

## VO(acac)<sub>2</sub> Supported on Ethylenediamine Functionalized Hydrous Zirconia Nano-Particles for Catalytic Epoxidation of Alkenes

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Hydrous zirconia nanoparticles were covalently functionalized by 3-(trimethoxysilyl)-propylchloride and ethylenediamine to support VO(acac)<sub>2</sub> complex. The prepared catalyst has been characterized by means of FT-IR spectroscopy, PXRD pattern, thermal analysis, elemental analysis, and scanning electron microscopy. Then it was used for the epoxidation of *cis*-cyclooctene. The catalytic procedure was subsequently investigated for each catalyst and followed by Gas-Liquid Chromatography. It was also applied repeatedly in the optimum reaction conditions to reveal its recycling ability. Then these conditions were used for successful epoxidation of other linear and non-linear alkenes.

**Keywords:** Hydrous Zirconia nanoparticles (ZNP), Bis-acetylacetonate-oxo-vanadium, Epoxidation, Ethylenediamine, 3-(Trimethoxysilyl)-propylchloride

### INTRODUCTION

In chemical procedures, economic and environmental concerns encouraged researchers to use less reactant and to obtain more products. By the way, in catalytic procedures, they are fortified to improve the reaction progress by yield, catalyst separation and catalyst recycling. Different types of vanadium complexes were used as efficient catalysts for various organic reactions. The complexes usually contained oxo-vanadium species such as bis(acetylacetonato)oxo-vanadium [1], vanadium containing MOFs [2] or heteropolyanions [3]. These are used in miscellaneous organic reactions such as alkene epoxidation [1-2] and aromatic oxidation [3]. Supporting of these catalysts on proper solid beds could improve both the catalytic activity and their separation from the reaction media [4-8]. Impregnation [9] and adsorption [10] are conventional and simplest methods for supporting active species of different catalysts on the surface of solid beds. But the absence of

suitable bonding interactions caused gradual elution of active species from the surface of beds especially in polar solvents. Therefore, new reports focused on the use of chemical bonding to support active species on catalytic beds [4-8]. On the basis of this strategy and in continuation of our studies on new catalytic protocols, here we report the preparation of ethylenediamine functionalized hydrous zirconia nanoparticles (en-ZNP) loaded VO(acac)<sub>2</sub> complex for efficient epoxidation of alkenes. Hydrous zirconia nanoparticles (ZNP) were produced through a sol-gel process [11] at room temperature without any other thermal treatment which survived all its surface hydroxyl groups. Therefore, it is an inorganic-insoluble solid support with extra hydroxyl groups on its surface which prepare a platform for further modification and functionalization. For the covalent bonding of en functional groups, ZNP, like other hydroxyl covered solid beds [4-8], reacted with (MeO)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>Cl. Then some of the chlorine atoms were replaced with en. This covalently anchored en groups on ZNP were used to anchored bis-acetylacetonate-oxo-vanadium complex. The resulting catalyst was then thoroughly characterized by different techniques including

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FTIR, XRD, FE-SEM and thermal analysis and its activity was extensively investigated toward epoxidation of some alkenes.

Epoxides are usual intermediates of wide range of organic chemicals which commonly produced by mild and selective oxidation of alkenes in the presence of metal based catalysts [4-8]. Most frequently, the epoxidation of *cis*-cyclooctene was used as a model to compare the activity of new catalysts with previous ones. In this research, the activities of these new catalysts were examined in the epoxidation of cyclooctene and some other alkenes.

## MATERIALS AND METHODS

The Required solvents and reagents were purchased from Merck or Fluka and used without further purification. IR spectra were recorded on a Rayleigh WQF-510A FT-IR instrument at  $4\text{ cm}^{-1}$  resolution using KBr pellets. Thermogravimetric analyses were carried out in Bahr STA-503 with a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  in air. Elemental analyses were carried out in a LECO TruSpec CHNS Analyzer. Electron microscopy was performed on a S360 Mv2300 scanning electron microscope. Gas-liquid chromatography (GLC) was carried out on a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200.

## EXPERIMENTAL

### Preparation of Supported Catalyst

Hydrous zirconia nanoparticles (ZNP) were prepared from dissolving zirconium oxychloride octa-hydrate (25 g, 77.6 mmol) in deionized water (225 mL) [11]. Ammonium hydroxide solution (5 M) was added to this solution dropwise up to pH 9. The obtained hydrogel was filtered off and the remained chloride ions were completely removed in a Soxhlet extractor with deionized water and the chloride free ZNP was dried at room temperature. The chlorine functionalized ZNP (Cl-ZNP) was prepared by refluxing 1.00 g of ZNP with MSPCl (400  $\mu\text{l}$ , 2.3 mmol) in dry toluene (50.0 mL) for 24 h. Then the solid substance obtained was filtered off, washed three times with dry toluene, and dried at  $100\text{ }^{\circ}\text{C}$  overnight. The ethylene-diamine functionalized ZNP (en-ZNP) was prepared by refluxing 1.00 g of Cl-ZNP with ethylene-di-amine (en:

1.0 mL, 15 mmol) in acetonitrile (50.0 mL) for 48 h in the presence of 2.5 mL (18 mmol) tri-ethylamine. Then the solid substance obtained was filtered off, washed three times with acetonitrile, and dried at  $100\text{ }^{\circ}\text{C}$  overnight.

