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Schiff base-functionalized boehmite nanoparticle-supported molybdenum and vanadium complexes: efficient catalysts for the epoxidation of alkenes

Mahdi Mirzaee*, Bahram Bahramian and Adonis Amoli

Boehmite nanoparticles, with high surface area and high degree of surface hydroxyl groups, were prepared via hydrothermal-assisted sol-gel processing of aluminium 2-butoxide. The produced powder was covalently functionalized with 3-(trimethoxysilyl)propylamine, and then, in order to support vanadium oxosulfate and molybdenum hexacarbonyl complexes, all the terminal amine groups were changed to Schiff bases by refluxing with salicylaldehyde. These catalysts were applied in the epoxidation of *cis*-cyclooctene and other olefins with *tert*-BuOOH in CCl₄. The catalytic procedures for both catalysts were optimized for various parameters such as solvent and oxidant. Recycling experiments revealed that these heterogeneous nano-catalysts could be repeatedly applied for the epoxidation of alkenes. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: boehmite nanoparticles; heterogeneous Schiff base catalysts; molybdenum hexacarbonyl; vanadium oxosulfate; olefin epoxidation

Introduction

Epoxides are known as some of the most valuable building blocks for producing commercially important chemicals such as chiral pharmaceuticals, pesticides, detergents, epoxy paints, agrochemicals, various polymers, surfactants, antistatic agents, corrosion protection agents, lubricating oils, textiles, sweeteners, cosmetics and perfumes.^[1–4] In the last decade, several soluble Schiff base complexes of Cr.^[4,5] Mo,^[4,6,7] Re,^[8] Ni,^[9] Co,^[10,11] Mn,^[12,13] V,^[14–17] Cu,^[18] Ru^[19] and Ti^[20] have been employed as active homogeneous catalysts in the epoxidation of alkenes. However, most of these catalysts are expensive and contaminate the environment. In that respect, the development of efficient methods for recovering and reusing them is very important from environmental and economic points of view.

One way to reach this goal is to immobilize the homogeneous catalysts on insoluble supports. This can also efficiently increase the reactivity of some catalysts by preventing the formation of oxo-bridged dimeric or polymeric complexes which are deleterious for catalytic activity.^[21,22] This has been the subject of numerous publications and reviews which addressed the application of several Schiff base-functionalized supports for various catalytic organic reactions. A variety of organic and inorganic materials can be used as insoluble supports. Organic insoluble supports include polymers such as polystyrene.^[23,24] Hybrid organic–inorganic materials such as zirconium poly(styrene phenylvinylphosphonate)phosphate^[25] have also been used for this purpose. Activated carbon,^[26] multiwall carbon nanotubes,^[21,27] nanostructured ordered carbon material,^[21,28] porous silica,^[29,30] MCM-41,^[31,32] SBA-15,^[21,33,34] zeolites^[1,21,35,36] and magnetic nanoparticles^[37] have also been used as insoluble supports. Inorganic supports generally have higher chemical stability and higher surface area than the organic ones.

Additionally, the surfaces of some metal oxides and metal hydroxides are covered with hydroxyl groups. These surface hydroxyl groups provide valuable sites which can be grafted with various functionalities in order to produce active and stable catalysts for liquid-phase organic reactions. Boehmite (γ -AlOOH) is one of these inorganic insoluble supports which contain extra hydroxyl groups on its surface. It has been used as an important precursor for the preparation of advanced catalysts, alumina and alumina-derived ceramics.^[38]

The research reported here used boehmite nanoparticles (BNPs) grafted with 3-(trimethoxysilyl)propylamine (MSPA) to anchor Schiff base and to support two complexes of molybdenum and vanadium. Then, these supported catalysts were used in the epoxidation of various olefin substrates.

Experimental

Materials and Methods

Solvents and reagents were purchased from Merck or Fluka and used without any further purification. IR spectra were recorded with a Bomem MB series FT-IR instrument at 4 cm⁻¹ resolution, using KBr pellets. ¹H NMR spectra were obtained in DMSO- d_6 using a Bruker Avance 300 MHz spectrometer. Powder X-ray diffraction (PXRD) patterns were collected with a Philips PW-1800 or STOE diffractometer with Cu K α radiation. Thermogravimetric (TG) analyses were

Correspondence to: Mahdi Mirzaee, Department of Chemistry, University of Shahrood, Shahrood, Iran. E-mail: mmirzaee@shahroodut.ac.ir

Department of Chemistry, University of Shahrood, Shahrood, Iran

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carried out with a Rheometric Scientific STA-1500 or BAHR Thermoanalyse GmbH with a heating rate of 10°C min⁻¹ in air. A 400 W Hg lamp was used for activation of hexacarbonyl molybdenum complex. Elemental analyses were carried out with a Hereans CHN-O-Rapid analyser. Electron microscopy was performed with a JEOL JSM-6360LV transmission electron microscope. Gas–liquid chromatography (GLC) was carried out with a Shimadzu GC-16A instrument using a 2 m column, packed with silicon DC-200.

