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ARTICLE

Epoxidation of cyclohexene with *tert*-butyl hydroperoxide catalyzed by mixed oxide V_2O_5–TiO_2

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TiO_2 and 20 wt% V_2O_5–TiO_2 catalysts were prepared by the sol–gel route and calcined at 500 °C. The mixed oxide presented the crystalline structures of TiO_2 anatase and V_2O_5 Shcherbinaite phases, with a BET (Brunauer–Emmett–Teller) surface area of 19 m^2/g. The catalytic material was tested for the epoxidation of cyclohexene by *tert*-butyl hydroperoxide at 80 °C. The activity and selectivity were investigated as a function of the reaction time as well as the amounts of the catalyst and solvent. The reaction followed second-order kinetics, and the best catalytic performance was observed after 6 hr of reaction time, with 150 mg of catalyst in *n*-heptane solvent. The epoxidation selectivity reached 76% at 48% conversion. The catalyst remained stable after two cycles.

KEYWORDS
epoxidation of cyclohexene and selectivity, mixed oxide, sol–gel, V_2O_5–TiO_2

1 | INTRODUCTION

One of today's industrial routes for the formation of simple epoxides is the chlorohydrin process, where alkenes react with chlorine in the presence of sodium hydroxide. The formation of epoxides via metal-catalyzed oxidation of alkenes represents the most elegant and environmentally friendly method for the production of this compound class.[1,2] Innovation and improvement in catalytic epoxidation methods, where molecular oxygen, hydrogen peroxide, or alkyl hydroperoxides are employed as the terminal oxidants, are highly desirable.[3,4] Hence, from the environmental and economic points of view, molecular oxygen and hydrogen peroxide should be the preferred oxidants, considering their high active oxygen content and the fact that there are no waste products; only water is formed. However, one of the major limitations when using molecular oxygen and hydrogen peroxide as terminal oxidants for the formation of epoxides is the poor product selectivity obtained through these processes.[5] Valderruten et al.[6] and Bellifa et al.[7] showed that mixed oxides produced by the sol–gel method are the most efficient and selective catalysts of this type of solids for the epoxidation of cyclohexene. High-valent early transition metals, such as titanium (IV) and vanadium (V), have been shown to efficiently catalyze the epoxidation of alkenes in homogeneous catalysis.[8] The most preferred oxidants using these catalysts are various alkyl hydroperoxides, such as the *tert*-butyl hydroperoxide (TBHP) or ethylbenzene hydroperoxide (EBHP). Amelioration the catalytic activity and selectivity for the epoxidation of cyclohexene with cumene hydroperoxide (CHP) as oxidant. In addition, the high surface area mesoporous silicas (MCM-41 and SBA-15) are more effective than amorphous silica as supports for these catalysts. Supporting $TiSi_3$ on the SBA-15 affords highly active cyclohexene epoxidation catalysts (0.25–1.77 wt% Ti loading), providing turnover frequencies (TOFs) of 500–1,500 hr^{-1} after 1 hr (TOFs are reduced by about half after calcination). These results demonstrate that oxygen-rich siloxide complexes of titanium are useful as precursors to supported epoxidation catalysts.[9] Though titanium has been used in several new applications of heterogeneous catalysis, it is not the case for vanadium. Indeed, the development of the solid titanium (IV)-silicate (TS-1) catalyst by chemists at Enichem[10] represents a breakthrough for epoxidation reactions.

Catalytic liquid-phase epoxidation of cyclohexene is a commercially important reaction that is used to produce cyclohexene oxide, which is an essential organic intermediate in the production of fine chemicals. Moreover, the production of epoxides paves the way to the development of mild and green chemical processes for the synthesis of adipic acid, which is the raw material used in the production of nylon 6,6.[11,12] The use of solid catalysts for cyclohexene epoxidation, using TBHP as oxidant, has been reported, with the formation of 2-cyclohexene-1-one, 2-cyclohexene-1-ol, and *trans*-cyclohexane-1,2-diol, besides cyclohexene oxide.[3,13–17]

Sasidharan et al.[18] studied the regioselective epoxidation of different types of double bonds located within the cyclic and acyclic parts of bulky olefins using large-pore titanium silicate Ti-β in the presence of dilute aqueous H_2O_2 as oxidant under mild liquid-phase conditions. Their experimental results revealed that the epoxidation tendency of various bulky olefins with different positional and/or geometric isomers over Ti- β follows the order: terminal –C C– > ring –C C– ≈ bicyclic ring –C C– > allylic C–H bond.

