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Effect of redox properties of ceria-supported vanadium oxides in the liquid phase cyclohexene oxidation

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Several VO\textsubscript{2}/CeO\textsubscript{2} based catalysts, with V loadings between 5 and 20 wt.%, were prepared by impregnation and subsequently dried, calcined and reduced at 673 K. The structural characterization of these materials was carried out using X-rays diffraction (XRD), N\textsubscript{2} adsorption–desorption at 77 K, UV–vis diffused reflectance spectroscopy (DR UV–vis) and Fourier-Transformed Infrared Spectroscopy (FTIR). Their catalytic activities in the epoxidation of cyclohexene, with TBHP as oxidant and heptane as solvent, were also examined. XRD results revealed a good dispersion of VO\textsubscript{2} species on ceria. FTIR and DR UV–visible spectroscopy techniques indicated that polymeric vanadyl species are present on all catalysts and a crystalline VO\textsubscript{2} phase appears on the 20 wt.% vanadium sample. Experimental results pointed out that catalysts activity decreases with increased vanadium loading, whereas the epoxy selectivity increased up to 90 % when vanadia loading reached 15 wt.%. In the case of 20 wt.%VO\textsubscript{2}/CeO\textsubscript{2}, the reaction switched towards a 100 % enol, enone selectivity. The presence of CeVO\textsubscript{2} was shown to influence the conversion and selectivity of the reaction.

In fact, using different supports and metal loadings, the surface structure\textsuperscript{14, 15}, number of surface sites number of surface sites, the acid–base\textsuperscript{11, 12} and redox properties\textsuperscript{13} can be intentionally monitored. Consequently, considerable attention has been focused on the preparation, characterization and evaluation of vanadium oxide catalysts deposited on various single or mixed oxides. Cerium-based materials were widely used as oxygen carriers\textsuperscript{16, 17}. The addition of a low amount of cerium can enhance the oxydo-reduction features of a given catalyst. Generally, the oxidation rate is limited by the oxygen transfer from the metal active sites to the metal/support interface, while ceria is able to enhance this oxygen transfer to efficiently catalyze the reaction. The redox properties of ceria (Ce\textsuperscript{4+}/Ce\textsuperscript{3+}) and the high lability of its lattice oxygen are among the most important factors that contribute to the catalytic reactivity in oxidation reactions\textsuperscript{18, 19}. The presence of vanadia on ceria affords interesting performances for oxidative dehydrogenation reactions\textsuperscript{20-22}. The surface polymeric vanadia species on ceria are more reducible than the isolated ones, according to \textit{in situ} Raman spectroscopy\textsuperscript{23}.

In general, interfaces between metal oxides supported on metal oxide substrates (supported on another metal oxide) have been less studied than those between metals supported on metal oxides\textsuperscript{24}. It has been established, in our previous studies\textsuperscript{24} on the liquid epoxidation reaction over mixed vanadium oxides, that the presence of catalysts with redox features directs the reaction toward epoxidation. However, increasing the strength of Lewis acid sites leads to allylic oxidation.

For the same purpose, we report in the present work the structural characterization of ceria supported vanadia catalysts, for various VO\textsubscript{2} loadings considered, using different physico-chemical techniques. Catalysts activity towards liquid phase epoxidation of...
cyclohexene is also investigated and correlated with different vanadia species on the supported catalysts. The effect of reaction parameters such as the catalyst weight, temperature, oxidant concentration, leaching and stability was also checked.

2. Experimental

2.1 Synthesis

2.1.1. Starting materials

The following chemicals were employed in the preparation of X wt.%V/CeO₂: Cerium (IV) oxide (CeO₂; Aldrich), ammonium metavanadate (NH₄VO₃; Strem chemicals, 99 %), nitric acid (Aldrich), cyclohexene (Aldrich 99 %), hydroperoxide tertio-butyl (TBHP; Aldrich 70 %) and heptane (Fluka 99 %).

