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1. Introduction

Alkene epoxidation is a very useful reaction in industrial organic synthesis. The resultant epoxides are essential precursors in the synthesis of various important substances such as plasticizers to perfumes and epoxy resins.1,2 The design of catalytic systems for complete oxidation of hydrocarbons is an important issue in environmental catalysis.3 Many studies have revealed the high catalytic activity of various supported vanadium oxides in a number of oxidation reactions.³⁻⁶ In fact, the choice of the support to be used depends on the reaction, because the catalytic activity depends not only on the number of active sites but also on their distribution on the surface and also on the vanadium loading in vanadium oxide-based materials.7 For example, VO_x catalysts supported on reducible supports, such as CeO₂, TiO₂, and ZrO₂ show significantly higher activity for oxidative dehydrogenation (ODH) reactions, compared to those supported on irreducible supports, such as Al₂O₃ and SiO2.8-12 Today, the new trend is moving towards the use of heterogeneous catalysts in the selective epoxidation of olefins. On the one hand; molecular sieve catalysts, containing redox metal ions incorporated in the framework, have been widely used,¹³ on the other, reducible supports for vanadia catalysts, such as ZrO₂ have received growing attention due to their thermal stability, and their redox and catalytic features as well.14

Investigation of the effect of VO_x/ZrO_2 structure on the catalytic activity in cyclohexene epoxidation

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Vanadium oxide catalysts were prepared by impregnation of ammonium metavanadate on monoclinic zirconia with a metal loading equal to 5 wt%. Further thermal treatment led to V_2O_5/ZrO_2 upon calcination at 400 °C and VO_2/ZrO_2 upon calcination at 400 °C, followed by reduction at the same temperature. The third compound underwent further heat treatment at 800 °C, under argon. The effect of high temperature treatment on the structure of the materials as well as on the catalytic properties of the vanadate species was investigated in the epoxidation of cyclohexene, with TBHP as the oxidant and heptane as the solvent. Structural characterization of these materials was carried out using ICP-OES, X-ray diffraction (XRD), N₂ adsorption–desorption at 77 K, UV-Vis diffuse reflectance spectroscopy (DR UV-Vis), Fourier-Transform Infrared Spectroscopy (FTIR) and pyridine adsorption followed by FTIR. The coexistence of a solid solution with polymeric vanadium species in the case of 5VZr-2 and 5VZr-3 with the formation of ZrV_2O_7 in the case of 5VZr-3, resulted in good catalytic performance, with up to 80% epoxide selectivity and 32% cyclohexene conversion. In the case of 5VZr-1, the appearance of the crystalline V_2O_5 phase decreased the catalytic activity in the cyclohexene reaction.

Structural characterization of supported vanadate species is of key importance, because the variation in the catalytic activity with the support can be partly attributed to the structure of vanadate species dispersed on the surface of various supports.¹⁵

The predominating opinion is that active vanadium-based catalysts possess a molecularly dispersed vanadium oxide phase which is typically more active than the bulk V₂O₅.³ It has been demonstrated that the strong influence of the support on the activity and selectivity is mainly due to the presence of the active species V–O-support.¹⁶ Deo and Wachs suggested the V–O-support bridging bond as a factor controlling both reactivity and reducibility of supported vanadium oxide catalysts.^{3,5} The same authors noted that the strength of V–O-support bond is a fundamental criterion of the oxidative activity of supported metal oxide catalysts.

In the present study, various zirconia-supported VO_x systems were prepared by impregnation. The V loading was chosen to be 5 wt% in accordance to earlier studies.^{17,18} The influence of thermal treatment on their structural properties was investigated. Their catalytic performances were tested in the cyclohexene epoxidation by *tert*-butylhydroperoxide.

2. Experimental

2.1. Synthesis

2.1.1 Raw materials. The following chemicals were used in the preparation of 5 wt% V/ZrO₂, namely zirconium(v) oxide (ZrO₂; Prolabo), ammonium metavanadate (NH₄VO₃; Strem chemicals, 99%), nitric acid (Aldrich), cyclohexene (Aldrich)



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99%), hydroperoxide tertio-butyl TBHP (Aldrich 70%) and heptane (Fluka 99%).