Preparation of BNPs

Aluminium 2-butoxide was synthesized from aluminium and 2-butanol according to the general preparation procedure of aluminium alkoxides.^[39] The prepared aluminium alkoxide was vacuum-distilled in order to obtain a high-guality aluminium alkoxide precursor. For hydrothermal-assisted hydrolysis, according to our previous report,^[40] aluminium 2-butoxide was diluted in 2-butanol to 50% and was loaded in a glass container. The glass container was placed in a 300 ml stainless steel autoclave. The gap between the autoclave chamber and the glass container was covered with 50 ml of distilled water and then the autoclave was heated at 100°C. Aluminium 2-butoxide was hydrolysed by diffusion of water vapour into solution in the hydrothermal chamber. All manipulations of aluminium alkoxide were carried out in a Schlenk line. The transference into the autoclave was performed in a moisture-free atmosphere in order to prevent hydrolysis of aluminium alkoxide before introducing it into the hydrothermal chamber. After 5 h, the autoclave was cooled and the produced powder was filtered off and dried at 100°C overnight. The BNPs thus produced were used as catalytic support.

Preparation of Molybdenum and Vanadium Complexes Supported on Functionalized BNPs

As the first step in the preparation of functionalized BNPs, 1.00 g of BNPs was refluxed with MSPA (61 μ l, 0.35 mmol) in dry toluene (50.0 ml) for 24 h (Scheme 1). The amine-functionalized BNPs (AFBNPs) as a white solid was filtered off, washed three times with dry toluene and dried at 100°C overnight. Then as the second step, 1.00 g of AFBNPs was refluxed with an equivalent amount of 2-hydroxybenzaldehyde (36.5 μ l, 0.35 mmol) in ethanol (20.0 ml) for 12 h (Scheme 1). Then the resulting imine-functionalized BNPs (IFBNPs) were filtered off, washed three times with hot ethanol and dried at 100°C overnight.



Scheme 1. Preparation of AFBNPs, IFBNPs, Mo-IFBNPs and V-IFBNPs.

 $Mo(CO)_6$ and $VO(SO_4) \cdot H_2O$ complexes were used for supporting on IFBNPs (Scheme 1). For this purpose, $Mo(CO)_6$ (0.276 g, 1.05 mmol) was activated under ultraviolet light in THF (20.0 ml) for 30 min. Then this activated molybdenum complex was added to dry IFBNPs and the mixture was refluxed for 6 h. The mixture was cooled, filtered and the precipitate was washed several times with THF and dried at 100°C overnight. In a similar procedure, $VO(SO_4)$. H_2O (0.200 g, 1.05 mmol) was refluxed with IFBNPs in ethanol (20 ml) for 7 h and the powder produced was washed several times with ethanol and dried at 100°C overnight.

Catalytic Epoxidation of Alkenes

In a typical process, a 25 ml round-bottom flask, equipped with a magnetic stirrer bar and a condenser, was charged with alkene (0.7 mmol), oxidant, catalyst (Mo-IFBNPs or V-IFBNPs) and solvent, and the mixture was refluxed. The reaction progress was monitored using GLC. Since different alkenes have different reactivity towards oxidation, these reactions were continued until no further progress was observed. The details of the reaction conditions are summarized in Tables 1 and 2.

Catalyst Recycling

In a typical experiment, after recovering the catalyst from the reaction mixture at optimum conditions, it was washed several times with CCl_4 , and then used in the same procedure under the same conditions. The detailed procedures of the recycling experiment are summarized in Table 3.

Results and Discussion

There are various methods for the preparation of BNPs. Among them, a hydrothermal-assisted sol–gel process with aluminium alkoxide was used here.^[40] It has some advantages, such as preparation in a one-pot process and processing at low temperature. Then BNPs were grafted with MSPA, and their amine group was converted to Schiff base in order to support two different complexes of molybdenum and vanadium. These supported catalysts were used in the epoxidation of *cis*-cyclooctene. The catalytic procedures for both catalysts were optimized for different parameters such as catalyst, solvent and oxidant. Then both catalysts were used for the catalytic epoxidation of different olefins under optimum conditions. In addition, recycling experiments were done to reveal the reusability of these catalysts.

Preparation and Characterization of Molybdenum and Vanadium Complexes Supported on Functionalized BNPs

BNPs were prepared by hydrothermal-assisted sol-gel processing of aluminium 2-butoxide solution in 2-butanol. The most promising property of these hydrothermally processed BNPs is the formation of crystalline single-phase product with no organic residue.^[40] This is confirmed by the lack of C-H stretching vibration in the IR spectrum and also the lack of organic residue ignition in TG/differential scanning calorimetry (DSC) thermograms in addition to the XRD pattern of this sample. The IR spectrum of BNPs (Fig. 1(a)) only shows the characteristic bands of boehmite.^[40] The PXRD pattern of BNPs (Fig. 2(a)) also confirms crystallization of single-phase boehmite.^[40] In the TG/DSC curve of BNPs (Fig. 3(a)), there are two endothermic peaks below 100°C and around 450°C. The first one is due to the elimination of physically adsorbed water, and