VO(acac)<sub>2</sub> complex was then used to support on ZNP, Cl-ZNP, or en-ZNP. For this purpose, 50 mL acetonitrile was added to VO(acac)<sub>2</sub> (0.6 g, 2.2 mmol) and ZNP, Cl-ZNP or en-ZNP (1.00 g) and the mixture was refluxed for 12 h. Then the mixture was cooled down, filtered off and the precipitate was washed three times with acetonitrile and dried at  $100\text{ }^{\circ}\text{C}$  overnight.

### Catalytic Epoxidation of Alkenes

In a typical process, an appropriate round bottom flask equipped with a magnetic stirrer bar and a condenser was charged with an alkene, an oxidant, the catalyst (V-en-ZNP) and solvent, and the mixture was then refluxed. All the reactions were performed at least two times, and the reaction progress was monitored by GLC. Since different alkenes have different reactivity toward oxidation, these reactions were continued until no further progress was observed. The characterizations of the main products and byproducts were performed by comparison of their retention times with those for the standard samples. The alkene conversions and product selectivity were calculated using their peak areas by the standard addition method.

### Catalyst Recycling

In a typical experiment, after recovering the catalyst from the reaction mixture at the optimum experimental conditions, it was washed several times with CCl<sub>4</sub>, and then used in the same procedure under the same conditions.

## RESULTS AND DISCUSSION

Conventional sol-gel processing on zirconium oxychloride was used here for the preparation of ZNP [11]. Then it was grafted with MSPCl and en since it showed no acceptable interaction with VO(acac)<sub>2</sub>. Then the prepared catalysts were applied in the model reaction which is epoxidation of *cis*-cyclooctene and optimized for some crucial parameters such as the ratio of the catalyst, type of solvent, type and ratio of the oxidant. Hot filtration was also used to confirm the heterogenic character of all catalytic

procedures. Then they were used for the epoxidation of different alkenes under the optimum experimental conditions. In addition, recycling experiments were carried out to reveal the reusability of these catalysts.

### Preparation and Characterization of Supported Catalysts

It was proved that, for an efficient epoxidation of alkenes in mild conditions, the presence of a catalyst containing an active metal site was vital because the oxidant could coordinate to this site, and be activated for the epoxidation process. However, ZNP, Cl-ZNP and en-ZNP showed no reactivity in the epoxidation of alkenes. Furthermore, supporting the VO(acac)<sub>2</sub> on ZNP or Cl-ZNP failed (Scheme 1). The IR spectra and ICP analyses showed no evidence that could confirm an acceptable interaction between them even after 20 h reflux. Consequently, in continuation of our studies on use of pending  $\equiv\text{O}_3\text{Si}(\text{CH}_2)_3\text{X}$  (X = NH<sub>2</sub> or Cl) groups to support metal complexes on solid beds [4-8], here we tried to support VO(acac)<sub>2</sub> onto the surface of en-ZNP. VO(acac)<sub>2</sub> could be coordinated to the surface pending amine groups of en-ZNP by reflux in acetonitrile solution (Scheme 1).

Figure 1 shows the FT-IR spectra of ZNP, Cl-ZNP, en-ZNP, and supported VO(acac)<sub>2</sub> on en-ZNP. All of them clearly contain the characteristic broad vibration band of ZNP at 3300-3400 cm<sup>-1</sup>, which was assigned to the surface hydroxyl groups of ZNP. ZNP also had a distinguishable Zr-OH related vibration at 471 cm<sup>-1</sup> in the IR spectrum (Fig. 1a). The IR spectrum for Cl-ZNP (Fig. 1b) showed three new bands at 2927, 976 and 648 cm<sup>-1</sup> in addition to the ZNP characteristic bands, which was assigned to the C-H, Si-O and C-Cl stretching vibrations of the grafted 3-(tri-methoxy)silylpropylchloride groups, respectively. The IR spectrum for en-ZNP (Fig. 1c) showed a new band at 1269 cm<sup>-1</sup> in addition to the Cl-ZNP characteristic bands, which was assigned to the C-N stretching vibrations of the grafted amine groups. Their N-H stretching vibrations over 3000 cm<sup>-1</sup> was covered by broad bands of ZNP hydroxyl group vibrations in this region. The IR spectrum for V-en-ZNP (Fig. 1d) showed a new band at 977 cm<sup>-1</sup> in addition to the en-ZNP, which was assigned to the V=O stretching vibrations of the supported vanadium complex.

ICP and elemental analysis confirmed the lack of

vanadium, carbon and nitrogen content in ZNP. The elemental analysis also showed that the nitrogen content of en-ZNP was 3.6%, which means that 1.28 mmol of the pending en groups was covalently bonded to the surface of 1.00 g of ZNP. Determination of the vanadium content in V-en-ZNP according to the ICP analysis showed that approximately 72% of the nitrogen sites on en-ZNP were used to anchor 0.92 mmol of VO(acac)<sub>2</sub> on 1.00 g V-en-ZNP.

