

Catalytic Activity of a Reusable Polymer-Anchored Nickel(II)–Phenanthroline Complex on the Oxidation of Various Organic Substrates

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ABSTRACT: A polymer-anchored nickel(II)–phenanthroline complex [polyNi(II)–phen] was synthesized and used effectively as a reusable catalyst in various oxidation reactions in the presence of *tert*-butylhydroperoxide as an oxidant in acetonitrile medium. The catalyst was characterized with elemental analysis, atomic absorption spectrometry (AAS), thermogravimetric analysis, scanning electron microscopy, and spectrometric methods such as diffuse reflectance spectroscopy, ultraviolet–visible spectroscopy, and Fourier transform infrared spectroscopy. The study of the effects of the time, temperature, oxidant, catalyst concentration, molar

ratio of substrate to oxidant, and solvent in the oxidation of styrene individually gave the optimized reaction conditions. Under optimized conditions, the catalyst exhibited good conversions for the oxidation reactions of various olefins, alkanes, aromatic alcohols, and thioethers. The catalyst was easily recovered by simple filtration and reused for more than five times with consistent catalytic activity. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3789–3798, 2012

Key words: catalysts; heterogeneous polymers; polymer synthesis and characterization; recycling

INTRODUCTION

The oxidation of organic substrates has been extensively studied, and olefin oxidation is especially interesting because of the industrial importance of this type of reaction.^{1,2} Among the products of the olefin oxidation reaction, epoxides are extremely important because they are widely used in the production of epoxy resins, paints, perfumes, surfactants pharmaceuticals, and polymer and are also intermediates in many organic syntheses.^{3,4} Benzaldehyde, the oxidation product of toluene, and its derivatives, are also an important intermediate for chemical syntheses and are applied in scores of areas, such as perfumes, pharmaceuticals, dyestuffs, and agrochemicals.⁵ The oxidation of alcohols to carbonyl compounds is a fundamental transformation in organic chemistry, both at the laboratory and industry levels.⁶ Furthermore, the oxidative conversion of the hydroxyl group has also attracted much interest in the biorefinery field recently.⁷ Particularly, the oxidation of primary alcohols to aldehydes is significant because they find wide application as intermediates in fine chemicals, chiefly in the perfume industry.^{8,9} The

oxidation of sulfides (thioethers) to sulfoxides, that is, sulfoxidase activity, has been considered as one of the important catalytic reactions also.

The design of new metal catalysts for the selective oxidation of organic molecules is an area of considerable interest in homogeneous molecular catalysis. Recent trends in the immobilization of transition-metal complexes on insoluble supports (mainly, organic polymers) appear to be a good way for heterogenizing homogeneous catalysts. Such types of heterogenized–homogeneous catalytic systems not only offer the combined advantages of homogeneous (mild conditions) and heterogeneous (easy separation) catalysts but also impose extreme shape selectivity in catalytic process.^{10,11} The heterogenization of a catalyst on an inert support prolongs the life of the catalyst and makes it separate easily from the reaction mixture. The catalysts on crosslinked supports with pores of molecular dimension have shown significant increases in their selectivity and activity because of the high concentration of active sites within the small pores.¹² The efficiency of catalysts on inert supports has been found to be high¹³ in comparison to the unsupported state of the catalysts¹⁴ because, in the unsupported state, the aggregation of the catalysts reduces their efficiency. Insoluble crosslinked polymers are used widely as they are inert, nontoxic, thermally stable, and easily recycled.¹⁵ Although various inorganic supports, such as mesoporous silica, zeolites, porous alumina, Y-zeolite, epoxy resins, clays, ion-exchange resins, and modified MCM-41 (is an ordered

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mesoporous material, displaying a honeycomb-like structure of uniform mesopores),^{16–21} have been used for anchoring homogeneous complexes, organic polymer supports have been better employed as they are able to provide preferential stereochemistry for catalysts and reactants¹³ in the presence of solvents in comparison to rigid inorganic supports. Immobilization of the complexes in polymer supports often present advantages for industrial applications, and the catalytic potentials of immobilized metal complexes in organic transformations have been reviewed in detail by several groups.^{22,23} Functionalized porous crosslinked polymer beads have displayed significant influence on various reactions^{24–26} and have been used as reagents,^{27,28} chelating agents for the separation of metal ions, and also as potential sorbents.^{29,30} The metal complexes supported on polymers have shown excellent catalytic activity for hydrogenation³¹ and enantiomeric epoxidation of alkenes³² in comparison to homogenized catalysts.³³ Predominantly polymer-supported transition-metal complexes were found to be efficient heterogeneous catalysts for the oxidation of various olefins and alcohols^{34–36} under mild reaction conditions. Recently, the use of chloromethylated polystyrene (**1**) crosslinked with divinylbenzene as a solid support to immobilize metal complexes with catalytic potential for various oxidation reactions^{37–40} has been well recognized.

A major objective lies in the design and synthesis of polymeric supports with appropriate functional groups for attachment to the active metal centers. Styrene–divinylbenzene copolymer, the most commonly employed support, has been chemically modified into a ligand having a variety of coordination sites, such as β -diketones ($\text{O} \curvearrowright \text{O}$), dipyridylamine ($\text{N} \curvearrowright \text{N}$), diphosphine ($\text{P} \curvearrowright \text{P}$), glycine ($\text{N} \curvearrowright \text{O}$), and ethylenediamine ($\text{N} \curvearrowright \text{N}$).^{41–43} 1,10-Phenanthroline ($\text{N} \curvearrowright \text{N}$) is the parent of an important class of chelating agents. In our work, 5-amino-1,10-phenanthroline was preferred, as a ligand, mainly because of two factors. One, it is rigid and provides two aromatic nitrogens whose unshared electron pairs are beautifully placed to act cooperatively in binding cations, and the amine group in the 5 position can provide the attachment of the polymer support in opposition to the metal, such that the metal is less crowded to bind with the oxidant and facilitate the reaction. This heteroaromatic moiety can also provide a further binding site for metal cations.⁴⁴

Transition-metal complexes have also attracted a lot of attention as possible oxidation catalysts for the selective oxidation of olefins in mild conditions. Several transition-metal-based homogeneous systems, such as palladium, ruthenium, manganese, copper, vanadium, and iron,^{45–48} have been reported for the oxidation of alcohols, alkanes, and olefins. So in this article, we report on the synthesis and characterization of Ni(II) supported on a functionalized polystyrene–phen ligand, and we examined it as a possible

catalyst in the oxidation of styrene and other olefins, alkanes, aromatic alcohols, and thioethers in the presence of *tert*-butylhydroperoxide (TBHP) as a terminal oxidant at ambient temperature in acetonitrile (ACN) solvent with admirable results. The effects of different experimental parameters, such as time, temperature, oxidant, molar ratio of oxidant to substrate, and solvent on the catalytic oxidation reaction of styrene were investigated to optimize the reaction conditions. We also determined that the polymer-anchored catalyst could be reused more than five times without much loss in its activity.