Table 1. Epoxidation of <i>cis</i> -cylooctene under reflux conditions ^{a,b}							
Entry	Catalyst (mg)	Solvent ^c	Oxidant	Catalyst loading (mol%) ^d	Oxidant/substrate molar ratio	Epoxide yield (%) ^e	
1	Mo-IFBNPs (40)	CH₃CN	TBHP	2.0	1.5	15	
2	Mo-IFBNPs (40)	CH₃OH	TBHP	2.0	1.5	No reaction	
3	Mo-IFBNPs (40)	(CH ₃) ₂ CO	TBHP	2.0	1.5	No reaction	
4	Mo-IFBNPs (40)	C ₆ H ₅ CH ₃	TBHP	2.0	1.5	25	
5	Mo-IFBNPs (40)	CH ₂ Cl ₂	TBHP	2.0	1.5	5	
6	Mo-IFBNPs (40)	CHCl₃	TBHP	2.0	1.5	35	
7	Mo-IFBNPs (40)	CCl ₄	TBHP	2.0	1.5	73	
8	Mo-IFBNPs (40)	CCl ₄	H_2O_2	2.0	1.5	3	
9	Mo-IFBNPs (40)	CH ₃ CN	H ₂ O ₂	2.0	1.5	2	
10	Mo-IFBNPs (40)	CCl ₄	H ₂ O ₂ ·CON ₂ H ₄	2.0	1.5	5	
11	Mo-IFBNPs (40)	CH ₃ CN	H ₂ O ₂ ·CON ₂ H ₄	2.0	1.5	2	
12	Mo-IFBNPs (40)	CCl₄	NalO ₄ ^f	2.0	1.5	No reaction	
13	Mo-IFBNPs (40)	CH₃CN	NalO ₄	2.0	1.5	No reaction	
14	Mo-IFBNPs (40)	CCl₄	TBHP	4.0	1.5	76	
15	Mo-IFBNPs (40)	CCl₄	TBHP	1.3	1.5	50	
16	Mo-IFBNPs (30)	CCl₄	TBHP	1.5	1.5	73	
17	Mo-IFBNPs (20)	CCI	TBHP	1.0	1.5	73	
18	Mo-IFBNPs (15)	CCI	ТВНР	0.75	1.5	73	
19	Mo-IFBNPs (10)	CCl	ТВНР	0.50	1.5	65	
20	Mo-IFBNPs (5)	CCI₄	TBHP	0.25	1.5	54	
21	Mo-IFBNPs (15)	CCI	ТВНР	0.75	1	45	
22	Mo-IFBNPs (15)	CCl	ТВНР	0.75	2	80	
23	Mo-IFBNPs (15)	CCI	TBHP	0.75	2.5	75	
24	Mo-IFBNPs (15)	CCI4	ТВНР	0.75	2	85	
25	Mo-IFBNPs (15)	CCl	ТВНР	0.75	2	95	
26	V-IFBNPs (20)	CH₂CN	ТВНР	1.0	1.5	8	
27	V-IFBNPs (20)	CH₃OH	TBHP	1.0	1.5	No reaction	
28	V-IFBNPs (20)	(CH ₂) ₂ CO	ТВНР	1.0	1.5	No reaction	
29	V-IFBNPs (20)	C _c H ₅ CH ₃	TBHP	1.0	1.5	27	
30	V-IFBNPs (20)	CH ₂ Cl ₂	ТВНР	1.0	1.5	12	
31	V-IFBNPs (20)	CHCl ₃	TBHP	1.0	1.5	21	
32	V-IFBNPs (20)	CCI	TBHP	1.0	1.5	45	
33	V-IFBNPs (20)	CCI	H ₂ O ₂	1.0	1.5	4	
34	V-IFBNPs (20)	CH₂CN	H ₂ O ₂	1.0	1.5	5	
35	V-IFBNPs (20)	CCI	H ₂ O ₂ ·CON ₂ H ₄	1.0	1.5	5	
36	V-IFBNPs (20)	CH₃CN	H ₂ O ₂ ·CON ₂ H ₄	1.0	1.5	2	
37	V-IFBNPs (20)	CCI₄	NalQ₄ ^f	1.0	1.5	No reaction	
38	V-IFBNPs (20)	CH₃CN	NalO₄	1.0	1.5	No reaction	
39	V-IFBNPs (5)	CCl₄	TBHP	0.25	1.5	20	
40	V-IFBNPs (10)	CCl ₄	TBHP	0.50	1.5	35	
41	V-IFBNPs (15)	CCl₄	TBHP	0.75	1.5	45	
42	V-IFBNPs (30)	CCl₄	ТВНР	1.5	1.5	45	
43	V-IFBNPs (40)	CCl₄	TBHP	2.0	1.5	45	
44	V-IFBNPs (15)	CCl₄	TBHP	0.75	1	28	
45	V-IFBNPs (15)	CCl₄	TBHP	0.75	2	50	
46	V-IFBNPs (15)	CCI	TBHP	0.75	2.5	52	
47	V-IFBNPs (15)	CCl₄	TBHP	0.75	2	56	
48	V-IFBNPs (15)	CCl ₄	TBHP	0.75	2	67	

^aRatio of pendant Schiff base group (mmol)/BNPs (g) is 0.35, except entry 8 (0.70) and entry 9 (0.23).

