyl species [59].





IR spectra of the sample diluted in KBr matrix were deconvoluted using the peakFit software in order to determine more accurately band frequencies and compare our solids to literature data. Deconvoluted infrared spectra of VO<sub>2</sub>-SiO<sub>2</sub> materials in the 1500–600 cm<sup>-1</sup> region are reproduced in Fig. 2. For 5 and 10 wt.%VO<sub>2</sub>-SiO<sub>2</sub>, absorption bands are observed at 1060 cm<sup>-1</sup> and the shoulder at 1190 cm<sup>-1</sup>, due to the asymmetric stretching vibrations of the three dimensional Si–O–Si network [53]. The band at 930 cm<sup>-1</sup> is generally assigned to a Si–O–V stretch mode [50, 53] and it is also postulated that both Si–O–V and V–O–V bridges can

contribute to this band [38, 61]. The band at 793 cm<sup>-1</sup> is assigned to symmetric stretching vibrations of the three dimensional Si–O–Si network [39, 45, 53, 55]. The absorption bands between 550 and 670 cm<sup>-1</sup> are attributed to the rocking modes of the V–O–V bonds [60, 62-63]. Concerning 15 and 20 wt.%VO<sub>2</sub>-SiO<sub>2</sub>, in addition to the bands previously described, another band appeared as a shoulder at ~1024 cm<sup>-1</sup>. It is usually assigned to the V=O stretching vibration in polyvanadate [63].



Fig. 2 Deconvoluted bands of room temperature IR spectra with ATR of the X wt.% VO<sub>2</sub>-SiO<sub>2</sub> materials

Pyridine adsorption was performed on the surface of 5, 10, 15 and 20 wt.%VO<sub>2</sub>-SiO<sub>2</sub> catalysts, and followed by IR spectroscopy. The bands of Brønsted acid sites (1538 cm<sup>-1</sup>) and Lewis acid sites (1448 cm<sup>-1</sup>) are characteristic of pyridine adsorption on the catalyst surface [64]. After pyridine adsorption on 5 wt.%VO<sub>2</sub>-SiO<sub>2</sub> catalyst, the IR-spectra exhibited both Lewis acid site bands and Brønsted acid site bands (Fig. 3). However, the IR-spectra of 10, 15 and 20 wt.%VO<sub>2</sub>-SiO<sub>2</sub>, shows only the Lewis acid sites adsorption. The quantification of these sites is shown in Table 2. The decrease in the number of Lewis acid sites is due to the coverage of these sites by the increasing amount of V in the catalyst. So, the total acidity is found to decrease at higher loadings [65]. This is explained by the stacking of the vanadyl species on the surface of silica which leads to a decrease in the number of adsorption sites exposed.



**Fig. 3** Infrared spectra of pyridine adsorbed on 5 wt.%VO<sub>2</sub>-SiO<sub>2</sub> at different temperatures (323 – 623 K, with a step of 50 K)

followed by infrared spectroscopy						
Catalyst	Lewis acid sites /µmol g <sup>-1</sup>	Brønsted acid sites /µmol g <sup>-1</sup>				
SiO <sub>2</sub>	0	0				
5%VO <sub>2</sub> -SiO <sub>2</sub>	70	10				
10%VO <sub>2</sub> -SiO <sub>2</sub>	4	0				
15%VO <sub>2</sub> . SiO <sub>2</sub>	6	0				
20%VO <sub>2-</sub> SiO <sub>2</sub>	10	0				

 Table 2 X wt.%VO2-SiO2 catalysts acidity at 423 K estimated by pyridine adsorption

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#### 3.2. Catalytic Activity Results

The oxidation of cyclohexene with TBHP in the presence of vanadium mixed oxides resulted in the formation of several products, as shown in Table 3. Through GC analysis, 1,2cyclohexanediol was not detected in the reaction product. In the absence of catalyst, cyclohexene gave only 12 % conversion; no epoxide was found. Since the SiO<sub>2</sub> catalytic test gave a similar result to the one with no catalyst, it can be said that the support was not active [66]. From the results in Table 3, we note that the conversion of cyclohexene increases when the vanadia loading rises to 15 wt.%, and decreases at higher vanadia loadings. The decrease in conversion of the catalysts beyond 15 wt.% is probably due to the transformation of isolated vanadium active sites into polymeric ones because of the agglomeration of vanadium oxide [67]. As shown in table 3, all the catalysts give epoxide as the major product, while selectivity decreases due to the appearance of the polymeric vanadium species (Fig. 1 and Fig. 2). Intermediate species adsorb on both monomeric or polymeric vanadium V-O-V promotes another reaction pathway and thereby reducing selectivity to epoxide [68].