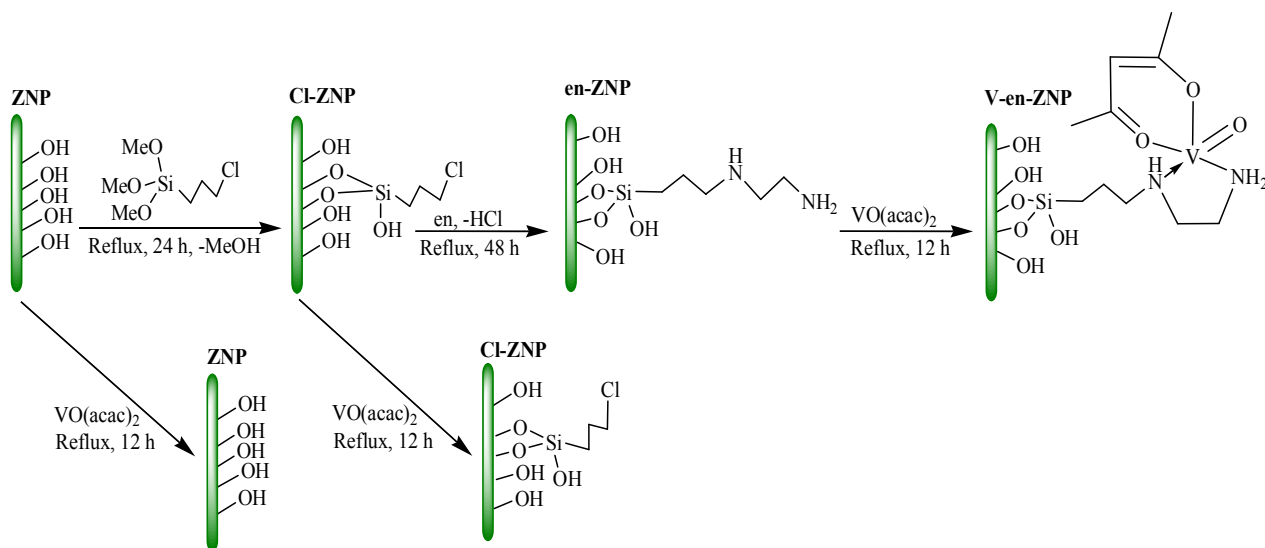
The PXRD pattern for ZNP was shown in Fig. 2 and confirmed the amorphous structure of it. In addition, PXRD patterns for Cl-ZNP, en-ZNP and V-en-ZNP were confirmed the amorphous structure of them. This also meant that vanadium complex was uniformly dispersed and not accumulated or crystallized onto the surface of en-ZNP; otherwise it could show its crystalline structure in the diffraction pattern.

In the TG curves of V-en-ZNP (Fig. 3), there is 7% weight loss below 200 °C which is accompanied by some endothermic peaks in DTA curve and could be attributed to the elimination of the physically-adsorbed and/or trapped water and other solvent molecules. There are also 10 and 15% weight losses at around 200-350 and 350-500 °C in TG curve, which are accompanied by exothermic peaks in the DTA curve and could be assigned to the ignition of organic pending groups and ligands of vanadium complex anchored to the surface of the catalyst, respectively.

Figure 4 shows the field emission scanning electron microscopy (FESEM) images of ZNP and V-en-ZNP. Uniform semi-spherical nanoparticles with over 50 nm diameter were seen in V-en-ZNP which the size of particles clearly grown by functionalization and supporting VO(acac)<sub>2</sub>.

### Alkene Epoxidation with TBHP Catalyzed by Supported Catalyst

Epoxidation of cyclooctene classically used as a model to validate the catalytic activity of the new catalysts since cyclooctene epoxide is its only product. Therefore, it was used in this research and the reaction conditions verified by changing some parameters including the solvent, oxidant and catalyst. The results showed that these catalysts, exclusively need *tert*-butylhydroperoxide (TBHP) to oxidize different alkenes in chlorinated solvents and other oxygen