EXPERIMENTAL

Materials and instruments

Analytical-grade reagents and freshly distilled solvents were used throughout the experiment. Liquid substrates were predistilled and dried by an appropriate molecular sieve. Distillation, purification of the solvents, and substrates were done by standard procedures.⁴⁹ 5-Amino-1,10-phenanthroline and chloromethylated poly(styrene–divinyl benzene) (2% crosslinks with 200–400-mesh size) were supplied by Sigma-Aldrich Chemical Co., (St. Louis, MA). Other reagents were obtained from Merck Co., (Darmstadt, Germany).

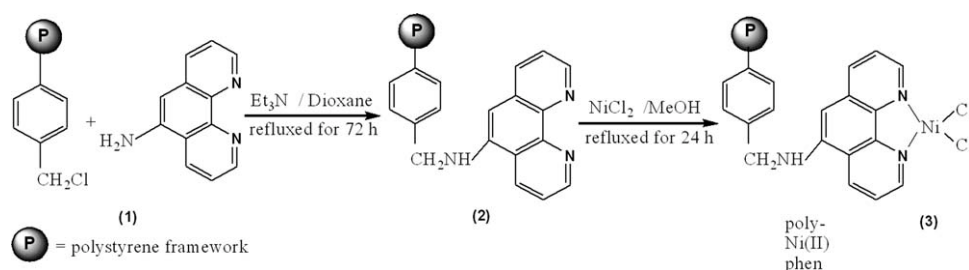
A PerkinElmer (Waltham, Massachusetts) 2400 C elemental analyzer was used to collect microanalytical data (C, H, and N). Fourier transform infrared (FTIR) spectra of the samples were recorded on a PerkinElmer FTIR 783 spectrophotometer with KBr pellets. A Mettler-Toledo TGA/SDTA 851 instrument was used for the thermogravimetric analysis (TGA). Morphologies of the functionalized polystyrene and complex were analyzed with a scanning electron microscope (Zeiss EVO40, United Kingdom) equipped with an energy-dispersive X-ray spectroscopy facility. Nickel content in the catalyst was determined with a Varian (Palo Alto, CA) AA240 atomic absorption spectrophotometer.

Synthesis of catalyst

The outline for the preparation of the polymer-anchored Ni(II) complex is given in Scheme 1.

Preparation of the polymer-bound ligand (**2**)

The polymer-anchored ligand was prepared as follows: **1** (1.2 g) was added to a solution of 5-amino-1,10-phenanthroline (0.983 g, 0.005 mol) in dioxane (100 mL). The mixture was heated to reflux with stirring. After refluxing for 1 h, triethylamine (0.5095 g, 0.005 mol) was added, and after 25 h, 0.2 g of triethylamine was added. With further refluxing for an additional 32 h, the suspension became a yellow–brown color. The mixture was cooled to room



Scheme 1 Synthesis of the polymer-supported Ni(II)-phen complex.

temperature and then filtered. The resin was washed with ethanol until the filtrate became colorless and was then dried *in vacuo*.

Synthesis of the polymer-anchored nickel(II)-phenanthroline complex [polyNi(II)-phen or 3]

The polymer-supported ligand (2 g) was placed in ethanol (10 mL) in a round-bottom flask. To this, an ethanolic solution (10 mL) of NiCl_2 (1% w/v) was added over a period of 45 min and refluxed for 8 h. Then, the brown colored solid complex was filtered, washed with ethanol, and dried *in vacuo*.

Procedure for catalytic oxidation

A mixture of 50 mg of catalyst, 10 mL of solvent (ACN), and 5 mmol of substrate was stirred in a 50-mL, two-necked round-bottom flask equipped with a condenser and placed in an oil bath at 60°C under vigorous stirring. Then, 10 mmol of TBHP (70% aqueous solution) was added. The resulting mixture was then refluxed for 8 h. After filtration, the filtrate was concentrated and then analyzed by a Varian 3400 gas chromatograph equipped with a 30-m CP-SIL8CB capillary column and a flame ionization detector. The products were determined with cyclohexanone as an internal standard. All reaction products were identified with an Agilent (Santa Clara, CA) gas chromatograph-mass spectrometer.

RESULTS AND DISCUSSION

Characterization of the polyNi(II)-phen

Because of the insolubility of the polymer-supported Ni(II) complex in all common organic solvents, its structural investigation was limited to its physicochem-

ical properties, chemical analysis, scanning electron microscopy (SEM), TGA, IR, and ultraviolet-visible (UV-vis) spectral data. Elemental analysis of the ligand and complex (Table I) supported the formulation of the complex. AAS analysis results suggest 1.1% Ni in the immobilized Ni(II)-phenanthroline (phen) complex.

SEM and energy-dispersive X-ray analysis (EDAX)

Scanning electron micrographs of the polymer-supported phen ligand and prepared Ni (II) catalyst were recorded to determine the morphological changes occurring on the surface of the polymer matrix. In Figure 1, the SEM images of the polymer-anchored ligand [Fig. 1(A)] and the immobilized Ni(II) complex on modified polystyrene [Fig. 1(B)] are shown. The SEM pictures show the morphological difference between the ligand and the catalyst. The existence of the nickel metals could be further proven by EDAX (Fig. 2).