Many recent studies have shown that the V_2O_5–TiO_2 catalyst can be used for the selective oxidation of saturated and unsaturated hydrocarbons such as cyclohexane, benzene, and *o*-xylene.[19–22] To our knowledge, no study using the V_2O_5–TiO_2 system for cyclohexene epoxidation has been reported so far.

After a preliminary paper on the sol–gel synthesis and characterization of various V_2O_5–TiO_2 mixed oxides,[23–25] the preparation and catalytic activity of 20 wt% V_2O_5–TiO_2 catalysts are described here. The prepared catalyst was characterized by X-ray diffraction (XRD) and nitrogen physisorption (specific surface area (SBET), pore size, and pore volume) in order to understand its behavior and performance as a solid catalyst for the epoxidation of cyclohexane, using TBHP as oxidizer. Furthermore, the kinetics, catalyst stability, catalyst mass, and the solvent effects on the epoxidation reaction were studied.

2 | RESULTS AND DISCUSSION

2.1 | Sample characterization

The results of XRD analysis of TiO_2 and 20 wt%V_2O_5–TiO_2 samples are shown in Figure 1. Typical diffraction peaks characteristic of TiO_2 anatase crystalline phase (ICDD-PDF 21–1272) and V_2O_5 Shcherbinaite crystalline phase (ICDD-PDF 041–1426) were observed. No rutile phase was detected in these oxides. These results are in line with the recently published synthesis of sulfated mixed vanadium oxide (25 wt% V_2O_5–TiO_2/SO_4^{2-}) prepared by the sol–gel route and calcined at 773 K[26]; both anatase (TiO_2) and Shcherbinaite (V_2O_5) were present when the wt% of SO_4^{2-} was <0.3. In this study, the crystalline vanadia phase appeared only when the calcination temperature reached 500 °C (not shown), indicating that vanadium oxide was present earlier in a highly dispersed manner. The quantitative composition was estimated from the intensity of the most intense diffraction peaks, and the I/I_{cor} factor was deduced from the corresponding powder diffraction files (1.60, (001) peak for V_2O_5; 3.30, (101) peak for anatase); the mass percentage of V_2O_5 is about 10%, i.e., half the expected value, thus showing that an important part of vanadium (about 10 wt% V_2O_5) was not present in the crystalline form. Therefore, the possibility of a partial substitution of Ti(IV) by V(IV) in the anatase structure cannot be ruled out; the initial oxidation number of vanadium introduced during the preparation procedure is IV. The average crystallite sizes of both phases are given in Table 1. V_2O_5 presented a slightly higher size (33 nm) compared to anatase (27 nm). The specific surface area showed a significant decrease when vanadium oxide was introduced into titanium oxide (40 and 19 m^2/g, respectively, for TiO_2 and V_2O_5–TiO_2) (Table 1), which is not in line with the variation of the titania's crystallite size. A simple cubic model, with six free faces, gave, as expected, higher values of the surface area; the calculated value for TiO_2 agrees with the experimental one (64 vs. 40 m^2/g), whereas the mixed oxide displays a larger difference (57 vs. 19 m^2/g). The pore volume and mean pore size data are found to be in line with the classical mesoporous cylindrical model (Table 1).