2.1.2 Synthesis of the system X wt.% VO₂/ CeO₂

Typical procedure for 5 wt.%VO₂/CeO₂: the 5 wt.%VO₂/CeO₂ catalyst used in this study was prepared by an impregnation procedure. Prior to impregnation, the CeO₂ support was calcined at 673 K, for 4 h. Ammonium metavanadate (NH₄VO₃) was used as the VO₂ precursor. A volume of 40 mL of nitric acid was added to 0.57 g of ammonium metavanadate and stirred for 2 h, then 4.75 g of CeO₂ were added to this solution. The resulting mixture was stirred for 24 h. It was next dried first at 60 °C for one night, then at 120 °C for another night, and then calcined in air at 400 °C, for 4 h. It was finally reduced, under hydrogen flow, at 400 °C, for 4 h. The materials obtained were green, a color that indicates the presence of reduced vanadium (IV) species. For the other catalysts, amounts of ammonium metavanadate, ceria and nitric acid where recalculated in order to obtain 10, 15 and 20 wt% loadings.

All catalysts under study in this paper are summarized in the following table 1:

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>V loading (%)</th>
<th>NH₄VO₃ (g)</th>
<th>CeO₂ (g)</th>
<th>HNO₃ (ml)</th>
<th>Thermal treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>V₂O₅/CeO₂</td>
<td>5</td>
<td>0.57</td>
<td>4.75</td>
<td>40</td>
<td>4h under air at 400°C</td>
</tr>
<tr>
<td>VO₂/CeO₂</td>
<td>5</td>
<td>0.57</td>
<td>4.75</td>
<td>40</td>
<td>4h under air at 400°C + 4h under H₂ at 400°C</td>
</tr>
<tr>
<td>VO₂/CeO₂</td>
<td>10</td>
<td>1.13</td>
<td>4.50</td>
<td>80</td>
<td>4h under air at 400°C + 4h under H₂ at 400°C</td>
</tr>
<tr>
<td>VO₂/CeO₂</td>
<td>15</td>
<td>1.71</td>
<td>4.25</td>
<td>120</td>
<td>4h under air at 400°C + 4h under H₂ at 400°C</td>
</tr>
<tr>
<td>VO₂/CeO₂</td>
<td>20</td>
<td>2.27</td>
<td>4.00</td>
<td>160</td>
<td>4h under air at 400°C + 4h under H₂ at 400°C</td>
</tr>
<tr>
<td>VO₂/CeO₂</td>
<td>5</td>
<td>0.57</td>
<td>4.75</td>
<td>80</td>
<td>4h under air at 400°C + 4h under H₂ at 400°C + 4h under Ar at 800°C</td>
</tr>
</tbody>
</table>

2.2. Catalyst characterization

All catalysts were characterized by X-ray powder diffraction (XRD), using a Bruker D5005 diffractometer with Cu Kα radiation (λ = 1.5406 Å), in the range of 20 = 10 ° - 80 °, with a step of 0.02 ° and an acquisition time of 1s. Elemental analysis was performed using atomic absorption with a Perkin Elmer Analyst 300 spectrometer. The prepared samples were analyzed by thermal analysis (TGA / DTA) using an SDT Q600 instrument. The 20-30 mg sample mass was introduced into a platinum crucible, which is supported by the beam of a balance in the oven. The analysis was performed in air with a temperature ramp of 5 K/min in the range 298 - 1473 K. These analyses have been carried out in the Laboratory of Catalysis in Organic Chemistry (LACCO, UMR6503) Poitiers University, France. The BET surface area was determined from N₂ adsorption/desorption. They are calculated following the expressions below:

2.3. Catalytic experiments

The catalytic epoxidation of cyclohexene, with tertio-butylhydroperoxide TBHP (Aldrich, 70 wt.% in H₂O) as an oxidant, was carried out in a two-necked 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 of TBHP (5.5 mL) 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. More than 90 % of the initial TBHP is transferred in the organic phase to be used in the catalytic reaction. Secondly, 29 mmol (3 mL) of cyclohexene, 0.1 g of catalyst and the TBHP-heptane mixture (organic phase) were all mixed in a 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 an Agile HP-FFAP capillary column. A flame ionization detector (FID) was used to analyze 0.5 µL of the sample. Before GC analysis, the remaining TBHP was decomposed by introducing an excess of triphenylphosphine (Aldrich). Meanwhile, an iodometric titration was performed at the end of the reaction (after 6 h) in order to control the remaining TBHP in the reaction mixture (results reported as % TBHP consumption in tables 4-8). The catalytic performances were reported in terms of cyclohexene conversion, selectivity towards products and Turnover Frequency. They are calculated following the expressions below:
3. Results and discussion