FTIR spectroscopic studies

The modes of attachment of metals onto the support were confirmed by comparison of the FTIR spectral bands of the polymers before and after loading with Ni(II) metal, both in the mid ($4000\text{--}400\text{ cm}^{-1}$) and far ($600\text{--}50\text{ cm}^{-1}$) IR regions (Table I). The IR spectrum of pure 1 showed an absorption band at 1261 cm^{-1} due to the presence of C-Cl groups, which was absent in 2 and the catalyst (3). IR spectra showed that a stretching vibration for N-H appeared at 3371 cm^{-1} for 2 and its complex. The stretching vibrations of C=N and C=C double bonds appeared as follows: at 1613 and 1596 cm^{-1} for polyphenanthroline (polyphen) and at 1622 and 1601 cm^{-1} for polyNi(II)-phen. These were

TABLE I
Chemical Composition and IR Stretching Frequencies of the Polymer-Anchored Ligand and Complex

Compound	Color	Cl (%)	C (%)	N (%)	H (%)	Ni (%)	IR (cm^{-1} , KBr) ^a					
							C=C	C=N	C-Cl	N-H	Ni-N	Ni-Cl
1	Colorless	23.2	70.8		5.9				1261 (s)			
2	Yellow-brown		85.1	9.4	5.4		1596	1613	1261 (w)	3371		
3	Brown	16.7	59.3	6.6	3.8	1.1	1601	1622	1261 (w)	3371	240	247

^a IR spectra measured as KBr pellets. s, strong; w, weak.

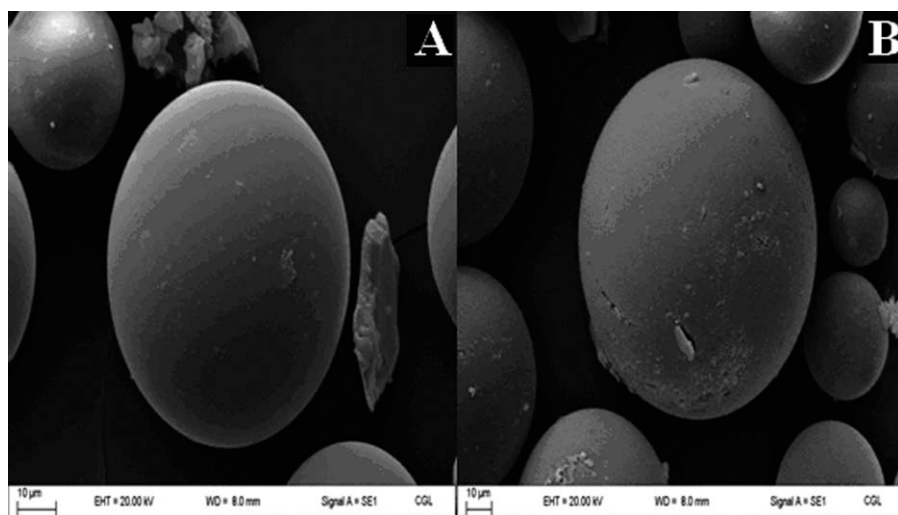


Figure 1 Field emission SEM images of the (A) polyphen ligand and (B) polyNi(II)-phen complex.

different because the phenyl backbones were influenced by the metal ion. In the far IR data, two bands due to $\nu(\text{Ni-N})$ at 240 cm^{-1} (phen nitrogen)¹⁷ and $\nu(\text{Ni-Cl})$ at 247 cm^{-1} were observed; this confirmed the formation of the metal complex.

TGA studies

The thermal stability of the polymer-supported ligand and Ni(II) complex (Fig. 3) were investigated at a heating rate of $10^\circ\text{C}/\text{min}$ in air over a

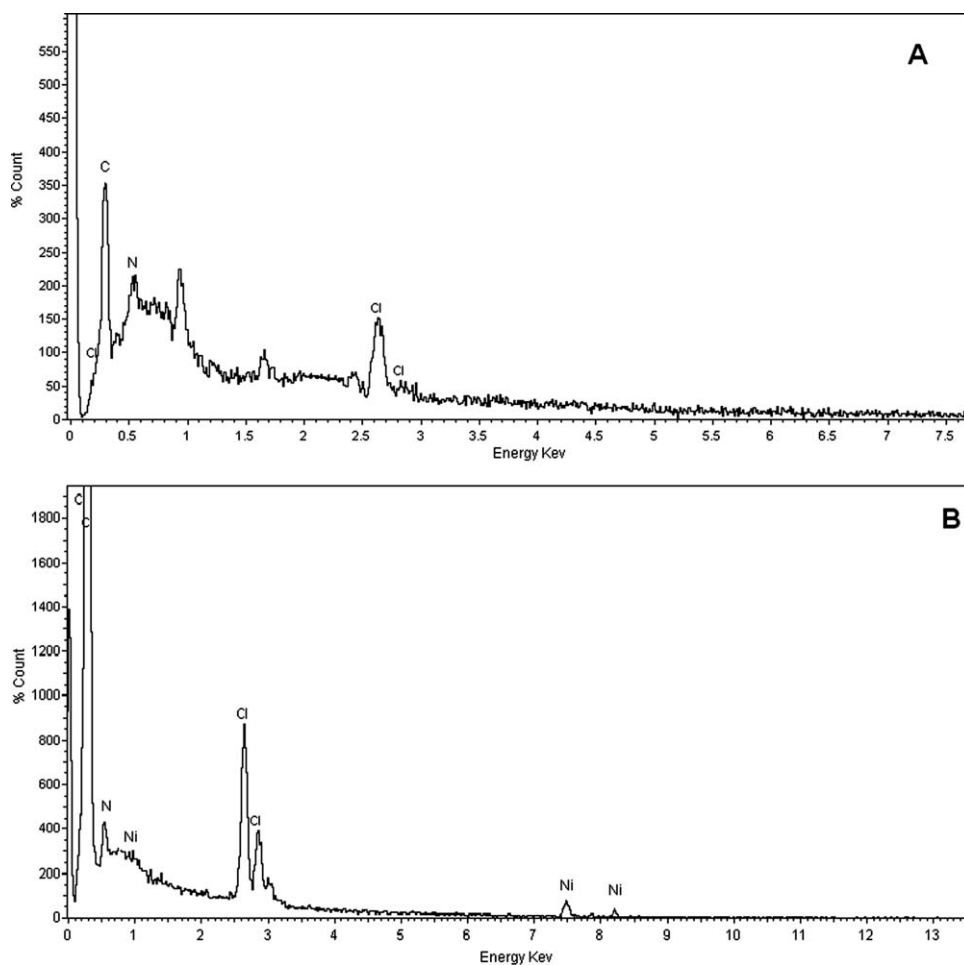


Figure 2 EDAX data of the (A) polyphen ligand and (B) polyNi(II)-phen complex [Fig. 2(B)].