^bTimes of reactions are 150 min for Mo-IFBNPs and 90 min for V-IFBNPs.

^cAmount of solvent is 3 ml except entries 24 and 47 (2 ml) and entries 25 and 48 (1 ml).

^dCalculated for 0.7 mmol cyclooctene.

^eGLC yields are based on the starting cyclooctene.

^fTetrabutylphosphonium bromide was used as phase transfer reagent.

Table 2. Epoxidation of various olefins with TBHP catalysed by Mo-IFBNPs or V-IFBNPs under refluxing condition ^a							
Entry	Alkene	Mo-IFBNPs catalyst ^b		V-IFBNPs catalyst ^b			
		Conversion (%)	Epoxide (%)	Time (h)	Conversion (%)	Epoxide (%)	Time (h)
1	Cyclooctene	96	96	2	92	92	3.5
2	Cyclohexene	98 ^c	89	2	92 ^c	84	3.5
3	1-Octene	70	70	6	61	61	12
4	1-Hexene	71	71	4	65	65	12
5	Styrene	86 ^d	80	6	90 ^d	58	12
6	α -Methyl styrene	98 ^e	89	2	94 ^e	85	3.5
7	α-Pinene	72	72	4	71	71	3.5
8	trans-Stilbene	96 ^f	96 (trans) ^g	4	92 ^f	92 (trans) ^g	12
9	cis-Stilbene	94 ^f	81 (<i>cis</i>) and 13 (<i>trans</i>) ^h	3	91 ^f	79 (<i>cis</i>) and 12 (<i>trans</i>) ^h	6

^aReaction conditions: alkene (0.7 mmol), TBHP (1.4 mmol), catalyst (15 mg), CCl₄ (1 ml).

^bGLC yield based on the starting alkenes.

^cBy-product is 9% for Mo-IFBNPs and 8% for V-IFBNPs.

^dBy-product is 6% for Mo-IFBNPs and 32% for V-IFBNPs.

^eBy-product is 9% for both catalysts.

^fBoth ¹H NMR and GLC data confirm the reported yields.

⁹*Trans* isomer is the only product according to ¹H NMR data.

^hCis and trans isomers are both produced according to ¹H NMR data.

Table 3. Epoxidation of *cis*-cylooctene with TBHP under reflux conditions using recycled catalysts

Cycle number							
-)	Mo-IFBNPs	catalyst ^a	V-IFBNPs catalyst ^a				
	Epoxide yield (%) ^b	TOF (h ⁻¹)	Epoxide yield (%) ^b	TOF (h ⁻¹)			
1	95	44	92	29			
2	95	44	92	29			
3	94	44	92	29			
4	94	44	90	28			
5	93	43	89	28			
6	91	42	87	27			
7	90	42	85	26			
8	88	41	83	26			
9	85	39	80	25			
10	80	37	75	23			
^a Reaction condition: 0.7 mmol cyclooctene, 1.4 mmol TBHP, 15 mg							

catalyst, 1 ml CCl₄, 120 min for Mo-IFBNPs and 180 min for V-IFBNPs. ^bGLC yields are based on the starting cyclooctene.

the other is attributed to dehydroxylation of boehmite and crystallization of γ -alumina. The absence of C–H stretching vibrations in the IR spectrum and also the absence of an exothermic peak at around 250°C in the TG/DSC curve of BNPs confirm loss of all organic residue in the hydrothermally processed BNPs. Inductively coupled plasma (ICP) and elemental analyses also confirm the lack of molybdenum or vanadium and carbon and nitrogen content in BNPs, respectively. The calculation of particle size from the PXRD pattern according to the Scherer equation shows 10 nm particles for BNPs. This is confirmed by the transmission electron microscopy image of BNPs (Fig. 4). In this image, needle-shaped BNPs are seen over 50 nm long and up to 10 nm in width. Effective surface area of the BNPs is 326 m² g⁻¹ according to BET experiments.