3.1. Physico-chemical characterization

3.1.1 Powder XRD analysis

The X-ray reflection peaks of ceria were observed at \( \theta \sim 28.57^\circ, 33.11^\circ, 47.53^\circ \) and \( 56.37^\circ \) [ICDD pattern 43-1002], corresponding to Miller indices (111), (200), (220) and (311), respectively (Fig. 1). This shows a typical crystal structure of the cubic fluorite-type ceria. The diffraction patterns of X wt.%\( \text{VO}_2/\text{CeO}_2 \), calcined and reduced at 673 K, showed lines due to ceria, but no lines characteristic of \( \text{VO}_2 \) were seen (Fig. 1). This indicates that vanadia was finely dispersed on the ceria surface for this sample.

\[ \text{Fig. 1 X-ray diffraction (XRD) patterns of the CeO}_2 \text{ and X wt.%VO}_2/\text{CeO}_2 \text{ systems.} \]

3.1.2 Surface area measurements

The surface areas of X wt.%\( \text{VO}_2/\text{CeO}_2 \) supported oxides, measured by \( \text{N}_2 \) adsorption, according to the BET method, are shown in Table 2. The results show that the commercial ceria, used in this study, has no surface area. However, the latter increases upon impregnation of vanadium oxide on ceria. This phenomenon may be attributed most likely to the vanadium surface area which increases with the vanadium loading. An unusual phenomena of hydration–dissolution and re-precipitation of the support during the preparation procedure has been reported on V/\( \text{CeO}_2 \) \text{[21]} and V/MgO \text{[22]} systems. In these cases, the support partly dissolves in the acidic V-containing precursor solution, and then precipitates on evaporation of water, thus generating a V-loaded material with a larger surface area than the initial support. However, it does not seem to be the case here, as the formation of ceria with smaller size should be accompanied by broader XRD peaks.

\[ \text{Table 2 Textural characteristics, as determined by N}_2 \text{ adsorption, for different samples.} \]

3.1.3 Scanning Electron Microscopy (SEM) with EDX

SEM micrographs of 5 wt.%\( \text{VO}_2/\text{CeO}_2 \) sample (Fig. 2), show the presence of spherical fine particles, which are gathered into larger grains that coexist with other small geometric particles. EDX analysis indicates a vanadium content of 4.89%.

\[ \text{Fig. 2 SEM micrograph with EDX spectrum of 5 wt.%VO}_2/\text{CeO}_2 \text{ sample.} \]

For a comparison purpose, the experimental vanadium loading determined by atomic absorption is 5.78%, for this same sample. The difference between these values may be explained by the fact that EDX is a very localized surface analysis while atomic absorption is a global and bulk analysis, so that if the vanadium distribution is not very homogenous, the results may differ.

3.1.4 TGA/DTA analysis

Fig. 3 illustrates the TGA/DTA analysis of 5 wt.%\( \text{VO}_2/\text{CeO}_2 \), conducted before calcination and reduction at 400°C. An
endothermic peak, observed from room temperature to 200 °C for supported catalysts, can be attributed to the removal of water. The small endothermic peak at 600 °C may be attributed to the fusion of VO₉₂ and to the formation of CeVO₄. Around 950 °C, new phases may be formed. The total weight loss of the sample is about 3 %, in the temperature range 25 – 1200 °C.

Fig. 3 Thermal gravimetric analysis of the 5wt.% VO₂/CeO₂ sample, before thermal treatment at 400 °C.

3.1.5 DR UV–vis spectroscopy

The UV-Vis DRS spectroscopy was used to investigate the structure of supported vanadia catalysts, as the ligand-to-metal charge transfer (LMCT) transitions of V⁴⁺ appear in the 200 – 500 nm region, and the d-d transition bands in the 600–800 nm region. The UV-Vis spectra of the samples are shown in Fig. 4.