2.1.2 Synthesis of the system 5wt% VO_x/ZrO₂. The impregnation procedure was used to prepare the 5 wt% $VO_x/$ ZrO₂ catalysts used in present study.¹⁹ Prior to impregnation, the ZrO₂ support was calcined at 673 K for 4 h. Ammonium metavanadate (NH₄VO₃) was used as a vanadium precursor. A quantity of 40 mL of nitric acid was added to 0.57 g of ammonium metavanadate and stirred for 2 h, and then 4.75 g of ZrO₂ were added to this solution. The resulting mixture was stirred for 24 h, at room temperature, and subsequently dried at 60 °C for one night and at 120 °C for another night. The resulting solid was calcined under flowing air at 400 °C, for 4 h. The calcined sample (noted 5VZr-1) was further reduced under hydrogen flow, at 400 °C, for 4 h. The reduced material (noted 5VZr-2) exhibited a green color, indicating the presence of reduced vanadium (+4) species.²⁰ Finally, the reduced 5VZr-2 sample underwent another thermal treatment under argon flow (28 mL min⁻¹), at 800 °C, for 4 h. It will be noted 5VZr-3.

2.2. Catalyst characterization

All catalysts were characterized by X-rays powder diffraction (XRD) using a Bruker D5005 diffractometer (Cu K α radiation, $\lambda =$ 1.54060 Å) in the range of $2\theta = 10-80^\circ$, with a step of 0.02° and an acquisition time of 1 s. Elemental analysis was performed using atomic absorption with a Perkin Elmer Analyst 300 Atomic Absorption 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⁻¹ in the range 298–1473 K. XRD, ATG and elemental analysis were carried out in the Institute of Chemistry of Mediums and Materials of Poitiers (IC2MP) at the Faculty of Science, Poitiers University, France. The BET surface areas were determined from N₂ adsorption/desorption isotherms at 77 K, using a Quantachrom instrument. Prior to absorption measurements, the sample was outgassed at 300 °C, for 3 h, under 30% nitrogen in helium flow. The FTIR spectra of the solid samples were recorded, using an Agilent Technologies Cary 60 series FTIR spectrometer, with ATR accessories, in a measuring range of 400-4000 cm⁻¹. The UV-visible spectra (200–800 nm) of these samples were measured on a Perkin Elmer UV-Vis spectrometer equipped with a Cary 4/5 diffuse reflection sphere. The baseline was set to zero with the help of an MgO reference. The Scanning Electron Microscopy (SEM) with EDX (Energy Dispersive X-ray) analysis was performed using a Hitachi TM-1000 apparatus, at an acceleration voltage of 150 kV. FTIR spectroscopy 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 a liquid nitrogen cooled MCT-detector. A mass ranging from 18 to 20 mg of the catalyst sample was pressed into a self-supported wafer of approximately 2 cm in diameter, then evacuated at 400 °C for 4 h, and finally cooled down to 20 °C. A known amount of pyridine was then introduced into the cell, at room temperature, and the wafer was

degassed at 150 °C, for 15 min, to remove the physisorbed fraction. Finally, the adsorbed pyridine was followed by evacuation for 15 min, at different temperatures. The IR spectrum thus obtained was used to calculate the number of acid sites on the sample, by measuring the peak area of the adsorbed pyridine.

2.3. Catalytic experiments

The catalytic epoxidation of cyclohexene with tert-Butyl hydroperoxyde TBHP (Aldrich, 70 wt% in H2O) as 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 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 then magnetically stirred for 24 h. Next, the organic phase was separated from the aqueous phase. In order 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 was transferred into the organic phase to be used in the catalytic reaction. The amount of 29 mmol (3 mL) of cyclohexene with 0.1 g of catalyst and the TBHP-heptane admixture were all mixed in a magnetic stirrerglass reactor, at 65 °C for 6 h. The reaction products were analyzed 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 also used and 0.5 µL of the sample was analyzed. Prior the GC analysis, the remaining TBHP was decomposed by introducing an excess of triphenylphosphine (Aldrich). In parallel, and in order to control the remaining TBHP in the reaction mixture, an iodometric titration was performed at the end of the reaction, after 6 h (results reported as % TBHP consumption in Table 3).