BNPs themselves have promising catalytic properties for the multi-component synthesis of highly substituted imidazoles which was done in our research group and reported elsewhere.^[41] In addition, it was proved that for efficient epoxidation of olefins under mild conditions, a catalyst that contains an active metal site is vital. An oxidant could coordinate to this site and be activated for the epoxidation process. But BNPs show low reactivity in epoxidation of olefins as Choudhary and co-workers reported.^[42] Consequently we have changed our strategy and tried to functionalize BNPs with a Schiff base in two steps. During the first step, by refluxing a mixture of BNPs and MSPA in dry toluene for 24 h, -O₃Si(CH₂)₃NH₂ group is grafted on the hydroxyl-covered surface of BNPs (Scheme 1) and AFBNPs are thus produced. The IR spectrum of AFBNPs (Fig. 1(b)) shows a new band at 1553 cm^{-1} which is assigned to the N-H stretching vibrations of grafted amine groups in addition to the BNP characteristic bands. Elemental analysis shows that the nitrogen content of AFBNPs is 0.46%, which means that 0.33 mmol of pendant amine groups are covalently bound to the surface of 1.00 g of BNPs. ICP analysis also shows there are no molybdenum or vanadium contaminants in AFBNPs and they shows no reactivity in catalytic epoxidation of olefins as predictable according to the above discussion. In the second step, pendant amine groups of AFBNPs are changed to Schiff base by refluxing a mixture of AFBNPs and 2-hydroxybenzaldehyde in ethanol for 12 h which produces IFBNPs (Scheme 1). In addition to the BNP characteristic bands, the IR spectrum of IFBNPs (Fig. 1(c)) shows a sharp band at 1663 cm^{-1} which is assigned to the C=N stretching vibration of azomethine (imine) group. Elemental analysis shows that the nitrogen content of IFBNPs is 0.46%, which means all the pendant amine groups are changed to imine by this reaction. ICP analysis also confirms the lack of molybdenum or vanadium content in IFBNPs and they show no reactivity in catalytic epoxidation of olefins.

The IFBNPs were then used for supporting molybdenum and vanadium complexes. For this purpose, $Mo(CO)_6$ and $VO(SO_4) \cdot H_2O$ were used. But $Mo(CO)_6$ is not labile in ligand substitution reaction so its solution in THF was activated by irradiation with UV light. This process resulted in the formation of $Mo(CO)_5$ (THF) complex which substituted its THF ligand with coordinating atoms of imine group





Figure 1. FT-IR spectra of (a) BNPs, (b) AFBNPs, (c) IFBNPs, (d) Mo-IFBNPs and (e) V-IFBNPs.

on BNPs, after refluxing for 6 h (Mo-IFBNPs). VO(SO₄)·H₂O complex was also refluxed with IFBNPs in ethanol for 7 h to support the vanadium complex on the IFBNPs (V-IFBNPs).

The IR spectrum of Mo-IFBNPs (Fig. 1(d)) shows some new weak bands at around 1800–1900 cm^{-1} due to the carbonyl stretching vibration of coordinated molybdenum complex. On the one hand, the lower symmetry of the molybdenum complex as a result of coordination is evidenced by the redshift and splitting of carbonyl stretching vibrations^[43]; on the other hand, the low metal content of the catalyst is evidenced by the weakness of them. ICP analysis shows that approximately 90% of Schiff base sites on IFBNPs are used for anchoring 0.3 mmol of molybdenum complex on 1.00 g of Mo-IFBNPs. The PXRD pattern of Mo-IFBNPs (Fig. 2(b)) confirms the retention of the crystalline structure after functionalization and metal loading. In the TG/DTA curve of Mo-IFBNPs (Fig. 3(b)) there is an endothermic peak below 100°C with 7% weight loss in the TG curve due to the elimination of physically adsorbed water. There is also an exothermic peak at around 350°C with 13% weight loss in the TG curve due to the ignition of organic parts of pendant groups on BNPs. This thermogram also shows 12% weight loss in the range 400-500°C which is accompanied by an endothermic



Figure 2. XRD patterns of (a) BNPs, (b) Mo-IFBNPs and (c) V-IFBNPs.

peak in the DTA curve due to the dehydroxylation of boehmite and the crystallization of γ -alumina similar to BNPs. The calculation of particle size from the PXRD pattern of Mo-IFBNPs, according to the Scherer equation, shows no change in particle size in comparison to BNPs.

The IR spectrum of V-IFBNPs (Fig. 1(e)) shows a new band due to the V=O stretching vibration of VO(SO₄) complex at 970 cm⁻¹, confirming the coordination of vanadium complex to the functionalized BNPs. ICP analysis also shows that over 90% of Schiff base sites on IFBNPs are used for anchoring 0.31 mmol of vanadium complex on 1.00 g of V-IFBNPs, which is comparable to the metal loading in Mo-IFBNPs. The PXRD pattern of V-IFBNPs (Fig. 2(c)) also confirms the retention of the crystalline structure after metal loading. In the TG/DTA curve of V-IFBNPs (Fig. 3(c)) there is an endothermic peak below 100°C with 9% weight loss in the TG curve due to the elimination of physically adsorbed water. Similar to the molybdenum counterpart, there is an exothermic peak at around 300°C with 7% weight loss in the TG curve of V-IFBNPs due to the ignition of organic parts of IFBNPs. Additionally, analogous to BNPs and Mo-AFBNPs, this thermogram shows 12% weight loss in the range 400–550°C which is accompanied by an endothermic peak in the DTA curve and assigned similarly. The calculation of particle size from the PXRD pattern of V-IFBNPs, according to the Scherer equation and similar to the molybdenum counterpart, shows no change in particle size in comparison to BNPs.