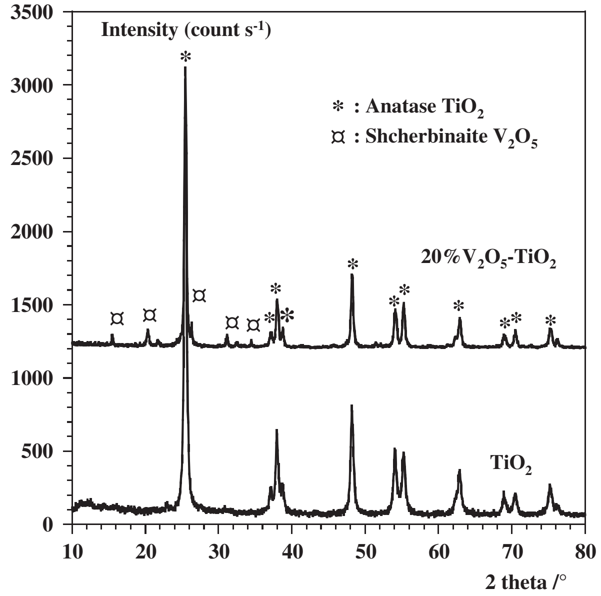


FIGURE 1 X-ray diffraction (XRD) patterns of TiO_2 and 20%V_2O_5–TiO_2 catalysts

Our data can be usefully compared to recent published results; a close value of the surface area (22 m^2/g) was found for sulfated 1% V_2O_5–TiO_2 prepared by sol–gel procedure and calcined at the same temperature (500 °C).[27] Rodella et al.[25] prepared V_2O_5/TiO_2 catalysts using ammonium vanadate as the vanadium precursor and V_2O_5 mass loading up to 9%. After calcination at 450 °C, the surface area was

TABLE 1 XRD crystallite size, N_2 physisorption data, cubic crystallite model, and cylindrical pore model

Sample	XRD mean size/nm	S_{BET}/m^2·g^{-1}	S_{XRD}^{a}/m^2.g^{-1}	Pore volume/cm^3·g^{-1}	Pore size/nm	Cylindrical pore model^b
TiO_2	24	40	64	0.093	9.0	3,900
20%V_2O_5–TiO_2	27 (TiO_2) 33 (V_2O_5)	19	57	0.14	30	4,100

[a] S_{XRD}: Calculated from the mean size and a cubic model with six free faces.
[b] S_{BET}.(pore size)/(pore volume) (calculated value with the same units: 4,000).

found to be 87 m^2/g; no separate vanadium oxide phase could be seen by XRD, which is in good agreement with our results. Bellifa et al.[22] prepared 20 wt%V_2O_5–TiO_2 directly from V_2O_5 by an acidic sol–gel route; after calcination at 300 °C under oxygen flow, the specific surface area was found to be 27 m^2/g; the presence of crystalline V_2O_5 oxide could be observed from the diffractogram besides the anatase and rutile phases. In a more recent paper, Debecker et al.[19] used a non-hydrolytic sol–gel method where $TiCl_4$ and $VOCl_3$ were employed as oxide precursors in diisopropyl ether. The final calcination temperature was 500 °C and the V_2O_5 mass percentage was increased up to 10% (specific surface area 71 m^2/g); again, no separate vanadium oxide phase could be observed.

2.2 | Catalytic tests

2.2.1 | Preliminary tests

The oxidation of cyclohexane using TBHP was investigated at temperatures 70 and 80 °C (Table 2). Cyclohexene was oxidized into cyclohexene oxide (C_6 epoxide), cyclohexenol (C_6 enol), cyclohexenone (C_6 enone), cyclohexanone (C_6 one), and *trans*-1,2-cyclohexanediol (C_6 trans) (Scheme. 1). The catalytic performances of both catalysts in terms of cyclohexene conversion and epoxide selectivity are presented in Table 2. At 70 °C, the conversion is 10% and the selectivity to cyclohexenol is 100%, in the absence or presence of TiO_2, which means that titania here has no influence. The mixed-oxide catalyst leads to a significant increase in cyclohexene conversion (38%) and epoxide selectivity (74%). The very low level of cyclohexenol selectivity (6%) and the presence of the other oxidation products agree with the presence of a catalytic transformation of C_6 enol as a side-reaction. At 80 °C, the cyclohexene conversion increases slightly for a blank test and in the presence of TiO_2 (13 and 14%); the cyclohexenol selectivity remains high, besides a low formation of epoxide and oxidation products. In the presence of V_2O_5–TiO_2, the conversion and epoxide selectivity increase to 46 and 79%, respectively. Despite the difficulty in analyzing quantitatively the remaining TBHP by iodine titration under the reaction conditions, the conversion data are in good agreement with the disappearance of one TBHP molecule for each cyclohexene molecule, as expected for the formation of epoxides (Table 2). The cyclohexene conversion and the yield of products versus time in presence of 150 mg of V_2O_5–TiO_2 catalyst are presented in Figure 2.

2.2.2 | Influence of the catalyst mass

Cyclohexene conversion and the product selectivity were determined at 80 °C for different masses of the mixed-oxide catalyst (10, 25, 100, 150, and 250 mg). The results are presented in Table 3, and the kinetic data are shown in Figure 3. The conversion percentage increases as the mass is increased from 25 to 100 mg; the same remark can be made for the selectivity in epoxide. Then, the conversion remains stable for the catalyst mass of 250 mg, while the selectivity changes; it drops in epoxide but rises mainly in C_6 one and C_6 diol products. Higher cyclohexene conversion (48%) and epoxide selectivity (76%) were observed for 150 mg of the catalyst. More experimental work is needed in order to explain these results.