The catalytic performances were reported in terms of the cyclohexene conversion, selectivity towards products and turnover frequency (TOF). They were calculated by means of the expressions below:

 $\frac{\text{Conversion}(\%) =}{\frac{\text{moles of initial substrate} - \text{moles of residual substrate}}{\text{moles of initial substrate}} \times 100$

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

$$TOF(h^{-1}) = \frac{nbr \text{ of epoxide molecules}}{nbr V \text{ sites } \times \text{ time}}$$

3. Results and discussion

3.1. Physico-chemical characterization

3.1.1 ICP-OES. The 5VZr-2 sample, with a theoretical vanadium content of 5 wt%, was analyzed by ICP-OES. The results showed that vanadium which was actually deposited on zirconium is 4.27 wt%, indicating a 14% loss of vanadium during the synthesis procedure.

3.1.2 Powder XRD analysis. X-rays diffractograms of ZrO₂, 5VZr-1, 5VZr-2 and 5VZr-3 are shown in Fig. 1.

ZrO₂ exhibits a monoclinic structure [ICDD pattern 037-1484], with an average crystallite size of 30 nm. The deposition of vanadium oxide on the support and the heat treatment do not affect the structure of the material, therefore the monoclinic structure is conserved. However, in the case of 5VZr-1, the crystalline phase of V_2O_5 appears [ICDD pattern 041-1426], with an average crystallite size of 45 nm. Moreover, the diffraction peaks of 5VZr-2 and 5VZr-3 diffraction show a slight shift towards smaller angles compared to the ICDD reference (zoom on the two most intense peaks). This shift suggests the formation of a solid solution resulting from the distortion of the ZrO_2 lattice by insertion of V^{4+} cations. At 800 °C, 5VZr-3 diffractogram presents new low-intensity peaks at $2\theta = 20.8$, 23, 25 and 27° , corresponding to the formation of a new crystalline phase ZrV₂O₇ [ICDD pattern 016-422]. This new crystalline phase, which appears at high temperatures, may originate from the intimate contact between dispersed surface vanadium oxide species and the zirconia support.16,21

3.1.3 Surface area measurements. Table 1 show that all materials have a very low surface area and porosity that decreases even further upon high temperature treatment.



Fig. 1 X-rays diffraction (XRD) patterns of the ZrO_2 and 5wt% V_xO_y/ZrO_2 systems.

Table 1 Textural characteristics, as determined by N_2 adsorption/ desorption for different samples

Material	Temperature treatment (°C)	$S_{\rm BET} \ \left({{ m m}^2 \ { m g}^{ - 1}} ight)$	Pore volume $(cm^3 g^{-1})$	Pore size (Å)
ZrO ₂	400	<10	0.02	173
5VZr-1	400	<10	0.02	94
5VZr-2	400	<10	0.02	87
5VZr-3	800	${\sim}0$	_	_

3.1.4 TGA/DTA analysis. Fig. 2 illustrates the TGA/DTA analysis of 5VZr-2 material before any thermal treatment (dried sample). An endothermic peak, observed between room temperature and 200 °C, can be attributed to water removal.²² A Small endothermic peak, beyond 600 °C, may be imputed to phase transformation, leading to the formation of ZrV_2O_7 .^{22,23} Over 950 °C, further phase transitions may have occurred.^{22,24} The total weight loss of the sample was found equal to about 2% in the temperature range 25 to 1200 °C, which corresponds perfectly to what was expected theoretically (transformation of ammonium metavanadate to V_2O_5).

3.1.5 DR UV-Vis spectroscopy. Over the past few years, this technique has been increasingly involved in the characterization of vanadia catalysts.^{6,25–27} In fact, the ligand-to-metal charge transfer (LMCT) transitions of vanadium appear in the 200–500 nm region and the d–d transition bands in the 600–800 nm region, due to d–d electron transfer of V^{4+} .²⁸ The energy of oxygen-to-vanadium charge transfer absorption band, which is correlated with the minimum diffuse reflectance, is strongly influenced by the number of ligands surrounding the central vanadium ion. It can therefore be used to obtain very useful information on the coordination of vanadium ions in different surface species, in supported vanadia catalysts.^{29,30}

The UV-Vis spectra of the samples are shown in Fig. 3, and may be interpreted as follows:

(a) The bands around 220 nm are most likely due to charge transfer between Zr^{4+} and oxygen.^{31,32}

(b) The band of vanadium species, observed in the 300-350 nm region, should be assigned to the charge-transfer



Fig. 2 Thermal gravimetric analysis of the 5VZr-2 sample, before thermal treatment.