Alkene Epoxidation with *tert*-Butylhydroperoxide Catalysed by Mo-IFBNPs and V-IFBNPs

With the purpose of achieving optimized conditions for the title reaction, epoxidation of cyclooctene was investigated by changing various parameters including solvent, oxidant, catalyst and reaction time. The experiments show that with these catalysts, *tert*butylhydroperoxide (TBHP) is the only oxidizing system that can achieve the epoxidation of cyclooctene in CCl₄. Other oxygen



Figure 3. Thermal analyses curves of (a) BNPs , (b) $\mathsf{Mo}\text{-}\mathsf{IFBNPs}$ and (c) $\mathsf{V}\text{-}\mathsf{IFBNPs}.$



Figure 4. Transmission electron microscopy image of BNPs.

sources such as hydrogen peroxide, sodium periodate (in the presence of 0.01 g of tetrabutyl phosphonium bromide as phase transfer reagent) and urea–hydrogen peroxide in CCl₄ or CH₃CN do not show any activity (Table 1, entries 1, 7–13, 26, 32–38). In addition, under mild conditions, the epoxidation of cyclooctene using TBHP does not proceed in the absence of catalyst.

In a first step, the effect of solvent was investigated; consequently, protic and aprotic solvents with various polarity and coordinating ability were used in the epoxidation of cyclooctene with TBHP. The observed trend (Table 1, entries 1–7, 26–32) is the same as that of literature reports on homogeneous alkene epoxidation by $Mo(CO)_6$ catalyst.^[44] Coordinating solvents such as CH₃CN and CH₃OH compete with TBHP to occupy the coordination sites on the transition metal catalyst. Therefore in the presence of these solvents, the observed yields are low. Among other solvents, CCl₄ leads to the highest yield of epoxide product for both Mo-IFBNPs and V-IFBNPs catalysts. This could be attributed to the higher boiling point of CCl₄ in comparison to the other solvents investigated.

In the next step, the amount of pendant Schiff base groups anchored on BNPs (Table 1, entries 7, 14 and 15) was changed. For this purpose, 0.35 (entry 7), 0.7 (entry 14) and 0.23 (entry 15) mmol of MSPA were used in order to anchor to 1.00 g of BNPs and convert them to Schiff base. After supporting Mo(CO)₆ on the functionalized BNPs under the same conditions, these catalysts were used for the epoxidation of 0.7 mmol of cyclooctene with 1.05 mmol of TBHP. The results show that after 2.5 h, the conversions for entries 7 and 14 are about the same and higher than that for entry 15; therefore 0.35 mmol of pendant Schiff base group per gram of BNPs was selected for other investigations.

As another parameter, the amount of catalysts was changed in the epoxidation of cyclooctene with TBHP. The results (Table 1, entries 7, 16–20, 32, 39–43) show that by increasing the amount of both Mo-IFBNPs and V-IFBNPs catalysts up to 15 mg, the yield of cyclooctene epoxide increases.

The ratio of oxidant to substrate is one of the most crucial parameters in catalytic epoxidation processes. The results (Table 1, entries 18, 21–23, 41, 44–46) for Mo-IFBNPs and V-IFBNPs show that the optimum ratio of oxidant to substrate for both catalysts is 2. Although increasing this ratio to 2.5 does not change the yields significantly, decreasing the ratio to 1 reduces the yields.

As the last parameter, the amount of solvent was investigated. The results (Table 1, entries 22, 24, 25, 45, 47, 48) show that by decreasing the amount of solvent for both catalysts from 3 to 1 ml, the yield of cyclooctene epoxide increases.

Figure 5 shows the effect of reaction time on the epoxidation of cyclooctene with TBHP. Comparing the reactivity of Mo-IFBNPs and V-IFBNPs catalysts reveals that the former is more reactive, and after 2 h the conversion reaches a maximum and becomes constant. But the supported vanadium complex needs 3.5 h to reach this point.

These new catalysts, Mo-IFBNPs and V-IFBNPs, can also be used for the epoxidation of a wide range of substituted alkenes (Table 2). Blank experiments, performed without catalysts or BNPs, show a very low conversion even after 5 h reflux. However, in the presence of these catalysts, a wide range of both cyclic and linear alkenes can efficiently and selectively be converted to epoxides. Based on the epoxidation mechanism suggested earlier,^[45] higher electron donating ability of olefin double bond is expected to show greater epoxidation reactivity. Therefore, cyclooctene and cyclohexene with inner double bonds should exhibit greater activity in comparison to 1-hexene and 1-octene which contain terminal double bonds. *trans*-Stilbene is also completely converted to epoxide using Schiff base-functionalized BNPs for catalytic epoxidation of alkenes



Figure 5. Epoxidation of 0.7 mmol of *cis*-cyclooctene with 1.4 mmol of TBHP catalysed by 15 mg of Mo-IFBNPs or V-IFBNPs in 3 ml of CCl_4 under reflux conditions.