For clarity purposes, the attribution of the characteristic bands according to literature is reported in the following Table 3:

<table>
<thead>
<tr>
<th>Band (nm)</th>
<th>Attribution</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>225 and 278</td>
<td>Ce⁴⁺ ← O⁻ and Ce⁴⁺ ← O⁻ charge transfers, Tetrahedral V⁴⁺ monomeric species.</td>
<td>18, 39, 40</td>
</tr>
<tr>
<td>240-280</td>
<td>Tetrahedral V⁴⁺ monomeric species.</td>
<td>41</td>
</tr>
<tr>
<td>270-300</td>
<td>Tetrahedral V⁴⁺ monomeric species.</td>
<td>41-46</td>
</tr>
<tr>
<td>300-350</td>
<td>Tetrahedral V⁴⁺ polymeric species.</td>
<td>41-44</td>
</tr>
<tr>
<td>350-400</td>
<td>Octahedral V⁵⁺ monomeric species.</td>
<td>41, 45-48</td>
</tr>
<tr>
<td>400-500</td>
<td>Octahedral V⁵⁺ monomeric species.</td>
<td>41-44, 46, 49-51</td>
</tr>
<tr>
<td>500-550</td>
<td>Presence of V₂O₅ crystalline.</td>
<td>43, 52, 53</td>
</tr>
<tr>
<td>550-800</td>
<td>Transition d-d of vanadium (IV).</td>
<td>46, 49, 52</td>
</tr>
<tr>
<td>600-800</td>
<td>Presence of CeVO₄</td>
<td>54</td>
</tr>
</tbody>
</table>

For all samples, the results indicate the presence of the d-d transition band attributed to V⁴⁺ cations. The bands around 225 nm and 278 nm are most likely due to Ce⁴⁺ ← O⁻ and Ce⁴⁺ ← O⁻ charge transfers, respectively. The band of vanadium species, noted in the region 300 - 350 nm, should be assigned to charge-transfer transitions involving oxygen and vanadium (IV) in tetrahedral coordination, present as polymeric species. The band in the region 400 - 500 nm is attributed to octahedral V⁴⁺ polymeric species. Jian et al. showed the presence of monovanadyl species for low vanadium contents (0.1 and 1 %), and the presence of polyvanadyl species for a higher vanadium content (4 %). In the case of 20 wt.% vanadium, the band of crystalline VO₂ appears at 547 nm. Using XRD and UV-Vis, Gu et al. and Duarte de Farias et al. noted the presence of the V₂O₅ crystalline phase, in 20 wt.% V₂O₅/CeO₂ and 18 wt.% V₂O₅/CeO₂, respectively. The absence of crystalline VO₂ diffraction peak in the case of 20 wt.% V₂O₅/CeO₂ may be due to the small size crystallites, which are most likely smaller than the detection limit of the XRD technique.

Fig. 4 Diffuse-reflectance UV-Vis deconvoluted spectra of the X wt.% VO₂/CeO₂ materials.

3.1.6 FT-IR absorption with ATR

The infrared spectra were deconvoluted by the deconvolution software PeakFit. Deconvoluted infrared spectra of VO₂/CeO₂ materials, in the 1500 – 500 cm⁻¹ region, are reproduced in Fig. 5. From deconvolution, the following bands are obtained:
In the case of 20 wt.% VO\textsubscript{2}/CeO\textsubscript{2}, the appearance of a new band, centered at 991 cm\textsuperscript{-1}, is attributed to the crystalline phase of the vanadium oxide\textsuperscript{61, 65}. The FTIR and UV-Visible spectroscopy results are found to be in good agreement.