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Fig. 3 Diffuse-reflectance UV-Vis deconvoluted spectra of the 5 wt% $V_x O_y/ZrO_2$ materials.

transitions involving oxygen and vanadium species in tetrahedral coordination, present as polymeric species.^{33–35} The band in the 400–500 nm region is attributed to octahedral vanadium polymeric species.^{33,36,37}

(c) In the case of 5VZr-1, the band at ${\sim}570$ nm is due to the presence of crystallized $V_2O_5.^{33,38,39}$

(d) In the case of 5VZr-2 and 5VZr-3, the band in the 600–700 nm region is due to the V^{4+} species d–d transition.

(e) In the case of 5VZr-3, the existence of a band at 765 nm should be due to the presence of ZrV_2O_7 , evidenced by XRD.

Gao *et al.*²⁶ found that in the case of $4\% V_2O_5/ZrO_2$, the polymerized surface VO₄ species are predominant.

3.1.6 FTIR-ATR absorption. Deconvoluted infrared spectra were determined using the peakFit deconvolution software. Deconvoluted infrared spectra of 5 wt% V_xO_y/ZrO_2 materials in the 1500–500 cm⁻¹ region are reported in Fig. 4. After deconvolution, the following adsorption bands are revealed:

(a) between 530 and 650 $\rm cm^{-1},$ attributed to the rocking modes of the V–O–V bonds, $^{\rm 33,40,41}$

(b) around 710–750 cm⁻¹, representing stretching vibration of the V–O–V bonds,²⁸

(c) at 1000 cm⁻¹, being the asymmetric stretching vibration of the V=O bond in the polyvanadate,^{42,43}



Fig. 4 FTIR-ATR deconvoluted spectra of 5 wt% V_xO_y/ZrO_2 materials, at room temperature.

(d) in the case of 5VZr-1, a new band centered at 911 cm⁻¹ is observed, it is attributed to the crystal phase of the vanadium oxide (V₂O₅),^{7,43}

(e) in the case of 5VZr-3, the band at 867 cm⁻¹ may be due to the presence of ZrV_2O_7 phase, detected by XRD.

The results of the FTIR spectroscopy are correlated with those of UV-Visible and XRD analyses.

3.1.7 Measurement of surface acidity. Pyridine adsorption was performed on the surface of 5VZr-2 catalyst, and followed by IR spectroscopy. The bands corresponding to Brønsted acid sites (1538 cm⁻¹) and Lewis acid sites (1448 cm⁻¹) are characteristic of pyridine adsorption on the catalyst surface.⁴⁴ After pyridine adsorption on 5VZr-2 catalyst, the IR-spectra exhibited both Lewis acid site bands and Brønsted acid site bands (Fig. 5). The quantification of these sites is shown in Table 2. The number of Lewis acid sites decreases with increasing evacuation temperature. Elassal *et al.*⁷ found small amounts of Lewis acid sites in catalysts 4, 5 and 6% V₂O₅/ZrO₂. ZrO₂ itself has very weak acidity.^{13,45} When vanadium is inserted in the ZrO₂ lattice, in order to form the solid solution, the acidity of the oxide remains unchanged.

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Fig. 5 Infrared spectra of pyridine adsorption on 5VZr-2, at different temperatures (from 50 to 350 $^\circ$ C, in steps of 50 $^\circ$ C).