Mo-IFBNPs and V-IFBNPs catalysts. Surprisingly, *trans*-Stilbene gives only *trans*-epoxide. This reflects the high selectivity of these catalysts in the epoxidation of alkenes.

On the basis of Sobczak's ideas^[45] and other experimental and theoretical reports,^[44,46–48] probable mechanisms are proposed for the epoxidation of cyclooctene with TBHP catalysed by Mo-IFBNPs and V-IFBNPs (Schemes 2 and 3). According to our experimental results, reaction rates are of first order depending on catalyst and substrate concentrations. There are also some crucial stages in these processes. V-IFBNPs catalyst initially contains oxo ligand at its metal centre, but for Mo-IFNBPs, in the first step, pendant molybdenum complex is oxidized and an oxo-molybdenum complex is formed. The next step for both catalysts involves transferring TBHP proton to a terminal oxygen atom of these oxo complexes which results in coordination of *tert*-butylperoxide anion to



Scheme 2. Proposed mechanism for the epoxidation of olefin with TBHP catalysed by Mo-IFBNPs.



Scheme 3. Proposed mechanism for the epoxidation of olefin with TBHP catalysed by V-IFBNPs.

Lewis acidic metal centres. Then, the olefin substrate coordinates to the metal centre and, as a nucleophile, inserts into the metaloxygen bond of coordinated peroxide electrophile anion. This mechanism easily explains the faster reaction of electron-rich olefins in comparison to electron-poor olefins. In the next step, epoxide product is formed and *tert*-butylperoxide anion is converted into *tert*-butoxide anion. Then the peroxide product is released and the catalytic cycle continued by substitution of a new *tert*-butylperoxide instead of *tert*-butoxide anion.

Catalyst Recovery and Reuse

As discussed earlier, the reusability of solid supported catalysts is one of their most important benefits. Therefore, the reusability of Mo-IFBNPs and V-IFBNPs catalysts was monitored by means of multiple sequential epoxidations of cyclooctene with TBHP (Table 3). After each cycle, the reaction mixture was centrifuged and the supernatant solutions were analysed using ICP. This analysis shows that there is no metal contaminant in the supernatant solution. This also confirms that metal ions do not leach from the heterogeneous catalysts and the reactions proceed entirely under heterogeneous conditions. But after ten cycles of recovering both catalysts, they lose 15–17% of their activities in the epoxidation of olefins. The reason for this phenomenon is not clear now and needs more investigation in the future.

Conclusions

We have successfully prepared new hybrid heterogeneous catalysts by anchoring oxosulfate vanadium(IV) and hexacarbonyl molybdenum complexes to BNPs which are functionalized with Schiff base. These catalysts show good catalytic activities in the epoxidation of various important olefin substrates under entirely heterogeneous conditions. The results show that solvents have a crucial effect on the catalytic reactions, and maximum conversion is observed in CCl₄.

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References

- [1] B. Qi, X. H. Lu, S. Y. Fang, J. Lei, Y. L. Dong, D. Zhou, Q. H. Xia, J. Mol. Catal. A 2011, 334, 44.
- [2] S. Bhunia, S. Koner, Polyhedron 2011, 30, 1857.
- [3] W. Xiaoli, W. Gongde, W. Fang, W. Wei, S. Yuhan, Chin. J. Catal. 2011, 32, 1812.
- [4] A. A. Abdel Aziz, J. Mol. Struc. 2010, 979, 77.
- [5] D. Chatterjee, S. Basak, J. Muzart, J. Mol. Catal. A 2007, 271, 270.
- [6] C. Bibal, J. C. Daran, S. Deroover, R. Poli, Polyhedron 2010, 29, 639.
- [7] M. Moshref-Javadi, M. Moghadam, I. Mohammadpoor-Baltork, S. Tangestaninejad, V. Mirkhani, H. Kargar, M. Nawaz-Tahir, *Polyhedron* 2014, 72, 19.
- [8] P. Altmann, M. Cokoja, F. E. Kühn, J. Organometal. Chem. 2012, 701, 51.
- [9] V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor-Baltork, E. Shams, N. Rasouli, *Appl. Catal. A* 2008, 334, 106.
- [10] S. Shit, D. Saha, D. Saha, T. N. Guru Row, C. Rizzoli, Inorg. Chim. Acta 2014, 415, 103.
- [11] D. Saha, T. Maity, R. Bera, S. Koner, Polyhedron 2013, 56, 230.
- [12] P. Mukherjee, P. Kar, S. Ianelli, A. Ghosh, *Inorg. Chim. Acta* **2011**, *365*, 318.
- [13] P. Suresh, S. Srimurugan, R. T. Dere, R. V. Ragavan, V. S. Gopinath, *Tetrahedron Asym.* **2013**, *24*, 669.
- [14] C. Cordelle, D. Agustin, J. C. Daran, R. Poli, *Inorg. Chim. Acta* 2010, 364, 144.
- [15] G. Grivani, A. Dehno-Khalaji, V. Tahmasebi, K. Gotoh, H. Ishida, Polyhedron 2012, 31, 265.
- [16] G. Grivani, V. Tahmasebi, A. Dehno-Khalaji, K. Fejfarová, M. Dušek, Polyhedron 2013, 51, 60.
- [17] G. Grivani, G. Bruno, H. Amiri-Rudbari, A. Dehno-Khalaji, P. Pourteimouri, Inorg. Chem. Commun. 2012, 18, 15.
- [18] Z. Abbasi, M. Behzad, A. Ghaffari, H. Amiri-Rudbari, G. Bruno, Inorg. Chim. Acta 2014, 414, 78.
- [19] D. Chatterjee, J. Mol. Catal. A 2009, 310, 174.
- [20] K. M. Parida, M. Sahoo, S. Singha, J. Catal. 2010, 276, 161.
- [21] M. Sutradhar, L. M. D. R. S. Martins, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Coord. Chem. Rev.* in press. doi:10.1016/j. ccr.2015.01.020. Available online from 10 February 2015.
- [22] Z. Li, S. Wu, Y. Ma, H. Liu, J. Hu, L. Liu, Q. Huo, J. Guan, Q. Kan, Trans. Met. Chem. 2013, 38, 243.
- [23] G. Grivani, A. Akherati, Inorg. Chem. Commun. 2013, 28, 90.
- [24] B. Gao, Y. Li, N. Shi, React. Funct. Polym. 2013, 73, 1573.