### 3.2. Catalytic activity

Generally, cyclohexane oxidation gives mainly cyclohexane oxide (epoxide), cyclohexane diols, cyclohexenol (Enol), cyclohexenone (Enone), cyclohexanol (Ol) and cyclohexanone (One) (Fig. 6)\textsuperscript{66-69}. Oxidation of cyclohexene with TBHP, in the presence of vanadium supported oxides, resulted in the formation of several products, as shown in Table 4. Through GC analysis, 1,2-cyclohexanediol was not detected in the reaction mixture\textsuperscript{70, 71}. In the absence of catalyst, cyclohexene gave only 12\% conversion; no epoxide was found\textsuperscript{72}. Since the CeO\textsubscript{2} catalytic test gave a result similar to the one without catalyst, it can be concluded that the support was not active\textsuperscript{31}. According to the results reported in Table 4, activity decreases with increased vanadium loading; this is due to the saturation of the surface with adsorbed species, whereas the epoxide selectivity increases up to 90\% when the vanadia loading rises up to 15 wt.\%. However, the 20 wt.% VO\textsubscript{2}/CeO\textsubscript{2} catalyst directs the reaction towards the allylic oxidation where a selectivity of 100\% towards enol and enone is reached.

Fig. 6: Different possible products of cyclohexene oxidation reaction.

Thus, the similar surface structure as well as the similar surface acidity and redox property might be responsible for the identical behavior of these catalysts for the selective oxidation of cyclohexene. In fact, the structural characterizations given above show that 5, 10 et 15 wt.% VO\textsubscript{2}/CeO\textsubscript{2} materials have only polymeric sites, while the 20 wt.% VO\textsubscript{2}/CeO\textsubscript{2} catalyst possesses a significant amount of crystalline VO\textsubscript{2} on the surface and exhibits a significant surface acidity\textsuperscript{31, 73}. Consequently, this sample directs the selectivity towards cyclohexenol and cyclohexenone. There might be three types of V–O bonds in the supported VO\textsubscript{2} catalysts, i.e. V–O, V–O–V and V–O–support\textsuperscript{5}.

### Table 4 Oxidation of cyclohexene, using different supported catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Activity</th>
<th>TOF (h\textsuperscript{-1})</th>
<th>Epoxide</th>
<th>Enone</th>
<th>One</th>
<th>Enol</th>
<th>Ol</th>
<th>Diol</th>
<th>TBHP consumption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% VO\textsubscript{2}/CeO\textsubscript{2}</td>
<td>45</td>
<td>17.1</td>
<td>77</td>
<td>18</td>
<td>/</td>
<td>5</td>
<td>/</td>
<td>/</td>
<td>50</td>
</tr>
<tr>
<td>10% VO\textsubscript{2}/CeO\textsubscript{2}</td>
<td>28</td>
<td>5.5</td>
<td>80</td>
<td>11</td>
<td>/</td>
<td>9</td>
<td>/</td>
<td>/</td>
<td>82</td>
</tr>
<tr>
<td>15% VO\textsubscript{2}/CeO\textsubscript{2}</td>
<td>20</td>
<td>3.0</td>
<td>90</td>
<td>6</td>
<td>/</td>
<td>4</td>
<td>/</td>
<td>/</td>
<td>68</td>
</tr>
<tr>
<td>20% VO\textsubscript{2}/CeO\textsubscript{2}</td>
<td>5</td>
<td>0.0</td>
<td>/</td>
<td>64</td>
<td>/</td>
<td>36</td>
<td>/</td>
<td>/</td>
<td>98</td>
</tr>
</tbody>
</table>

Reaction conditions: cyclohexene 29 mmol, TBHP 38.45 mmol, Heptane 25 mL, 0.1 g catalyst, reaction time 6 h, reaction temperature 65 °C.
The redox property of catalysts might have mainly originated from the V–O–support bonds, instead of the V–O–V bonds, as bulk VO₂ is mainly acidic rather than redox. Weckhuysen and Keller⁵ ascribed the activity of selective oxidation of methanol to formaldehyde to the V–O–support bonds in the supported vanadia catalysts, after comparing the effects of different supports. It is difficult to determine the surface density of the V–O–support bonds directly. However, it is reasonable to infer that the highest density of the surface V–O–support bonds might be reached when the loading of VO₂ is lower than the monolayer capacity, since once the loading reaches the monolayer capacity, the surface vanadium species would form a two-dimensional network in which V–O–V may be the most popular bonds.