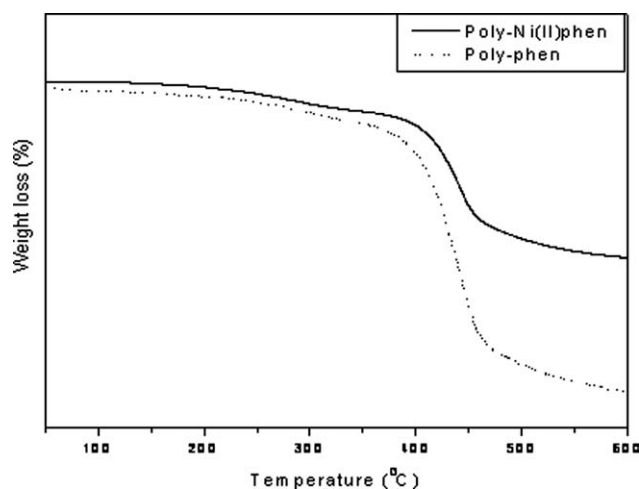


Figure 3 Thermal studies of polyNi(II)-phen.

temperature range of 30–600°C. It was seen that the thermal stability of the metal complex was slightly greater than that of its precursor polyphen ligand. The complex was stable up to 350°C, and above this temperature, it decomposed. Thermogravimetric study suggested that the polymer-supported Ni(II) complex degraded at considerably higher temperatures.

Electronic spectral studies

The electronic spectrum (Fig. 4) of the polymer-supported Ni(II)-phen was recorded in diffuse reflectance mode as a BaSO₄ disc because of the solubility limitations. The main absorptions were at about 330 and 350–420 nm. The absorption around 330 nm may have been due to $\pi \rightarrow \pi^*$ transitions of the phenyl moieties. The absorption around 350–410 nm was due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition of the phen moiety. In the complex, the bands around 387–423

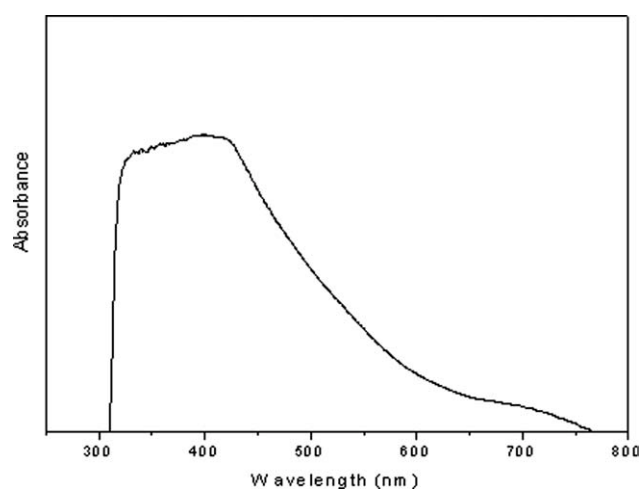


Figure 4 Diffuse reflectance spectroscopy–UV–vis absorption spectra of the polyNi(II)-phen complex.

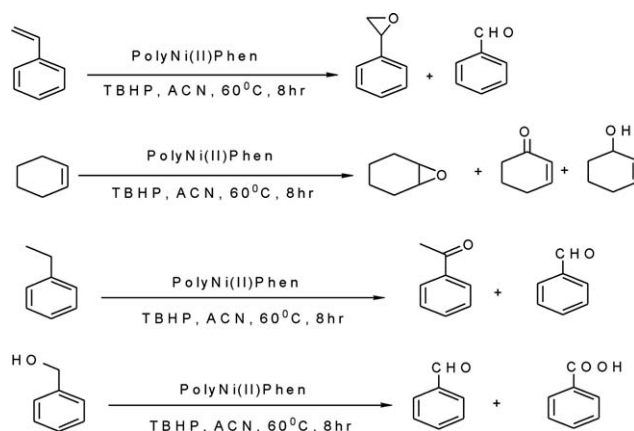
nm assigned to $d-d$ transition were due to the presence of Ni(II) ion,⁵⁰ but these peaks were not observed well because of overlapping, so there was a broad shoulder around 350–420 nm.

Catalytic activity

Here, we studied the performance of the polymer-anchored nickel catalyst on the oxidation of styrene with TBHP in ACN solvent. The main products of the olefin oxidations were epoxide and aldehyde (Scheme 2). The oxidation of styrene produced styrene oxide as the main product and also benzaldehyde in small yield. Blank experiments revealed that no reaction occurred in the absence of either the catalyst or the oxidant. Taking the oxidation reaction of styrene to styrene oxide and benzaldehyde as the model reaction, we successfully determined the effects of time, temperature, catalyst amount, oxidant, substrate–oxidant molar ratio, and solvent with the nickel catalyst. The oxidation in the presence of this catalyst under the same reaction conditions was also done with other substrates, such as ethyl benzene, toluene, benzyl alcohol, and diphenyl sulfide, with good conversion percentages and excellent product selectivity.

Effect of the solvent

The oxidation of styrene was examined with different solvents. The selected solvent should possess certain criteria, such as it should be stable and it should dissolve the substrate and oxidant. Table II shows the influence of the solvent on the conversion of styrene and the selectivity of styrene oxide with the polymer-supported Ni(II)-phen complex as a catalyst. The selectivity of styrene oxide was in the following order: ACN > H₂O > MeOH > (Me)₂CO > MePh. The results indicate that the epoxidation reaction did not proceed in toluene solvent.



Scheme 2 Various oxidation reactions with polyNi(II)-phen.

TABLE II
Styrene Epoxidation with Different Solvents^a

Entry	Solvent	Time (h)	Conversion (%) ^b	Selectivity(%) ^b	
				Styrene oxide	Benzaldehyde
1	Toluene	8	0	0	0
2	Me ₂ O	8	8	25	75
3	MeOH	8	20	18	82
4	H ₂ O	8	50	65	35
5	ACN	8	92	89	11

^a Reaction conditions: catalyst (9 wt % to styrene), styrene (5 mmol), solvent (10 mL), TBHP (10 mmol), 60°C.

^b Determined by GC.

Additionally, poor conversion and selectivity were found when the reaction was carried out in acetone media. The reaction, however, showed low activity and epoxidation selectivity in methanol; the main product was benzaldehyde. For this reaction, the nickel catalyst exhibited the highest catalytic activity and selectivity for styrene oxide in ACN media because it was a polar solvent, had a high dielectric constant, and dissolved a wide range of chemical compounds.