- [25] Z. Hu, X. Fu, Y. Li, Inorg. Chem. Commun. 2011, 14, 497.
- [26] A. R. Silva, V. Budarin, J. H. Clark, B. de Castro, C. Freire, *Carbon* 2005, 43, 2096.
- [27] M. Masteri-Farahani, S. Abednatanzi, *Inorg. Chem. Commun.* 2013, 37, 39.
- [28] S. Dorbes, C. Pereira, M. Andrade, D. Barros, A. M. Pereira, S. L. H. Rebelo, J. P. Araújo, J. Pires, A. P. Carvalho, C. Freire, *Micropor. Mesopor. Mater.* 2012, 160, 67.
- [29] S. Bhunia, S. Koner, Polyhedron 2011, 30, 1857.
- [30] P. Visuvamithiran, M. Palanichamy, K. Shanthi, V. Murugesan, Appl. Catal. A 2013, 462–463, 31.
- [31] S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork, K. Ghani, *Catal. Commun.* **2009**, *10*, 853.
- [32] W. Xiaoli, W. Gongde, W. Fang, W. Wei, S. Yuhan, Chin. J. Catal. 2011, 32, 1812.
- [33] Y. Yang, J. Guan, P. Qiu, Q. Kan, Appl. Surf. Sci. 2010, 256, 3346.
- [34] Z. Li, L. Liu, J. Hu, H. Liu, S. Wu, Q. Huo, J. Guan, Q. Kan, Appl. Organometal. Chem. 2012, 26, 252.
- [35] M. R. Maurya, P. Saini, A. Kumar, J. C. Pessoa, Eur. J. Inorg. Chem. 2011, 4846.
- [36] M. R. Maurya, M. Bisht, A. Kumar, M. L. Kuznetsov, F. Avecilla, J. C. Pessoa, *Dalton Trans.* **2011**, *40*, 6968.
- [37] M. Mohammadikish, M. Masteri-Farahani, S. Mahdavi, J. Magn. Magn. Mater. 2014, 354, 317.
- [38] M. Trueba, S. P. Trasatti, Eur. J. Inorg. Chem. 2005, 3393.
- [39] D. C. Bradley, R. C. Mehrotra, I. P. Rothwell, A. Singh, Alkoxo and Aryloxo Derivatives of Metals, Academic Press, London, 2001.
- [40] M. M. Amini, M. Mirzaee, J. Sol-Gel Sci. Technol. 2005, 36, 19.
- [41] A. Keivanloo, M. Bakherad, E. Imanifar, M. Mirzaee, Appl. Catal A 2013, 467, 291.
- [42] V. R. Choudhary, N. S. Patil, N. K. Chaudhari, S. K. Bhargava, J. Mol. Catal. A 2005, 227, 217.
- [43] A. C. Gomes, S. M. Bruno, S. Gago1, R. P. Lopes, D. A. Machado, A. P. Carminatti, A. A. Valente, M. Pillinger, I. S. Gonçalves, J. Organometal. Chem. 2011, 696, 3543.
- [44] B. Cornils, W. A. Hermann, *Applied Homogeneous Catalysis with Organometallic Compounds*, Wiley, Weinheim, **1996**.
- [45] J. Sobczak, J. J. Ziolkowski, J. Mol. Catal. A **1981**, 13, 11.
- [46] S. Huber, M. Cokoja, F. E. Kühn, J. Organometal. Chem. 2014, 751, 25.
- [47] H. Vrubel, K. J. Cluffi, G. P. Ricci, F. S. Nunes, S. Nakagaki, *Appl. Catal. A* 2009, 368, 139.
- [48] S. Rayati, F. Ashouri, C. R. Chimie 2012, 15, 679.