Scheme 1. Attempt to support VO(acac)<sub>2</sub> on ZNP, Cl-ZNP and en-ZNP

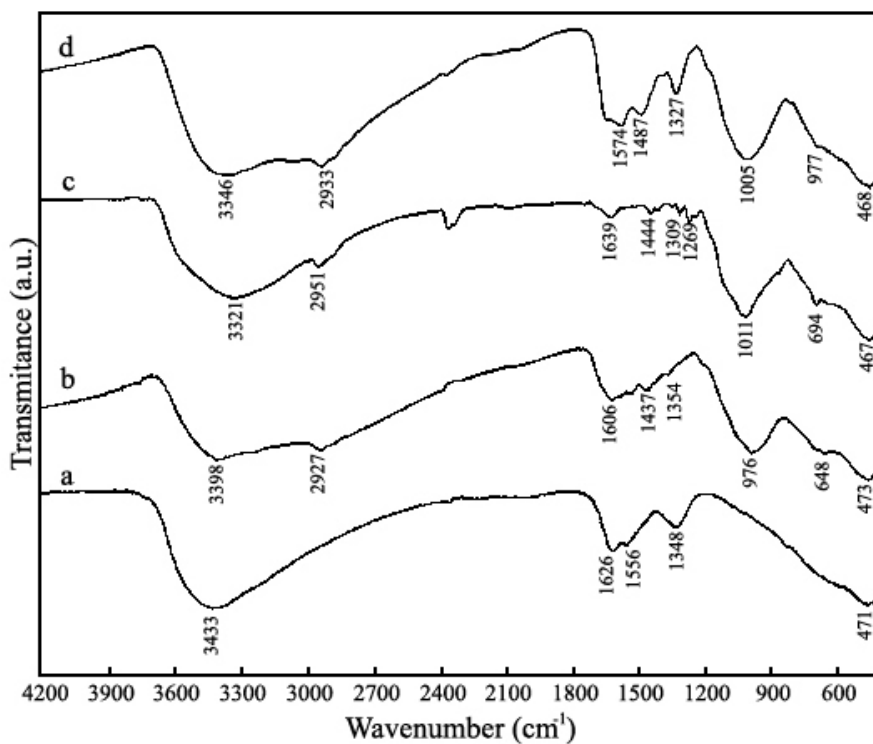


Fig. 1. FT-IR spectra of a) ZNP, b) Cl-ZNP, c) en-ZNP and d) V-en-ZNP.

sources such as hydrogen peroxide, urea-hydrogen peroxide, air, oxygen gas and sodium periodate, even in the presence of 0.01 g of tetrabutylphosphonium bromide as the

phase-transfer reagent, had not acceptable activity. It seems that the protic solvents, which were inevitably present with those oxidants, competed to bind to the metal centers and

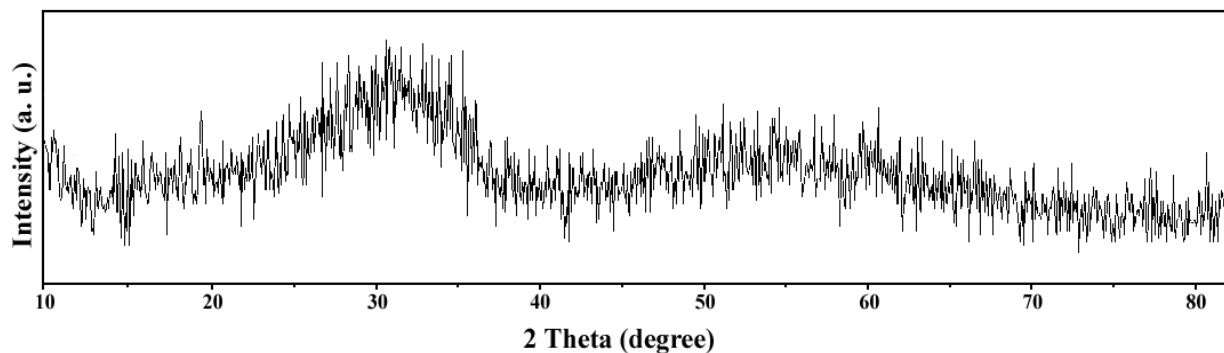


Fig. 2. PXRD pattern of ZNP.

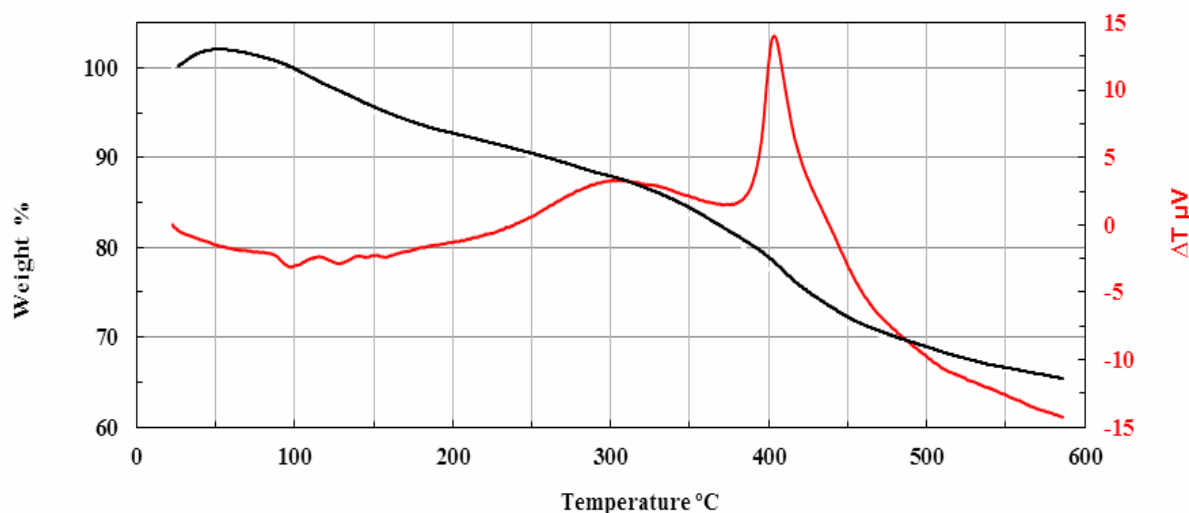


Fig. 3. Thermal analysis diagram of V-en-ZNP.