Effect of the reaction temperature

To determine the best temperature, the oxidation of styrene was thoroughly investigated at different temperatures with Ni(II)-phen as the catalyst. The oxidation reaction was carried out at various reaction temperatures from 40 to 80°C with a 1 : 2 mmol ratio of styrene to TBHP with ACN as the solvent for a duration of 8 h, and the results are shown in Figure 5. The optimum temperature was found to be 60°C. Lower temperatures did not favor the formation of products because the catalyst was less active. At higher temperatures, the yield and selectivity of the product decreased.

Effect of the oxidant

In this study, the effects of different oxidants, such as TBHP, H₂O₂, PhIO (Iodosylbenzene), and molecular oxygen, over this catalyst were examined in the oxidation reaction of styrene. The results of this study are given in Table III. Almost no conversion was observed when molecular oxygen was used as an oxidant. TBHP was the best oxidant among the three oxidants that were used in the catalytic oxidation reaction in this study. Oxidants such as H₂O₂ and PhIO were clearly less efficient than TBHP, as was evident from the percentage conversion of styrene. The significant difference in the styrene oxide yield when TBHP was used in comparison to hydrogen peroxide could be explained by nickel hydroper-

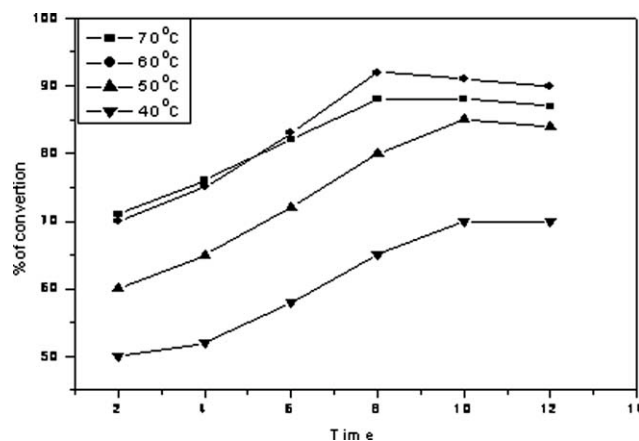


Figure 5 Effect of the temperature on the oxidation of styrene with polyNi(II)-phen complex as a catalyst. Reaction conditions: styrene (5 mmol), ACN (10 mL), TBHP (10 mmol), and catalyst (9 wt % to styrene).

oxo species, which could form at the surface of the active site of the metal catalyst (Scheme 3). The stability of tertiary carbocation explained why the reaction was better with TBHP than with H₂O₂.⁵¹

Effect of the substrate-to-oxidant (styrene-to-TBHP) ratio

The liquid-phase oxidation of styrene was carried out with three different millimolar ratios of styrene to TBHP. In all cases, styrene oxide was obtained as a major product with benzaldehyde as a byproduct. It was observed that the highest conversion of styrene (92%) and selectivity (89%) for styrene oxide were obtained at a styrene-to-TBHP millimolar ratio of 1 : 2 over the heterogeneous Ni (II) catalyst at 60°C for 8 h, as shown in Figure 6. When the

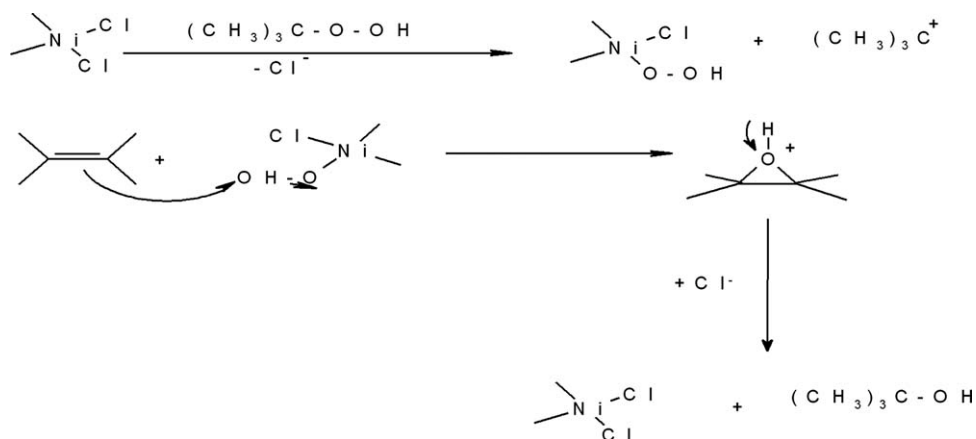
TABLE III
Oxidation of Styrene with Different Oxidants^a

Entry	Oxidant	Time (h)	Conversion (%) ^b	Selectivity (%) ^b	
				Styrene oxide	Benzaldehyde
1	None	8	0	0	0
2	PhIO	8	15	75	25
3	O ₂	8	8	70	30
4	TBHP	8	92	89	11
	(1 : 2) ^c				
	TBHP				
5	TBHP	8	70	92	8
	(1 : 1)				
	TBHP				
5	TBHP	8	68	95	5
	(1 : 0.5)				
5	H ₂ O ₂	8	60	35	64

^a Reaction conditions: catalyst (9 wt % to styrene), styrene (5 mmol), ACN (10 mL), oxidant (10 mmol), and temperature = 60°C.

^b Determined by GC.

^c The substrate-to-oxidant ratio appears in parentheses in this column.



Scheme 3

millimolar ratio of styrene to TBHP was increased from 1 : 1 to 1 : 2, the conversion and the selectivity of styrene oxide increased, and the selectivity of the byproducts decreased. The catalytic activity was found to decrease when the styrene-to-oxidant millimolar ratio was 1 : 3; probably a high oxygen concentration produced by more oxidant inhibited the process of the reaction. Thus, the optimal millimolar ratio of styrene to TBHP was 1 : 2.

Effect of the catalyst amount

The amount of catalyst was varied from 4.8 to 19% (wt % catalyst to styrene) with the same millimolar ratio of styrene to TBHP at 1 : 2 and a reaction temperature of 60°C. The reaction was carried out for 8 h, and the products were analyzed. The results are presented in Figure 7. With the increase in catalyst amount from 4.8 to 9% (wt % catalyst to styrene), the conversion of styrene increased to the maximum, 92%. This was due to the availability of more active

sites, which favored the accessibility of a large number of molecules of substrates and oxidant to the catalyst. Styrene conversion was nearly the same with a further increase of the catalyst amount to 19% (wt % of catalyst to styrene).