 Table 2
 Acidity of 5VZr-2 catalysts at different temperatures, estimated by pyridine adsorption and followed by infrared spectroscopy

Temperature (°C)	Lewis acid sites (μmol g ⁻¹)
50	29
100	26
150	15
200	9
250	4
300	2

3.2. Catalytic activity results

Generally, the cyclohexene oxidation reaction leads mainly to the formation of cyclohexene oxide (epoxide) and cyclohexane diols, besides cyclohexenol (Enol), cyclohexenone (Enone), cyclohexanol (Ol) and cyclohexanone (One) (Fig. 6).⁴⁶⁻⁵²

It is well established that the VO_x active species has a significant impact on the catalytic performance of vanadiumsupported catalysts,^{53,54} due to the presence of surface redox as well as acidic sites.^{17,55,56} Using GC analysis in all experiments, no 1,2-cyclohexanediol was detected in the reaction products.^{17,32,57} Without catalyst and with ZrO₂ alone, a very low conversion (2%) was observed and no epoxide was produced.^{32,49,58,59} The results of the catalytic tests of cyclohexene oxidation by TBHP at 70 °C, over different 5 wt%



Fig. 6 Different possible products of cyclohexene oxidation reaction.

 $V_x O_y/Zr O_2$ catalysts are summarized in Table 3. The highest performances were obtained over the reduced samples 5VZr-2 and 5VZr-3, due to the presence of the solid solution in both samples. 5VZr-3 is a better catalyst with a TOF = 49 h^{-1} , this may be explained by the presence of ZrV₂O₇ upon thermal treatment at 800 °C. Several studies have shown the importance of polymeric vanadium species for the catalytic activity in oxidation reactions over VO_x/ZrO₂ systems,^{3,6,26,58,60} as well as the formation of ZrV₂O₇ phase.^{16,61} However, a later study of the same system^{6,58,62} with different preparation methods, showed that bulk ZrV_2O_7 is quite selective. This suggests that some other factors, rather than V-O-Zr sites (since ZrV₂O₇ is exclusively composed of V-O-Zr functionalities), contribute to the catalytic activity in the oxidation reaction. In our case, one may suggest that the presence of reduced polymeric vanadium species in the solid solution is responsible for the increase in the catalytic activity and selectivity towards epoxide. This may be indicative of the relevance of the V-O-Zr bond, which is present in both zirconia-supported vanadium oxide and ZrV₂O₇ phase.¹⁶ The lower activity of 5VZr-1 must be ascribed to the presence of considerable amounts of crystalline V₂O₅ which decreases the number of surface polymeric sites.3,16,30,56,61

Finally, we discussed elsewhere¹⁷ the reaction mechanism for cyclohexene oxidation and we suggested that the epoxide production pathway is favored by redox features and by the presence of monomeric or polymeric vanadium sites.¹⁸

To our knowledge, no heterogeneous 5 wt% V_xO_y/ZrO_2 catalysts were used in the cyclohexene epoxidation reaction. The closest results to our work are summarized in Table 4. It can be observed that our catalysts (Table 3) present the best performances in terms of epoxide selectivity and conversion. Only M. Sharbatdaran *et al.*⁶³ reported an interesting conversion of 80% with a selectivity of 61% towards epoxide. However, it is worth underlining that these authors used an inorganic polymer of silica zirconia molybdate which is much more complex than our catalysts.

3.3. 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 5VZr-2 catalyst 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.*⁶⁸ and Farzaneh *et al.*⁶⁷ In addition, it was noted that the solution remains clear in the presence of TBHP and cyclohexene.⁶⁹ It can be stated from these results that no catalyst leaching occurs, and the reaction is really heterogeneous.

The results of the stability of 5VZr-2 catalyst during the epoxidation reaction of cyclohexene are shown in Table 5. They

Table 3	Oxidation of	cyclohexene,	using different	supported	catalysts
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		5()						
onv. (%)	TOF (h^{-1})	Epoxide	Enone	One	Enol	Ol	Diol	TBHP consumption (%)
	00				88	12		12
	00	_	_	_	_	_	_	8
	20	51	6	43	_	_	_	50
	42	80	_	15	5	_	_	50
	49	82	_	15	3	_	_	37
	nv. (%)	nv. (%) TOF (h ⁻¹) 00 00 20 42 49	$\begin{array}{c c} & & & \\ & & &$	$\begin{array}{c cccc} & & & & & \\ & $	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