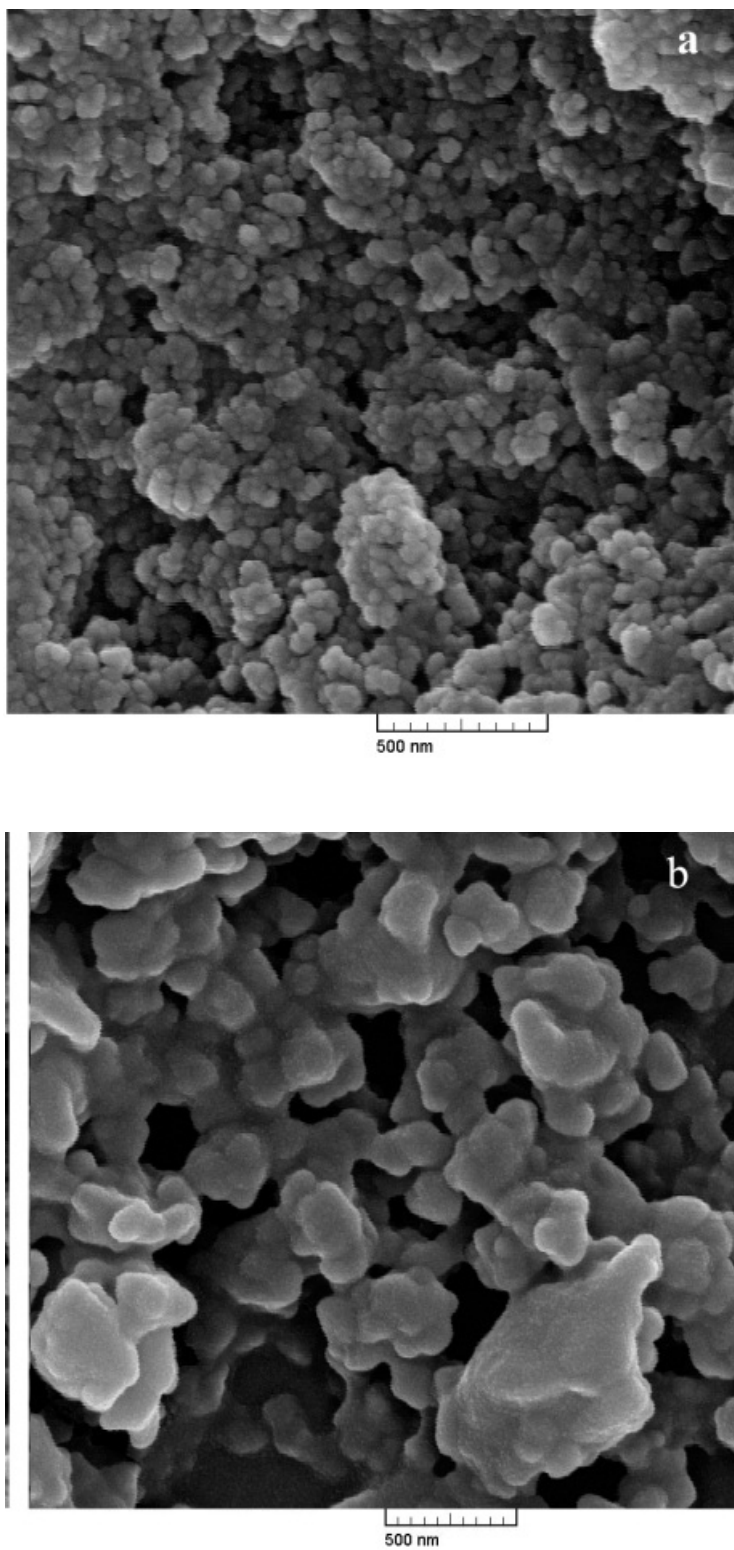
blocked the catalytic sites. Furthermore, under mild conditions, the epoxidation of *cis*-cyclooctene by TBHP did not proceed in the absence of metal contained catalyst, as pointed out above.

Studying the solvent effect in Table 1 (entries 1-7) showed the same trend as the other literature reports on homogeneous alkene epoxidation [4-8]. Coordinating solvents such as CH<sub>3</sub>CN and CH<sub>3</sub>OH compete with TBHP to occupy the coordination sites on the transition metal catalyst. Therefore, in the presence of these solvents, the observed yields are very low. Among other solvents, 1,2-dichloroethane (DCE) has the highest yield of epoxide

product for this catalyst.

As another parameter, the amount of catalyst was investigated in the epoxidation of *cis*-cyclooctene with TBHP. Table 1 (entries 7-10) confirm that increasing the amount of catalyst up to 15 mg increased the cyclooctene epoxide yields and then became constant.