Effect of the reaction time

The conversion of styrene was monitored and plotted as a function of reaction time (Fig. 8) at 60°C (styrene-to-TBHP millimolar ratio = 1 : 2). Under these reaction conditions, the conversion and selectivity simultaneously increased with time. The conversion increased with time and reached a maximum value of 92% at 8 h. When the reaction time increased, the conversion remained almost constant. The conversion and selectivity of epoxide were 92 and 89%, respectively, at 8 h.

Thus, the required parameters for the epoxidation of styrene, to get selectively styrene oxide, were as follows: styrene (5 mmol), TBHP (10 mmol), ACN solvent, catalyst (9 wt % to styrene), reaction time (8 h), and temperature (60°C). The major product,

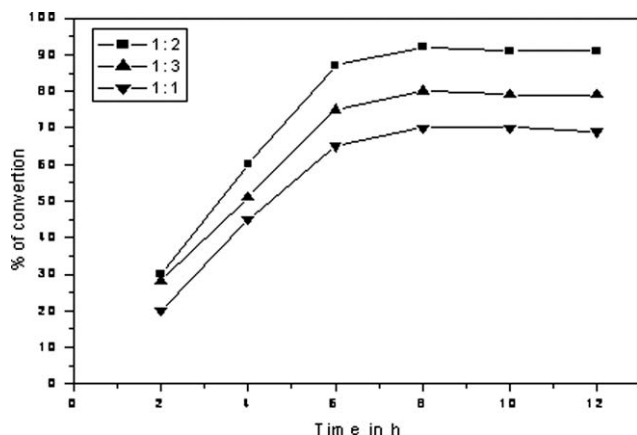


Figure 6 Effect of the substrate-to-oxidant molar ratio on the oxidation of styrene as a function of time with polyNi(II)-phen complex as a catalyst. Reaction conditions: ACN (10 mL), catalyst (9 wt % to styrene), temperature = 60°C, and time = 8 h.

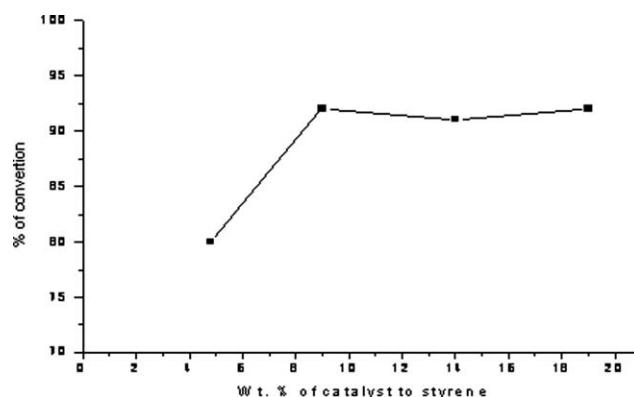


Figure 7 Effect of the amount of catalyst on the oxidation of styrene with polyNi(II)-phen complex as a catalyst. Reaction condition: styrene (5 mmol), ACN (10 mL), TBHP (10 mmol), temperature = 60°C, and time = 8 h.

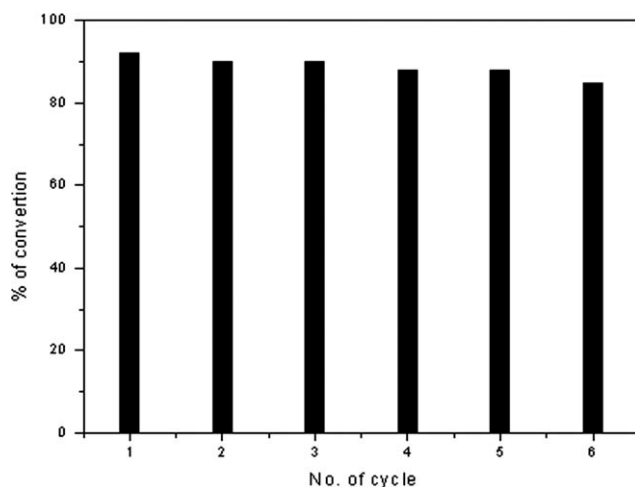


Figure 8 Recycling activity of the use of polyNi(II)-phen complex as a catalyst on the styrene oxidation reaction. Reaction conditions: styrene (5 mmol), ACN (10 mL), TBHP (10 mmol), catalyst (9 wt % to styrene), and temperature = 60°C for 8 h.

styrene oxide, was formed with 89% selectivity under these reaction conditions.

Catalytic oxidation with other organic substrates

To further explore the catalytic activity and selectivity of the catalyst, the oxidation of other olefins was investigated under optimized reaction conditions, which proved to be the best for styrene (Table IV). Cyclic olefins, such as cyclohexene and cyclooctene, were oxidized with high yields. The results show that the conversion was 54% with 94% epoxide selectivity in case of cyclooctene, whereas the oxida-

tion of cyclohexene gave 78% conversion and 68% epoxide selectivity with the allylic oxidation products cyclohexene-1-one and cyclohexene-1-ol to a small extent. α -Pinene and limonene showed moderate conversion with a high selectivity for epoxides.

The oxidation of benzyl alcohol and substituted benzyl alcohols produced benzaldehyde as the main product with benzoic acid in small yields, whereas 1-phenyl ethanol gave a keto product with 100% selectivity. Thioethers gave sulfoxide (S=O) products on oxidation (Table IV).

The oxidation of ethyl benzene carried out under these reaction conditions resulted in acetophenone and benzaldehyde as the major products with selectivities of 65 and 35%, respectively. On oxidation, toluene gave benzaldehyde with 100% selectivity (Table IV).

The polymer-anchored Ni(II)-phen complex catalyst was highly active for the oxidation of styrene, cyclohexene, ethyl benzene, and so on. Many heterogeneous transition-metal catalysts have been reported in the literature^{52–55} for the oxidation reaction, and the details are shown in (Table V). A comparison of this catalytic system with the previously reported system revealed that this catalyst gave better yields than the other catalyst within a reasonable reaction time and reaction temperature.