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		Activity			
Catalyst	Substrate	Conversion (%)	$_{(h^{-1})}^{\rm TOF}$	Epoxide selectivity (%)	Ref.
α-ZrP·Fe(Salen)	Cyclohexene, TBHP as oxidant, benzene as solvent, 80 °C, 5 h, 0.066 g catalyst	13		21	64
Au/ZrO ₂	Cyclohexene, TBHP as oxidant, reflux, 6 h, 70 °C, 0.1 g catalyst	29		18	32
SZ1-Mo	Cyclohexene, TBHP as oxidant, CH ₃ CN as solvent, reflux, 8 h, 0.05 g catalyst	80		61	63
VO ₂ /CeO ₂	Cyclohexene, TBHP as oxidant, heptane as solvent, 65 °C, 6 h, 0.100 g catalyst	45	17.1	77	18
ZrO ₂ -SiO ₂	Cyclohexene, H_2O_2 as oxidant, MeOH as solvent, 90 °C, 24 h, 0.040 g catalyst	28	—	0	24
ZrO ₂ -SiO ₂	Cyclohexene, TBHP as oxidant, 60 °C, 7 h, 0.020 g catalyst	<1		<1	65
[VO(hacen)]-Y	Cyclohexene, TBHP as oxidant, 70 °C, 12 h, 0.025 g catalyst	27.51		36.47	66
VO ₂ -SiO ₂	Cyclohexene, TBHP as oxidant, heptane	21		83	47
VO ₂ -TiO ₂	as solvent, 65 °C, 6 h, 0.100 g catalyst	13		21	
VO ₂ -Al ₂ O ₃		17		0	
V ₂ O ₅ -TiO ₂	Cyclohexene, TBHP as oxidant, heptane as solvent, 80 °C, 6 h, 0.100 g catalyst	46		75	46
Vanadium– chromium–bentonite	Cyclohexene, TBHP as oxidant, heptane as solvent, 70 °C, 6 h, 0.100 g catalyst	32		69	50
V-MCM-41	Cyclohexene, TBHP as oxidant, chloroform as solvent, 65 °C, 6 h, 0.200 g catalyst	27		92	67

indicate that this material is stable during 2 cycles of the reaction. A slight decrease in the catalytic performances occurs from the 3^{rd} one.

Table	5	Results	of	the	stability	of	5VZr-2	during	the	epoxidation
reaction	on	of cyclol	nex	ene	with TBF	HP^a				

Cycle	Conversion (%)	Epoxide selectivity (%)	$_{\left(h^{-1}\right) }^{TOF}$	TBHP consumption (%)
1^{st}	28	80	42	50
2 nd	24	78	35	30
3 rd	15	78	22	17
4^{th}	12	55	12	17

 a Reaction conditions: cyclohexene 29 mmol, TBHP 38.45 mmol, heptane 25 mL, 0.1 g catalyst, reaction time 6 h, reaction temperature 65 $^\circ \rm C.$

4. Conclusions

A series of zirconia-supported vanadium oxide catalysts were prepared by impregnation process, with different temperature treatments. 5VZr-1 was obtained upon calcination at 400 °C of dried V/ZrO₂, 5VZr-2 was obtained upon reduction at 400 °C of 5VZr-1, and 5VZr-3 was obtained upon thermal treatment of 5VZr-2 under argon flow, at 800 °C. Characterization of these catalysts showed the presence of crystalline V₂O₅ and a small amount of Lewis acid sites on 5VZr-1. This system has proven to be an efficient catalyst for the selective epoxidation of cyclohexene with TBHP as oxidant and heptane as solvent (TOF = 20 h⁻¹). The epoxidation catalytic performances can be exalted (TOF = 42 h⁻¹) when a solid solution is formed with polymeric vanadium species (detected by UV-Vis, FTIR and XRD). These performances can be even higher (TOF = 49 h⁻¹) in the presence of ZrV_2O_7 in crystalline form (confirmed by XRD). This may be indicative of the relevance of the V–O–Zr bond, which is present in zirconia-supported vanadium oxide as well as in the ZrV_2O_7 phase. Meanwhile, the presence of the crystalline V_2O_5 phase decreases the epoxide selectivity.

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