The oxidant to substrate ratio is one of the most crucial parameters in the catalytic epoxidation processes. The results tabulated in Table 1 (entries 7 and 11-13) show that the optimum oxidant to substrate ratio for the catalyst was 2. Although, increasing this ratio over 2 did not affect the yield, but by decreasing, the yield lowered intensely.



**Fig. 4.** FESEM images of a) ZNP and b) V-en-ZNP.

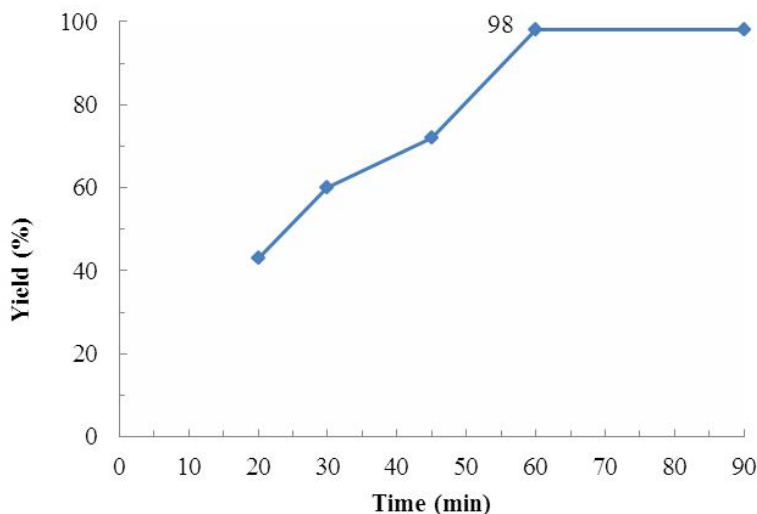
**Table 1.** Epoxidation of *cis*-cyclooctene under Reflux Conditions for 60 min

Entry	Catalyst (mg)	Solvent (mL)	Oxidant	Catalyst loading (mol%) <sup>a</sup>	Oxidant/Substrate molar ratio	Epoxide yield (%) <sup>b</sup>
1	V-en-ZNP (15)	CH <sub>3</sub> OH (1.5)	TBHP	2.76	2	3
2	V-en-ZNP (15)	CH <sub>3</sub> CN (1.5)	TBHP	2.76	2	7
3	V-en-ZNP (15)	CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> (1.5)	TBHP	2.76	2	25
4	V-en-ZNP (15)	CH <sub>2</sub> Cl <sub>2</sub> (1.5)	TBHP	2.76	2	42
5	V-en-ZNP (15)	CHCl <sub>3</sub> (1.5)	TBHP	2.76	2	69
6	V-en-ZNP (15)	CCl <sub>4</sub> (1.5)	TBHP	2.76	2	95
7	V-en-ZNP (15)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (1.5)	TBHP	2.76	2	98
8	V-en-ZNP (20)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (1.5)	TBHP	3.68	2	98
9	V-en-ZNP (10)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (1.5)	TBHP	1.84	2	41
10	V-en-ZNP (0)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (1.5)	TBHP	0	2	1
11	V-en-ZNP (15)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (1.5)	TBHP	2.76	2.5	98
12	V-en-ZNP (15)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (1.5)	TBHP	2.76	1.5	72
13	V-en-ZNP (15)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (1.5)	TBHP	2.76	1	65
14	V-en-ZNP (15)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (2)	TBHP	2.76	2	76
15	V-en-ZNP (15)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (1)	TBHP	2.76	2	88
16	V-en-ZNP (15)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (1.5) <sup>c</sup>	TBHP	2.76	2	10
17	V-en-ZNP (15)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (1.5) <sup>d</sup>	TBHP	2.76	2	57
18	V-en-ZNP (15)	CH <sub>3</sub> CN (1.5) <sup>d</sup>	H <sub>2</sub> O <sub>2</sub>	2.76	2	nd <sup>e</sup>
19	V-en-ZNP (15)	CH <sub>3</sub> CN (1.5) <sup>d</sup>	Urea-H <sub>2</sub> O <sub>2</sub>	2.76	2	nd
20	V-en-ZNP (15)	CH <sub>3</sub> CN (1.5) <sup>d</sup>	NaIO <sub>4</sub>	2.76	2	nd
21	V-en-ZNP (15)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (1.5) <sup>d</sup>	O <sub>2</sub> gas	2.76	-	nd
22	V-en-ZNP (15)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (1.5) <sup>d</sup>	Air	2.76	-	nd

<sup>a</sup>Calculated for 0.5 mmol cyclooctene. <sup>b</sup>GLC yields are based on the starting cyclooctene. <sup>c</sup>Temperature is 25 °C.<sup>d</sup>Temperature is 40 °C. <sup>e</sup>nd: not detected.

Figure 5 shows the time progress of the epoxidation of *cis*-cyclooctene with TBHP in the presence of V-en-ZNP which received to its maximum yield (98%) after 60 min.