Heterogeneity test

To determine whether the catalyst was actually functioning in a heterogeneous manner, a hot-filtration test was performed in the oxidation reaction. During the catalytic oxidation of styrene, the solid catalyst

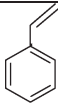
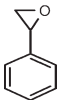
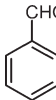




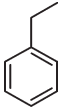


TABLE IV
Oxidation of Different Substrates with the Ni(II) Complex^a

Entry	Substrate Olephin	Conversion (%) ^b	Selectivity (%) ^b		
			Epoxide	Aldehyde/ketone	Alcohol
1	Styrene	92	89	11	—
2	Cyclohexene	78	68	24	8
3	Cyclooctene	54	94	—	6
5	α -Pinene	38	63	12	15
6	Limonene	32	65	12	13
7	Alkanes Ethyl benzene	65	Aldehyde 35	Ketone 65	—
8	Toluene	35	100	—	—
9	Alcohols Benzyl alcohol	78	Aldehyde 88	Ketone —	Carboxylic acid 12
10	4-Methylbenzyl alcohol	75	86	—	14
11	4-Nitrobenzyl alcohol	72	80	—	20
12	1-Phenyl ethanol	77	—	100	—
13	Thioethers Phenyl sulfide	55	Sulfoxide 100	—	—
14	Methylphenyl sulfide	48	100	—	—

^a Reaction conditions: catalyst (9 wt % to styrene), substrate (5 mmol), ACN (10 mL), oxidant (10 mmol), time = 8 h, and temperature = 60°C.

^b Determined by GC.

TABLE V
Comparison of the Polymer-Anchored Ni(II)-Phen Complex Catalyst with Other Transition-Metal Catalysts in Oxidation Reactions, as Reported in the Literature

Substrate	Catalyst	Conversion (%)	Selectivity of the product (%)			Reference
	PolyNi(II)-phen	92				This work
	Cu ₂ L-(μ _{1,1} -N ₃)(μ _{1,3} -N ₃)(μ _{1,1,1} -N ₃)/silica	88	84			52
	Vitamin B ₁₂ /MCM-41	60		8	92 benzoic acid	53
	Ru B	53.8	23.8	57.5	18.7 acetophenone	54
	Ru A	52.8	37.5	49.3	13.2	54
	PolyNi(II)-phen	78				This work
	Cu ₂ L-(μ _{1,1} -N ₃)(μ _{1,3} -N ₃)(μ _{1,1,1} -N ₃)/silica	76	84	24	8	52
	Vitamin B ₁₂ /MCM-41	70	—	25	—	53
	Ru B	65.2	2.55	36.9	25.4	54
	Ru A	53.9	trace	22.8	26.4	54
	PolyNi(II)-phen	65				This work
	6/Mn-MCM-41	57	82.2	17.8		55

Cu₂L, copper complex where L is ligand, 4-methyl-2,6 bis(phenylmethyliminomethyl)phenol; Ru A, 8% poly(S-DVB)_L-val Ru(III) complex; Ru B, 6% poly(S-DVB)_L-val Ru(III) complex; Mn, manganese.

was separated from the reaction mixture by filtration after 4 h of reaction, and the obtained filtrate was continually stirred under the same reaction conditions for a further 3 h. The gas chromatography (GC) analysis showed no increment in the conversion. AAS analysis of the filtrate confirmed that no nickel was present in the reaction mixture. The metal content of the recycled catalysts also remained unaltered; this indicated no leaching of the metal from the polymer support. It was noteworthy that the ACN remained completely colorless with the addition of catalysts. These results confirm that no leaching of the metal from the catalyst took place during the catalytic reaction.

Catalyst recyclability

The stability of the polyNi(II)-phen complex was studied in repeated styrene oxidation reactions. The catalyst was separated from the reaction mixture after each experiment by filtration, washed with methanol, and dried carefully before it was in the subsequent run. After the use of catalyst for five consecutive times, the styrene conversion was 85%. The nature of the recovered catalyst was followed

by IR and UV-vis spectra. The results indicate that the catalyst, after being reused several times, showed no change in its IR and UV-vis spectra. These observations show that polyNi(II)-phen complex remained intact after the first oxidation cycle. The results are presented in Figure 8.

CONCLUSIONS

The experimental results suggest that a Ni(II)-phen complex could be immobilized over a functionalized polystyrene surface. The heterogeneous catalyst showed a high catalytic activity in the styrene oxidation, with a conversion of 92%, and a high selectivity of styrene epoxide (89%). The immobilized nickel catalyst also showed excellent catalytic activity in the liquid-phase oxidation of other olefins (cyclohexene, cyclooctene, α -pinene, and limonene), alkanes (ethyl benzene and toluene), aromatic alcohols (benzyl alcohol and substituted benzyl alcohols), and thioethers (diphenyl sulfide and phenyl methyl sulfide) in the presence of TBHP as an oxidant. The excellent yield and selectivity of the catalyst toward the oxidation of olefins, alkanes, alcohols, and thioethers paves the way for designing ecofriendly catalysts. Its easy product recovery and

recycling efficiency, along with its high selectivity, make this catalyst useful for the synthesis of different fine chemicals under ecofriendly conditions and could open up new avenues for green chemistry.