2.2.3 | Kinetics of reaction

The results obtained for 150 mg of catalyst are considered to determine the reaction order and the rate constant; this corresponds to the highest conversion (56%) after 10 hr. The rate equation may be written as follows[28]:

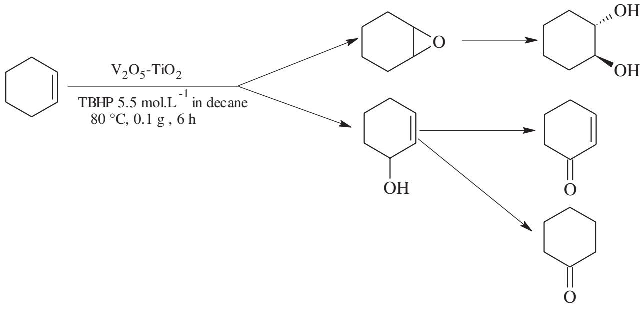
$$\text{Rate} = k[\text{C}_6\,\text{ene}]^{\alpha}\,[\text{TBHP}]^{\beta} = -d[\text{C}_6\,\text{ene}]/d(t),$$

where [C_6 ene] and [TBHP] represent the cyclohexene and TBHP concentrations, respectively, α and β are the

TABLE 2 Cyclohexene oxidation at two temperatures

				^{a}Selectivity/%				
Temperature/°C	Sample	^{b}Cyclohexene conversion/%	TBHP conversion/%	Epoxide	C_6 enol	C_6 enone	C_6 one	*trans*-C_6 diol
70	Blank test	10	—	0	100	0	0	0
	TiO_2	10	10	0	100	0	0	0
	20%V_2O_5–TiO_2	38	35	74	6	11	7	2
80	Blank test	13	10	6	88	4	2	0
	TiO_2	14	12	12	78	6	4	0
	20%V_2O_5–TiO_2	46	41	79	2	9	8	2

[a] *Epoxide*: cyclohexene epoxide; C_6 enol: 2-cyclohexenol; C_6 enone: 2-cyclohexenone; C_6 one: cyclohexanone; *trans*-C_6 diol: *trans*-1,2-cyclohexanediol.
[b] *Reaction conditions*: 3 mL cyclohexene; 25 mL heptane; 5 mL TBHP/decane; 100 mg catalyst; 6 hr.



SCHEME 1 Products identified during the oxidation of cyclohexene by TBHP

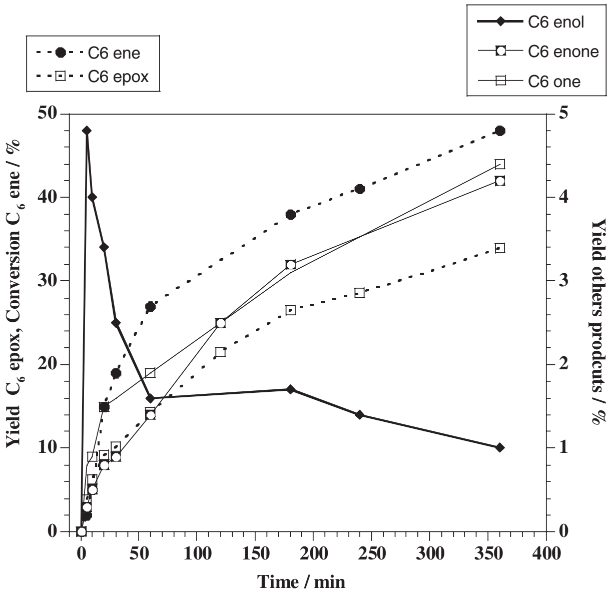


FIGURE 2 Cyclohexene conversion and product yield versus time in the presence of 150 mg of 20%V_2O_5–TiO_2: temperature 80 °C

respective kinetic reaction orders, and k is the second-order rate constant. Considering the classical assumption $\alpha = 1$ and $\beta = 1$, and taking into account the close initial concentrations of cyclohexene and TBHP, integration leads to the following equation:

$$1/[\mathrm{C_6\ ene}] = kt + 1/[\mathrm{C_6\ ene}]_{t=0}.$$

A plot of 1/[C_6 ene] versus time is displayed in Figure 4 for a time range extending from 20 min to 10 hr. The observed linear relationship is in agreement with the second-order dependence of the oxidation reaction. The rate constant k is equal to 2.14×10^{-3} L mol^{-1} min^{-1}. Analysis of the same data for a first-order reaction kinetics leads to a significantly lower correlation coefficient ($R = 0.97886$, figure not shown).