Catalanta	Conversion	Selectivity /%						TBHP
Catalysts	/%	Epoxide	Enone	One	Enol	01	Diol	Consumption
		Lpoinae		0.1.0	2	01	2101	/%
5%VO <sub>2</sub> -SiO <sub>2</sub>	21	84	/	12	4	/	/	24
10%VO <sub>2</sub> -SiO <sub>2</sub>	36	77	8	8	7	/	/	48
15%VO <sub>2</sub> -SiO <sub>2</sub>	46	63	2	35	/	/	/	45
20 %VO <sub>2</sub> -SiO <sub>2</sub>	39	58	4	38	/	/	/	61

Table 3 Cyclohexene oxidation over X wt.%VO<sub>2</sub>-SiO<sub>2</sub> catalysts

Reaction conditions: 29 mmol cyclohexene, 38.45 mmol TBHP, 25 mL Heptane, 0.1 g catalyst, 6 h, reaction temperature 338 K

The oxidation of cyclohexene with TBHP in the presence of vanadium mixed oxides 5 wt.%VO<sub>2</sub>-SiO<sub>2</sub>, 5 wt.%VO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and 5 wt.%VO<sub>2</sub>-TiO<sub>2</sub> was studied elsewhere [49]. High cyclohexene conversion is observed in the case of 5 wt.%VO<sub>2</sub>-SiO<sub>2</sub> (Table 4) due to highest surface area.

Catalysts	Conversion	Selectivity /%		TBHP	S <sub>BET</sub>	Lewis acid
	/ %0	Epoxide	Allylic oxidation	Consumption /%	$/m^2 g^{-1}$	sites /umol g <sup>-1</sup>
5%VO2-SiO2	21	84	16	24	390	70
5% VO_41_0	10	/	100	24	268	500
570 V O <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	10	/	100	20	308	399
5%VO <sub>2</sub> -TiO <sub>2</sub>	13	22	78	57	140	306

 Table 4 Cyclohexene oxidation vs. catalysts physico-chemical features [49].

These results show three different behaviors: (i) VO<sub>2</sub>-SiO<sub>2</sub> directs the reaction towards the epoxidation with a selectivity of 84 %; this is due to the presence of a weak Lewis acidity and a predominant redox character of vanadium oxide, (ii) VO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> directs the reaction towards the allylic oxidation, because of the strong Lewis acidity of alumina [9, 42], (iii) for VO<sub>2</sub>-TiO<sub>2</sub>, the major products of the allylic oxidation are obtained; due to the strong Lewis acid sites of the catalyst, but also a 22 % selectivity towards epoxide is observed due to the strong interaction between vanadium and titanium [62]. In conclusion, the catalyst 5wt.%VO<sub>2</sub>-SiO<sub>2</sub> has a higher catalytic activity in the cyclohexene epoxidation reaction due to the redox character of the vanadium oxide; which directs the reaction towards epoxidation. However, increasing the strength of Lewis acid sites leads to allylic oxidation. This reaction involves two paths. The first one is a direct epoxidation in the presence of redox catalysts which leads to the epoxide that becomes a diol in presence of water and acidic medium. The second one is an allylic oxidation, which in the presence of Lewis acid sites gives cyclohexenol, cyclohexenone and cyclohexanol, as shown on the following catalytic scheme (Fig. 4).



Fig. 4 Cyclohexene oxidation reaction scheme following two pathways

As it was found that  $5wt.\%VO_2$ -SiO<sub>2</sub> is the best catalyst, affording a high conversion of cyclohexene and a high epoxide selectivity under the optimized reaction conditions (i.e. reaction temperature 338 K, reaction time 6 h, 0.1 g of catalyst and a cyclohexene:TBHP molar ratio of 1:1.3), it was selected as the standard catalyst to study the influence of various parameters, such as cyclohexene to TBHP molar ratio and catalyst stability in the cyclohexene oxidation reaction.

#### 3.2.1. Effect of cyclohexene/TBHP molar ratio

The concentration of TBHP is also another important parameter affecting the cyclohexene oxide selectivity. While keeping the substrate (cyclohexene) amount constant, the effect of TBHP quantity was studied over a wide range of cyclohexene to TBHP molar ratio, i.e. from 0.5 to 2, with 5 wt.%VO<sub>2</sub>-SiO<sub>2</sub> catalyst.

 Table 6 Effect of cyclohexene/TBHP molar ratio on the cyclohexene epoxidation reaction with TBHP, for 5 wt.%VO<sub>2</sub>-SiO<sub>2</sub>

cyclohexene /TBHP	Conversion	Selectivity /%						TBHP Consumption
molar ratio	/%	Epoxide	Enone	One	Enol	Ol	Diol	%
1/2	39	82	3	12	3	/	/	40
1/1.3	21	84	/	12	4	/	/	24
1/1	18	77	5	9	9	/	/	35
1/0.5	14	85	5	4	6	/	/	35

Reaction conditions: 29 mmol cyclohexene, 25 mL Heptane, 0.1 g catalyst, 6 h, reaction temperature 338 K

Table 6 represents the cyclohexene conversion and product selectivity at various cyclohexene/TBHP molar ratios in the presence of 5wt.% VO<sub>2</sub>-SiO<sub>2</sub>. As shown, the cyclohexene conversion decreases while the cyclohexene/TBHP molar ratio increases and the epoxide selectivity remains almost unchanged. Anand et al. [70] attributed the decreasing conversion of cyclohexene when the cyclohexene/TBHP molar ratio increases to the fact that cyclohexene molecules occupy most of the active centers over the catalyst surface leaving less space for TBHP. In our case, when the cyclohexene/TBHP molar ratio increases, there is a competition between cyclohexene and TBHP; that is the more cyclohexene there is, the less TBHP is adsorbed on the active sites. Therefore conversion decreases. However, each time a TBHP molecule is adsorbed, it reacts with the cyclohexene adsorbed on an adjacent site to form the epoxide; selectivity remains constant.