The mechanism of the epoxidation reaction of cyclohexene with TBHP on vanadium mixed oxides was studied earlier²⁵ and it was shown that it occurs following two pathways: 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. The VO₂ loading in the 5 wt.%VO₂/CeO₂ was close to the monolayer capacity, as discussed above. This catalyst might possess the strongest redox ability among the catalysts under study in this work. In fact, it exhibits the highest activity for the selective epoxidation of cyclohexene (Fig. 7). The so-called highly dispersed vanadium species, mentioned above, can be taken as the isolated, dimeric and polymeric vanadium species. The surface V–O–Ce bonds seem to be important for the selective epoxidation of cyclohexene.

Table 5 summarizes several results reported in the literature dealing with cyclohexene epoxidation with TBHP on a wide range of vanadium based catalysts. It can be noticed that our catalysts, in particular 5 wt.% VO₂/CeO₂ are from the most interesting ones.
Since 5 wt.% VO₂/⁡CeO₂ is the best catalyst, affording a high conversion to cyclohexene and a high epoxide selectivity and a high TOF, it was chosen as a standard catalyst to study the influence of varying the parameters such as catalyst amount, cyclohexene to TBHP molar ratio, thermal treatment temperature and the stability of catalyst, upon the cyclohexene oxidation reaction.

### 3.2.1. Effect of the catalyst amount

To investigate the effect of the catalyst amount for the 5 wt.%VO₂/⁡CeO₂ sample, the following weights were considered: 0.025, 0.05, 0.1, 0.2 and 0.3 g. The results are summarized in table 6.

<table>
<thead>
<tr>
<th>Catalyst amount (g)</th>
<th>Activity</th>
<th>Selectivity (%)</th>
<th>TBHP consumption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conv (%)</td>
<td>TOF (h⁻¹)</td>
<td>Epoxide</td>
</tr>
<tr>
<td>0.025</td>
<td>33</td>
<td>46.8</td>
<td>72</td>
</tr>
<tr>
<td>0.05</td>
<td>38</td>
<td>28.0</td>
<td>75</td>
</tr>
<tr>
<td>0.1</td>
<td>45</td>
<td>17.1</td>
<td>77</td>
</tr>
<tr>
<td>0.2</td>
<td>42</td>
<td>7.6</td>
<td>74</td>
</tr>
<tr>
<td>0.3</td>
<td>43</td>
<td>4.9</td>
<td>70</td>
</tr>
</tbody>
</table>

Reaction conditions: cyclohexene 29 mmol, TBHP 38.45 mmol, Heptane 25 mL, reaction time 6 h, reaction temperature 65 °C.

From these results, TOF is seen to decrease with the amount of catalyst from 46.8 to 4.9. The selectivity to epoxide remains constant, around 77 %, regardless of the catalyst amount. When the catalyst mass is increasing, particle aggregation in the suspension might be more pronounced, resulting in poor reactant accessibility to pores, which subsequently gives a lower catalytic activity.

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

The concentration of TBHP is another important parameter affecting the cyclohexene epoxide selectivity. By keeping the substrate (cyclohexene) amount constant, the effect of TBHP amount was investigated over a wide range of cyclohexene to TBHP molar ratio ranging from 0.5 to 2, with 5 wt.% VO₂/⁡CeO₂ as catalyst. Table 7 represents the cyclohexene conversion, TOF and products selectivities at various cyclohexene/TBHP ratios, in the presence of 5 wt.% VO₂/⁡CeO₂. As it can obviously be seen, the cyclohexene conversion decreases as the cyclohexene/TBHP molar ratio rises and the epoxide selectivity increases as this molar ratio goes up. The best cyclohexene/TBHP ratio should be 1/1.3 and 1/1 with the highest TOF. Anand et al. attributed the decreasing cyclohexene conversion with the increase in cyclohexene/TBHP ratio to the fact that cyclohexene molecules occupy most of the active centers on the catalyst surface, thus leaving less space for TBHP. In our case, when the cyclohexene/TBHP molar ratio increases, there is a competition between cyclohexene and TBHP, so the more there is of cyclohexene, the less TBHP is adsorbed on the active sites, and therefore conversion decreases. However, each time a TBHP molecule is adsorbed, it reacts with the cyclohexene adsorbed on an adjacent site to form epoxide, and the selectivity increases.