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References

1. Szegedi, A.; Popova, M.; Minchev, C. *J Mater Sci* 2009, 44, 6710.
2. Onda, A.; Suzuki, Y.; Takemasa, S.; Kajiyoshi, K.; Yanagisawa, K. *J Mater Sci* 2008, 43, 4230.
3. Xia, Q. H.; Ge, H. Q.; Ye, C. P.; Liu, Z. M.; Su, K. X. *Chem Rev* 2005, 105, 1603.
4. Yudin, A. K. *Aziridines and Epoxides in Organic Synthesis*; Wiley-VCH: Weinheim, 2006.
5. Xian, Z.; Bin, W.; Ling, M.; Zhang, Z.; Fang, W. *Acta Pet Sinica (Pet Process Sect)* 2004, 20, 32.
6. (a) Hudlicky, M. *Oxidations in Organic Chemistry*; American Chemical Society: Washington, DC, 1990; (b) Tojo, G.; Fernandez, M. *Oxidation of Alcohols to Aldehydes and Ketones: A Guide to Current Common Practice*; Tojo, G., Ed.; Springer: New York, 2006.
7. Juben, G. W. H.; Chheda, N.; Dumesic, J. A. *Angew Chem* 2007, 119, 7298; *Angew Chem Int Ed* 2007, 46, 7164.
8. Enache, D. I.; Edwards, J. K.; Landon, P.; Solsona-Espriu, B.; Carley, A. F.; Herzing, A. A.; Watanabe, M.; Kiely, C. J.; Knight, D. W.; Hutchings, G. J. *Science* 2006, 311, 362.
9. Pillai, U. R.; Sahle-Demessie, E. *Appl Catal Gen* 2003, 245, 103.
10. Booth, R. J.; Hodges, J. C. *Acc Chem Res* 1999, 32, 18.
11. Gupta, K. C.; Sutar, A. K. *J Mol Catal A* 2008, 280, 173.
12. *Chemistry of Waste Minimization*; Sherrington, D. C.; Clark, J. H., Eds.; Chapman & Hall: London, 1995; p 141.
13. Dick, H. A.; Heck, R. F. *J Org Chem* 1975, 40, 1083.
14. Kamlesh, G.; Ram, R. N.; Soni, H. P. *J Mol Catal A* 2005, 242, 161.
15. Schlick, S.; Bortel, E.; Dyrek, K. *Acta Polym* 1996, 47, 1.
16. Soundiressane, T.; Selvakumar, S.; Ménage, S.; Hamelin, O.; Fontecave, M.; Singh, A. P. *J Mol Catal A* 2007, 270, 132.
17. Dinda, S.; Nandi, M.; Bhattacharyya, R. G.; Bhaumik, A. *J Mol Catal A* 2008, 287, 135.
18. Mureseanu, M.; Parvulescu, V.; Ene, R.; Cioatera, N.; Pasatoiu, T. D.; Andruh, M. *J Mater Sci* 2009, 44, 6795.
19. Mirkhani, V.; Moghadam, M.; Tangestaninejad, S.; Mohammadpoor-Baltork, I.; Shams, E.; Rasouli, N. *Appl Catal A* 2008, 334, 106.
20. Alvarez, L. X.; Christ, M. L.; Sorokin, A. B. *Appl Catal A* 2007, 325, 303.
21. Arnold, U.; Fan, F.; Habicht, W.; Döring, M. *J Catal* 2007, 245, 55.
22. Wolfgang, K. *Angew Chem Int Ed* 2003, 42, 1088.
23. Punniyamurthy, T.; Rout, L. *Coord Chem Rev* 2008, 252, 134.
24. Jian, X. G.; Yan, C.; Zhang, H. M.; Zhang, S. H.; Liu, C.; Zhao, P. *Chin Chem Lett* 2007, 18, 1269.
25. Kishida, T.; Yamauchi, T.; Komura, K.; Kubota, Y.; Sugi, Y. *J Mol Catal A* 2006, 246, 268.
26. Dygutsch, D. P.; Eilbracht, P. *Tetrahedron* 1996, 52, 5461.
27. Thomas, C. M.; Süß-Fink, G. *Coord Chem Rev* 2003, 243, 125.
28. Tamami, B.; Yeganeh, H. *React Funct Polym* 2002, 50, 101.
29. Chanda, M.; Sarkar, A.; Chen, Z. *J Polym Mater* 2004, 21, 21.
30. Chanda, M.; Sarkar, A.; Modak, J. *J Appl Polym Sci* 2004, 93, 883.
31. James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973.
32. Kunejky, R. I.; Khess, N. H.; Abdi, S. H. R.; Iyer, P. *React Funct Polym* 1997, 34, 153.
33. Roger, T. S.; Janda, K. D. *J Am Chem Soc* 2000, 122, 6929.
34. Gupta, K. C.; Sutar, A. K.; Lin, C. C. *Chem Rev* 2009, 253, 1926.
35. Fukahori, S.; Morikawa, M.; Ninomiya, J. *J Mater Sci* 2009, 44, 374.
36. Gupta, K. C.; Sutar, A. K. *J Mol Catal A* 2007, 272, 64.
37. Maurya, M. R.; Sikarwar, S.; Manikandan, P. *Appl Catal A* 2006, 315, 74.
38. Maurya, M. R.; Kumar, U.; Manikandan, P. *Eur J Inorg Chem* 2007, 2303.
39. Maurya, M. R.; Kumar, U.; Correia, I.; Adão, P.; Costa, P. J. *Eur J Inorg Chem* 2008, 577.
40. Cazaux, I.; Caze, C. *Eur Polym J* 1993, 29, 1615.
41. Sundell, M. J.; Nasman, J. H. *Chemtech* 1993, 23, 16.
42. Patel, D. R.; Dalal, M. K.; Ram, R. N. *J Mol Catal* 1996, 109, 141.
43. Sammes, P. G.; Yahioğlu, G. *Chem Soc Rev* 1994, 23, 327.
44. Hardacre, C.; Mullan, E. A.; Rooney, D. W.; Thompson, J. M. *J Catal* 2005, 232, 355.
45. Shi, F.; Tse, M.; Beller, M. *Chem Asian J* 2007, 2, 411.
46. Chhikara, B. S.; Chandra, R.; Tandon, V. *J Catal* 2005, 230, 436.
47. Trakarnpruk, W.; Dumrongpong, P. *J Mater Sci* 2006, 41, 3001.
48. Chimentao, R. J.; Medina, F.; Sueiras, J. E.; Fierro, J. L. G.; Cesteros, Y.; Salagre, P. *J Mater Sci* 2007, 42, 3307.
49. Vogel, A. I. *Textbook of Practical Organic Chemistry (Quantitative Analysis)*, 5th ed.; Longman: London, 1989.
50. Sacconi, L. *Trans Met Chem* 1968, 61, 943.
51. Chakraborty, J.; Nandi, M.; Mayer-Figge, H.; Sheldrick, W. S.; Sorace, L.; Bhaumik, A.; Banerjee, P. *Eur J Inorg Chem* 2007, 2007, 5033.
52. Roy, P.; Dhara, K.; Manassero, M.; Banerjee, P. *Inorg Chem Commun* 2008, 11, 265.
53. Farzanch, F.; Taghavi, J.; Malakooti, R.; Ghandhi, M. *J Mol Catal A* 2006, 244, 252.
54. Valodkara, V. B.; Tembeb, G. L.; Ravindranathan, M.; Rama, H. S. *React Funct Polym* 2003, 56, 1.
55. Parida, K. M.; Dash, S. S. *J Mol Catal A* 2009, 306, 54.