#### 3.2.2. Mechanism

The reaction mechanism of cyclohexene oxidation reaction is widely discussed in the literature where several intermediate complexes are proposed without a single mechanism to secure the agreement of all authors [12, 71-74]. Using  $O_2$  or  $H_2O_2$  as oxidant, a radical mechanism leading to the formation of a hydroperoxide reaction intermediate was evidenced [4, 13]. In the case of TBHP, on the basis of various studies reported in the literature [46, 75], we propose the following mechanism occurring in two pathways from the intermediate (A) formed between the catalyst and cyclohexene in the presence of TBHP (Fig. 5). tBuO<sup>-</sup>, formed throughout the reaction in parallel to intermediate A attacks either on the vanadium atom or on the C<sub>6</sub> ring leading to the different paths:

- Path 1 is a reaction producing epoxide which is favored by the redox and monomeric vanadium sites, but requires the presence of acidic sites;
- In path 2, the reactions occur with catalysts which have polymeric vanadium sites and Lewis acidic sites. This path, it is divided into two parts: the first one to form an unsaturated alcohol which undergoes a new oxidation reaction that gives cyclohexenone. The second one leads to the production of cyclohexanone by acidic transposition.



Fig. 5 Proposed mechanism for the cyclohexene epoxidation reaction by TBHP

#### 3.2.3. Leaching and stability

Leaching was carried out in order to observe if the passage of the catalyst into the organic phase occurs or not. For this purpose, cyclohexene reaction, in the presence of 5wt.%VO<sub>2</sub>-SiO<sub>2</sub>, was studied. After 6 hours of reaction, the organic phase and the solid phase were separated. A reaction was afterwards carried out with the organic phase for two hours, adding an amount of each reagent and heating to reflux temperature. The results of this reaction showed no production of epoxide, in agreement with the results reported by Farzaneh et al. [72], and Brutchey et al. [76]. In addition, the solution remains clear in the presence of TBHP

and cyclohexene [2]. These results show that we have no leaching of vanadium active species, as previously reported by Leus et al. [77]. Moreover, a catalyst analysis was carried out before and after catalytic test. These analyses showed a vanadium loading of 4.83 and 4.81 % respectively, indicating a relative vanadium loss of 0.4 % that may be negligible.

The results of the  $5wt.\%VO_2$ -SiO<sub>2</sub> catalyst stability upon cyclohexene epoxidation are shown in Table 7.

Cycle	Conversion	Epoxide Selectivity	TBHP Consumption
	/%	/%	/%
$1^{st}$	21	84	24
$2^{nd}$	29	87	30
3 <sup>rd</sup>	23	74	28
4 <sup>th</sup>	18	79	20
5%V2O5-SiO2	28	85	38

Table 7: 5 wt.%VO<sub>2</sub>-SiO<sub>2</sub> catalyst stability upon cyclohexene epoxidation with TBHP

Reaction conditions: 29 mmol cyclohexene, 38.45 mmol TBHP, 25 mL Heptane, 0.1 g catalyst, 6 h, reaction temperature 338 K

Results indicate that this catalyst is stable upon 4 reaction cycles. Indeed, the conversion of cyclohexene decreases from the third cycle because of the mass loss due to the filtration  $(0.0875 \text{ g in the } 3^{\text{rd}} \text{ cycle and } 0.0663 \text{ g in the } 4^{\text{th}} \text{ cycle})$  (see Table 5).

#### 4. Conclusion

The Xwt.%  $VO_2$ -SiO<sub>2</sub> mixed oxide materials were prepared by the sol-gel method. These materials were calcined and reduced at 673 K. The materials obtained showed a green color indicating the presence of reduced vanadium (IV) species. The XRD results revealed that  $VO_2$  is well dispersed on amorphous silica. The mixed oxides microporous surface area and acidic sites decrease with increasing vanadia loading. The samples UV-Vis spectra show that vanadyl species are incorporated in the support in a monomeric form. When the vanadium content increases, the polymeric vanadium species appear. This system has proven to be an efficient catalyst for the selective epoxidation of cyclohexene with TBHP as oxidant and heptane as solvent. A maximum selectivity for cyclohexene epoxidation (84 %) was observed for the 5wt.%VO<sub>2</sub>-SiO<sub>2</sub> catalyst at 338 K. This material is stable upon 4 reaction cycles. This reaction is really heterogeneous and no vanadium leaching was observed.

Finally, from the catalytic results reported in this paper, we suggest that the cyclohexene oxidation reaction involves two paths. The first one is a direct epoxidation, in the presence of

redox catalysts, leading to epoxide formation. The second one is an allylic oxidation in the presence of Lewis acid catalysts to give cyclohexenol, cyclohexenone, cyclohexanone and cyclohexanol.

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