Moreover, the heterogenic character of this catalyst was checked by the hot filtration test. For this purpose, the catalyst was removed by centrifuging the catalytic mixture



**Fig. 5.** Epoxidation of 0.5 mmol of *cis*-cyclooctene with 1.0 mmol of TBHP catalyzed by 15 mg of V-en-ZNP in 1.5 mL of  $C_2H_4Cl_2$  under reflux conditions.

in the middle of the optimization process (30 min), and the procedure was continued to reach an optimum time of reaction completion (60 min). The results obtained showed that when the catalyst was removed from the reaction medium, the catalytic procedure stopped and did not continue anymore. This test proves that the catalytic reaction is held in heterogeneous conditions, and the catalyst is not leached to the reaction medium.

We also studied the reaction progress in the presence of the related homogenous catalyst. The results obtained showed that by using  $VO(acac)_2$  as catalyst under the same experimental conditions for the heterogeneous counterpart, the reaction yields reduced to 73% after 60 min. The greater reactivity of this heterogeneous catalyst may be related to the homogenous dispersion of the catalytic active sites onto the surface of V-en-ZNP, which efficiently increased the effective collision of the reagents to the metal sites, and consequently, increased the cyclooctene epoxide yield in comparison to the homogeneous counterpart.



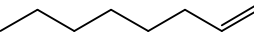
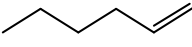
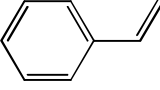
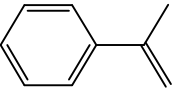
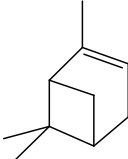
The newly prepared catalyst could be used for the epoxidation of different alkenes (Table 2). The blank experiment, performed without catalysts, with ZNP, Cl-ZNP or en-ZNP, showed a very low conversion even after 5 h reflux but in the presence of V-en-ZNP a wide range of both the cyclic and linear alkenes could competently and

selectively be changed to epoxides. According to the earlier proposed epoxidation mechanisms [4-8], higher electron-donating alkene showed more epoxidation reactivity. Therefore, cyclic alkenes such as cyclooctene and cyclohexene with inner double bonds exhibit more activities in comparison with their linear homologs, 1-hexene and 1-octene with terminal double bonds. Additionally, higher activity of cyclooctene than cyclohexene could be related to cyclooctene conformations which decrease the activation energy of the reaction [8]. In contrast, slower epoxidation of 1-octene than 1-hexene could be related to the higher steric hindrance of the hexyl group in comparison with the butyl group. The results show only a 3-8% reduction in the epoxide yields of different alkenes in comparison to the small-scale experiment and confirmed the ability of these catalytic protocols for use in industrial procedures.

Based on the previous reports [4-8], probable mechanisms were proposed for the epoxidation of cyclooctene with TBHP by the V-en-ZNP catalyst (Scheme 2). There are also some crucial stages in all of these processes. The first step for these catalysts involves the transfer of the TBHP hydroxyl proton to a terminal oxygen atom of the supported metal complex, which results in the coordination of the *tert*-butylperoxide anion to the Lewis acidic metal centers. Then the alkene substrate, as a



**Table 2.** Epoxidation of some Alkenes with TBHP Catalyzed by V-en-ZNP under Reflux Conditions

Entry	Alkene	V-en-ZNP catalyst <sup>a</sup>		
		Conversion (%) <sup>b</sup>	Epoxide (%) <sup>b</sup> (large scale) <sup>c</sup>	Time (min)
1		98	98(90)	60
2		92 <sup>d</sup>	81(77)	60
3		60	60(57)	180
4		65	65(59)	180
5		88 <sup>e</sup>	78(75)	150
6		92 <sup>f</sup>	87(82)	90
8		90	79	90

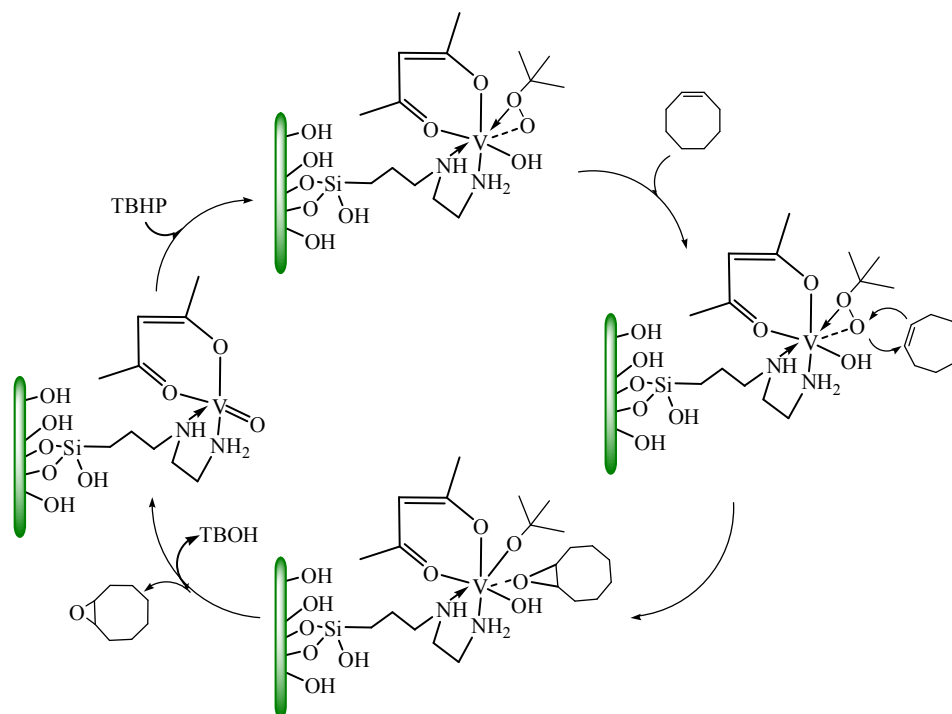
<sup>a</sup>GLC yield based on the starting alkenes. <sup>b</sup>Reaction conditions: alkene (0.5 mmol), TBHP (1.0 mmol), C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> (1.5 mL), catalyst (V-en-ZNP: 15 mg). <sup>c</sup>Large scale reaction conditions: alkene (10 mmol), TBHP (20 mmol), C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> (1 mL), catalyst (V-en-FZNP: 0.3 g). <sup>d</sup>The byproduct (cyclohexanone) is 11%. <sup>e</sup>The byproduct (benzaldehyde) is 10%. <sup>f</sup>The byproduct (acetophenone) is 5%.