### 3.2.3. Effect of thermal treatment

In order to check the effect of high-temperature thermal treatment, the 5 wt.%VO₂/⁡CeO₂ catalyst, previously calcined and reduced at 400 °C, was heated again for 4h, at 800 °C, under argon flow (28 mL min⁻¹), to obtain the 5 wt.%VO₂/⁡CeO₂ (800 °C). Catalyst 5 wt.%V₂O₅/⁡CeO₂ was obtained from dried V/⁡CeO₂ by calcination at 400 °C. These different treatments result in different V oxidation states (table 8). Indeed, V oxidation state is proven by the presence or not of the d-d transition bond in the DRUV-Vis spectra (figures 4 and 8) which is only present in the case of V⁴⁺.

The results of the effect of these treatments on the reaction of cyclohexene oxidation are summarized in table 8.

Results from table 7 show that the oxidation number +4 of VO₂ and +5 of V₂O₅, for the catalysts treated at 400 °C, do not induce any change in the catalytic activity of both catalysts. The redox properties of ceria (Ce⁴⁺/⁡Ce³⁺) and the high ability of its lattice oxygen are among the most important factors that contribute to the catalytic reactivity in epoxidation reactions.

The deposition of vanadium on the surface of cerium oxide increases and improves the CeO₂ ability to provide an oxygen from its own network which will oxidize the adsorbed cyclohexene, according to the reaction:

\[
\text{CeO}_2 + \text{xO}_2 \rightarrow \text{CeO}_{2-x} + x\text{O}_2
\]
Table 8 Effect of thermal treatment on the epoxidation reaction of cyclohexene, with TBHP.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>V oxidation state</th>
<th>Activity</th>
<th>Epoxide</th>
<th>Enone</th>
<th>One</th>
<th>Enol</th>
<th>Ol</th>
<th>Diol</th>
<th>Consumption of TBHP (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%(V_2O_5)/CeO_2</td>
<td>+5</td>
<td>49</td>
<td>17.9</td>
<td>74</td>
<td>7</td>
<td>19</td>
<td>/</td>
<td>/</td>
<td>57</td>
</tr>
<tr>
<td>5%(VO_2)/CeO_2</td>
<td>+4</td>
<td>45</td>
<td>17.1</td>
<td>77</td>
<td>18</td>
<td>/</td>
<td>5</td>
<td>/</td>
<td>50</td>
</tr>
<tr>
<td>5%(VO_2)/CeO_2 (800 °C)</td>
<td>+4</td>
<td>21</td>
<td>5.1</td>
<td>49</td>
<td>13</td>
<td>31</td>
<td>7</td>
<td>/</td>
<td>22</td>
</tr>
</tbody>
</table>

Reaction conditions: cyclohexene 29 mmol, TBHP 38.45 mmol, Heptane 25 mL, 0.1 g catalyst, reaction time 6 h, reaction temperature 65 °C.

The 5wt.%V/CeO_2 catalysts treated at 400 °C contain the most reducible V species. Since this material contains detectable polyvanadate species (Fig. 8), it is proposed that this surface phase is responsible for cyclohexene epoxidation, and the bridging oxygen in V–O–V and V–O–Ce is most likely the key catalytic site. For the 5 wt.%\(VO_2\)/CeO_2 (800 °C) catalyst, cyclohexene conversion and selectivity decrease even if epoxide remains the major product. This decrease is due to the formation of a new crystalline phase (CeVO_4). The XRD powder patterns (Fig. 9) of the \(VO_2\)/CeO_2 sample, treated at 800 °C, reveal, in addition to sharp ceria lines, new smaller lines which can be seen at 20 ~ 18.33 ° and 24.06 °, respectively [ICDD pattern 12-0757]. These peaks are attributed to the formation of the CeVO_4 mixed phase which is at 10 % of total CeO_2. However, once CeVO_4 was formed, the activity for the epoxidation reaction decreased. It seems that the oxygen anions in CeVO_4 were less active and labile than those in CeO_2 and VO_2 since they were more strongly bonded in the CeVO_4 lattice. The reason may be simple; the valent states of Ce and V are relatively stabilized at +3 and +5, respectively, in CeVO_4, leading to the weakened redox ability of CeVO_4. Therefore, the catalyst with abundant surface of CeVO_4 exhibited low activity for the epoxidation of cyclohexene.