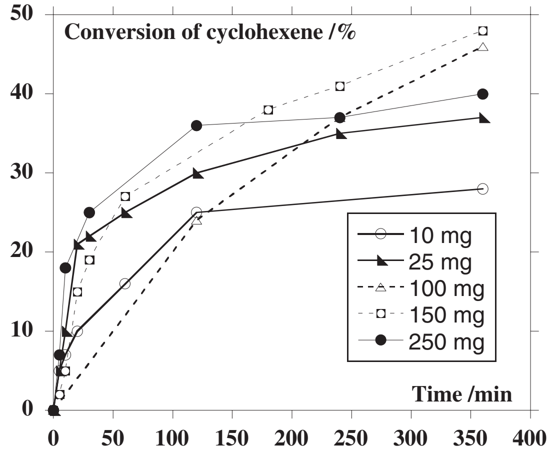


FIGURE 3 Cyclohexene conversion versus time for different 20%V_2O_5–TiO_2 catalyst masses: temperature 80 °C

2.2.4 | Solvent effect

The selection of the solvent is an important step in the reaction design. In order to identify suitable alternative solvents, it is interesting to have a classification system so that solvents with similar properties can be readily identified.[29] All solvents should have properties that fulfill some specific requirements related to the environment, safety, and health.[30]

Classification schemes have been proposed on the basis of different properties such as the dipole moment, dielectric constant, solubility, and polarity.[31] Table 4 shows the properties of the tested solvents. The behavior of cyclohexene oxidation by TBHP in various solvents is very strikingly different, as can be seen in Table 5 (80 °C, 100 mg of catalyst). Acetic acid gives the best conversion (52%) after 6 hr, followed by heptane (46%) and acetonitrile (37%), whereas propan-2-ol is only slightly better than the blank test (14%). The selectivity to epoxide is the highest for the nonpolar solvent *n*-heptane; it decreases to 50% in the two polar solvents acetonitrile and propan-2-ol. It can easily be noted that the

TABLE 3 Cyclohexene oxidation with different catalyst masses on 20%V_2O_5–TiO_2

		^{a}Selectivity/%				
Catalyst mass/mg	**^{b}Cyclohexene conversion/%**	**Epoxide**	**C_6 enol**	**C_6 enone**	**C_6 one**	***trans*-C_6 diol**
10	28	72	14	8	6	0
25	37	76	8	9	7	0
100	46	79	2	9	8	2
150	48	76	2	10	10	2
250	40	60	4	13	17	6

^{a} *Epoxide*: cyclohexene epoxide; C_6 enol: 2-cyclohexenol; C_6 enone: 2-cyclohexenone; C_6 one: cyclohexanone; *trans*-C_6 diol: *trans*-1,2-cyclohexanediol.
^{b} *Reaction conditions*: 3 mL cyclohexene; 25 mL heptane; 5 mL TBHP/decane; 80 °C; 6 hr.

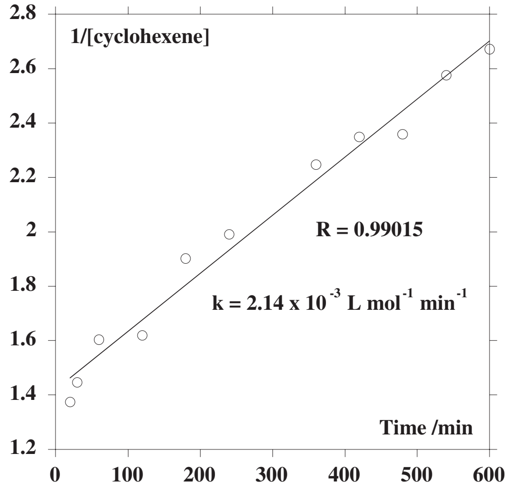


FIGURE 4 Pseudo-second-order kinetics of cyclohexene oxidation with 150 mg of 20%V_2O_5–TiO_2 catalyst at 80 °C