nucleophile, is inserted into the metal oxygen bond of the coordinated peroxide electrophile anion. This mechanism easily explains the faster reaction of the electron-rich alkenes in comparison to the electron-poor ones. In the next step, the epoxide product is formed, and the *tert*-butylperoxide anion is converted to the *tert*-butoxide anion. Then the peroxide product is released and the catalytic cycle is continued by substitution of a new *tert*-butylperoxide

instead of the *tert*-butoxide anion.

### Catalyst Recovery and Reuse

As discussed earlier, the reusability of the solid-supported catalysts is one of their most important benefits. Therefore, the reusability of this supported catalyst was monitored by means of the multiple sequential epoxidations of *cis*-cyclooctene with TBHP (Table 3). After each cycle,



Scheme 2. Proposed mechanism for epoxidation of alkenes with TBHP by V-en-ZNP

**Table 3.** Epoxidation of *cis*-cyclooctene with TBHP under Reflux Conditions Using Recycled V-en-ZNP Catalyst

Number of cycles	V-en-ZNP catalyst <sup>a</sup>			
	Epoxide yield (%) <sup>b</sup>	TOF (h <sup>-1</sup> ) <sup>c</sup>	V <sup>d</sup>	
			Leached (%) <sup>e</sup>	Content (mmol g <sup>-1</sup> ) <sup>f</sup>
0	98	35	ND	0.92
1	95	34	ND	0.92
2	92	33	ND	0.91
3	90	33	ND	0.90

<sup>a</sup>Reaction conditions: 0.5 mmol cyclooctene, 1.0 mmol TBHP, 1.5 mL C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, catalyst: 15 mg, time: 60 min. <sup>b</sup>GLC yields are based on the starting cyclooctene. <sup>c</sup>TOF = (mole of reactant) (yield/100)/(mole of catalyst) (time) <sup>d</sup>Determined by ICP analysis. ND: not detected. <sup>e</sup>Metal complexes leached from the catalysts into the catalytic solution medium. <sup>f</sup>Metal content of the recycled catalyst.

the reaction mixture was centrifuged, and the supernatant solution and recovered catalyst were analyzed by means of ICP. This analysis showed that there was no metal contaminant in the supernatant solution and no meaningful decrease in the metal loading of the recovered catalyst. It also confirmed that the metal ions did not leach from the heterogeneous catalysts and that the reactions were carried out entirely under the heterogeneous conditions. In addition, the catalytic activity for the recovered V-en-ZNP catalyst was retained successfully, up to three cycles.

TOF is a righteous parameter for the comparison of the catalytic activities, so we used it to show the benefits of our catalytic systems over the other reported catalytic protocols. Our recent reported catalytic protocol which contains vanadium oxo sulfate supported onto the Schiff base functionalized boehmite nanoparticles [5], has lower TOF (29 h<sup>-1</sup>) value in comparison to the newly prepared catalyst in the present research work. But, V-en-ZNP has comparable activity to our another catalytic protocol which contains vanadium oxo sulfate supported onto the amine functionalized boehmite nanoparticles [6] with TOF value of 39 h<sup>-1</sup>.

## CONCLUSIONS

We successfully prepared a new hybrid heterogeneous catalyst by anchoring acetylacetonate oxovanadium complex onto the surface of en-ZNP. This is an active catalyst for the epoxidation of various alkenes under entirely heterogeneous conditions.

Many vanadium complexes have been reported for the catalytic epoxidation of alkenes with TBHP and this new catalyst has comparable activity with all of the reported catalytic protocols in terms of cost, reaction time, selectivity, conversion, turn-over frequency (TOF), and reusability. In addition, 20-fold scale-up catalytic epoxidation experiments confirmed the industrial application of this newly prepared protocol.

There are some crucial factors that considerably change the yield. Among them, the type of solvent is the most predominant, and C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> as aprotic and hydrophobic solvent gave the best results.

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