3.2.4 Leaching and stability

Leaching was carried out to see whether the passage of the catalyst into the organic liquid phase occurs or not. For this, reactions of cyclohexene in the presence of the catalyst 5 wt.%\(VO_2\)/CeO_2 were studied. After 6 h of reaction time, the organic phase and the solid phase were separated by filtration. The reaction of the organic phase was started again for 2 hours, adding an amount of each reactant and heating to reflux temperature. The results of this reaction showed that no epoxide was produced; similar results were reported by Brutchey et al. and Farzaneh et al. In addition, it was noted that the solution remains clear in the presence of TBHP and cyclohexene. It can be stated from these results that no catalyst leaching occurs, and the reaction is really heterogeneous.

The results of the stability of catalyst 5 wt.%\(VO_2\)/CeO_2 during the epoxidation reaction of cyclohexene are shown in table 9. They indicate that this material is stable during 3 cycles of the reaction.

Table 9 Results of the stability of 5 wt.%\(VO_2\)/CeO_2 during the epoxidation reaction of cyclohexene with TBHP.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Conversion (%)</th>
<th>Epoxide Selectivity (%)</th>
<th>TOF (h⁻¹)</th>
<th>TBHP Consumption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>45</td>
<td>77</td>
<td>17.1</td>
<td>50</td>
</tr>
<tr>
<td>2nd</td>
<td>46</td>
<td>75</td>
<td>17.0</td>
<td>54</td>
</tr>
<tr>
<td>3rd</td>
<td>43</td>
<td>73</td>
<td>15.5</td>
<td>28</td>
</tr>
<tr>
<td>4th</td>
<td>18</td>
<td>42</td>
<td>3.7</td>
<td>25</td>
</tr>
</tbody>
</table>

Reaction conditions: cyclohexene 29 mmol, TBHP 38.45 mmol, Heptane 25 mL, 0.1 g catalyst, reaction time 6 h, reaction temperature 65 °C.
4. Conclusions

The X wt.% VO₂/CeO₂ supported oxide materials were prepared by the impregnation method. They were then calcined and reduced at 673 K. The materials obtained had a green color, which indicates the presence of reduced vanadium (IV) species. The XRD results revealed that VO₂ is dispersed on the ceria surface. The surface of supported oxides decreases with increasing vanadia loading. As it has been previously confirmed by FTIR results, UV-Vis spectra of the samples showed that vanadyl species are incorporated in the carrier in polymer form; in the case of 20 % by weight of vanadium, the samples showed that vanadyl species are incorporated in the carrier in polymer form; in the case of 20 % by weight of vanadium, the samples showed that vanadyl species are incorporated in the carrier in polymer form. Allylic oxidation is preponderant and leads to cyclohexenol and epoxidation product, while in the presence of acidic features, the reaction leads to an epoxidation product, while in the presence of acidic features, the reaction leads to an epoxidation product.

From all these cyclohexene oxidation results, it was evidenced that in the presence of redox catalysts, this reaction leads to an epoxidation product, while in the presence of acidic features, the reaction leads to an epoxidation product.

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References

Catalyst | Conversion (%) | Selectivity (%) | TBHP conversion (%)
--- | --- | --- | ---
5%VO$_2$O$_2$ | 45 | 77 | 18 | 5 | / | / | / | 50
10%VO$_2$O$_2$ | 21 | 60 | 11 | 9 | / | / | / | 82
15%VO$_2$O$_2$ | 20 | 60 | 6 | 4 | / | / | / | 68
20%VO$_2$O$_2$ | 5 | / | 64 | / | 36 | / | / | 98

Reaction conditions: Cyclohexene 29mmol; TBHP 38-45mmol; Heptane 25mL; 0.1g catalyst; 6h; reaction temperature 65 °C.