second major product is not the same for the two solvents; it is cyclohexanone in acetonitrile and cyclohexenol in propanol. One can thus see that acetonitrile promotes the classical enol–cetone transformation. In acetic acid, the major product is cyclohexanol, and the absence of epoxide is in agreement with the rapid transformation into *trans*-1,2 cyclohexanediol because epoxides are unstable in acid solvents. Epoxides can be cleaved in a regio- and stereo-selective manner under neutral conditions, with alcohols and acetic acid.[32] The conversion values are high in the presence of acetic acid and some vanadium species (V_2O_5); this may be due to the formation of stable peracids (peroxyacetic), which promote the oxidation of hydrocarbons.[33]A high conversion is observed in the case of acetonitrile (37%) with good epoxide selectivity (52%). The selectivity to epoxide obtained with acetonitrile as solvent results from the decreasing acidity, probably due to the coordination of acetonitrile through the nitrogen atom, leading to a decrease in the extent of the acid-catalyzed secondary reaction.[34] It is widely reported in the literature that the best solvent for oxidation is acetonitrile, which is a polar aprotic solvent.[35] Acetonitrile was more suitable for the epoxidation of cyclohexene on TS-1 than methanol because the reaction occurred mainly on the hydrophilic external surface.[36] In our case, heptane gives the best activity and selectivity, which means that there is an interaction between heptane as solvent and the vanadium species (V_2O_5). Catalysts based on metals such as chromium and vanadium have oxidation power. In the presence of heptane, they promote the oxidation reaction of cyclohexene with an epoxide selectivity.[17,37] The epoxidation of cyclohexane with TBHP and H_2O_2 on Tiβ-1 catalyst has been studied using CH_3OH as solvent. It has been shown that TBHP is more beneficial to the selective production of epoxide than H_2O_2. It is also assumed that a similar mechanism is operative for the epoxidation of cyclic alkenes with H_2O_2 and TBHP as oxidants. Obviously, the transition state involving Ti–OOR and cyclic alkenes must be much bulkier than that that relating to Ti–OOH and alkenes. This characteristic significantly retards the reaction rate of cyclic alkenes with TBHP, further decreasing the possibility of acid-catalyzed ring-opening secondary reaction of the epoxide molecule.[38]

2.2.5 | Recyclability of the reactions

Reutilization is one of the greatest advantages of heterogeneous catalysts; it can provide useful information about the intercalation process and catalytic stability during the successive catalytic cycles. The solid catalyst was recovered by filtration and dried in open air. After the first cycle, conversion decreased from 46 to 39% during the second cycle, and then remained stable (38% for the third cycle, Table 5). The selectivity showed slight changes only. These results suggest that the catalyst is stable during the catalytic reaction and is thus suitable for recycling.

3 | CONCLUSIONS

The mixed oxide 20 wt% V_2O_5–TiO_2 was prepared by the sol–gel method. Structural (XRD) and textural analyses (nitrogen physisorption) showed that V_2O_5–TiO_2 has the crystalline structure of the anatase phase, and the introduction of vanadium oxide decreases the specific surface area. Only half of the introduced vanadium was found as the minor crystalline phase V_2O_5, whereas the second half was well dispersed. This mixed oxide has proven to be an efficient catalyst for the selective epoxidation of cyclohexene by TBHP. Cyclohexene conversion was higher than 50%, and the maximum selectivity (79%) for epoxidation of cyclohexene was observed at the temperature of 80 °C in *n*-heptane. The oxidation reaction was shown to follow second-order kinetics.

TABLE 4 Properties of the solvents

Solvent designation	Solvent	T^a_{boi}	μ^b (debye)	ε_r^c	E_T^N	Polarity of constant
Nonpolar aprotic	*n*-Heptane	98	0	1.92	0.012	—
Polar aprotic	Acetonitrile	82	3.45	37.5	0.460	192.28
Polar aprotic	Acetic acid	118	1.68	6.15	0.648	214.02
Polar aprotic	Propanol-2	82	1.59	19.92	0.546	203.15

[a] Boiling point.
[b] Dipole moment (1 debye = 3,336 × 10^{-30} C m).
[c] Dielectric constant at 20 °C.

TABLE 5 Effect of solvent and number of cycles on cyclohexene oxidation

			[a]Selectivity (%)				
Solvent	**[b]Conversion (%)**	**TBHP (%)**	**Epoxide**	**C_6 enol**	**C_6 enone**	**C_6 one**	***trans*-C_6 diol**
Heptane cycle 1	46	41	79	2	9	8	2
Heptane cycle 2	39	35	76	6	8	6	4
Heptane cycle 3	38	35	74	9	11	6	0
Acetonitrile	37	30	52	9	10	29	0
Acetic acid	52	95	0	46	6	9	39
Propan-2-ol	14	10	51	28	14	7	0

[a] *Epoxide*: cyclohexene epoxide; C_6 enol: 2-cyclohexenol; C_6 enone: 2-cyclohexenone; C_6 one: cyclohexanone; *trans*-C_6 diol: *trans*-1,2-cyclohexanediol.
[b] *Reaction conditions*: 3 mL cyclohexene; 25 mL solvent; 5 mL TBHP/decane, 80 °C, 100 mg catalyst, 6 hr.

4 | EXPERIMENTAL

4.1 | Catalyst preparation

4.1.1 | Starting materials

Titanium tetrabutoxide ($Ti[OC_4H_9]_4$, Aldrich, 97%), vanadyl acetylacetonate ($VO[C_5H_7O_2]_2$, Merck), propan-2-ol (99,5%, Merck), acetic acid (Prolabo, 100%), cyclohexene (Aldrich, 98%), heptane (Fluka), and tertiobutylhydroperoxide solution (Aldrich, 5.5 mol/L in decane) were used in the experiments.

4.1.2 | Synthesis of TiO_2

Titanium butoxide (24.29 g, 0.0714 mol) and 0.50 mL of acetic acid (9.0 mmol) were dissolved in 50 mL of propan-2-ol, and the resulting mixture was stirred for 15 min. The white gel formed after the addition of 50 mL of H_2O was dried at 60 °C overnight, then at 120 °C for another night, and finally calcined at 500 °C for 4 hr under static air in a muffle furnace (heating rate of 5 °C/min).

4.1.3 | Synthesis of 20 wt% V_2O_5–TiO_2

The mixed oxide was prepared by the acid-catalyzed sol–gel method[39] using 3.499 g (0.0132 mol) of vanadyl acetylacetonate dissolved in water under stirring for 15 min. Then a mixture containing titanium butoxide (20.45 g, 0.0601 mol), acetic acid (0.50 mL, 9 mmol), and propan-2-ol (50 mL) was added into the first solution while stirring. The obtained green gel was first dried and then calcined, as previously done for TiO_2.

4.1.4 | Catalyst characterization

The surface area, pore size, and pore volume were determined using nitrogen adsorption at 77 K, on a Micromeritics Tristar 3000 apparatus, after heat pretreatment under vacuum for 6 hr at a temperature of 250 °C. The XRD measurements were carried out on a Bruker D5005 powder diffractometer for an angle 2θ ranging from 10 to 80° at a rate of 0.02° s^{-1}, using a monochromatized Cu Kα radiation source ($\lambda_{K\alpha\ 1} = 1.5406$ Å). The applied voltage and current were 50 kV and 35 mA, respectively. Identification of the crystalline phases was done by comparison with the references listed in the ICDD database. The average crystallite size was estimated using the Scherrer law.

4.2 | Catalytic activity evaluation

Cyclohexene oxidation reactions were carried out in a 100-mL, three-neck flask placed in a temperature-equilibrated water bath and equipped with a reflux condenser. A mixture containing 5 mL of TBHP in decane (27.3 mmol), 3 mL of cyclohexene (28.9 mmol), 25 mL of the solvent (heptane, acetonitrile, acetic acid or propan-2-ol), and 10–250 mg of the catalyst was prepared, and then magnetically stirred under atmospheric pressure at 70 or 80 °C with a speed of 460 rpm for 6–10 hr. The reaction mixture was analyzed by gas chromatography (GC) by taking aliquots (0.2 mL) at different reaction times. Before injection into the chromatograph, the aliquots were treated with 100 mg triphenylphosphine (TPP) in 1 mL hexane (minimum mol ratio TPP/TBHP = 3) to remove the remaining TBHP. A volume of 0.50 μL was injected into a Varian GC-450 gas chromatograph equipped with a CP-wax-52 B (25 m × 0.32 μm × 1.2 μm) column; a flame ionization detector (FID) was also used. The consumption of TBHP was determined by iodometric titration.

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