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Ni (II) schiff base complex immobilized on graphene oxide nano-sheets catalyzed epoxidation of alkenes

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Abstract Ni (II) schiff base complex was synthesized by the reaction of nickel acetate tetrahydrate with *N*, *N'*-Bis(2,4-di-hydroxybenzaldehyde)-1,2-cyclohexanediamine and supported on modified grapheme oxide nano-sheets using 3-chloropropyltrimethoxysilane as a reactive surface modifier. The heterogeneous nano-catalyst was characterized by Fourier transform infrared spectra, X-ray diffraction, thermogravimetric analysis, transmission electron microscopy, nitrogen adsorption–desorption isotherms and atomic absorption spectroscopy. This catalyst was used for the epoxidation of alkenes using tert-butyl hydroperoxide as oxidant, giving excellent conversions and selectivity. The catalyst showed great reusability and selectivity without significant loss of activity in the epoxidation reactions.

Keywords Ni (II) schiff base complex · Epoxidation · *t*-Butyl hydroperoxide · Graphene oxide

Introduction

Schiff bases and their complexes with the most of transition metals as stable complexes have a key role in coordination chemistry [1]. They can be prepared simply and cheaply for industrial applications. A various number of homogeneous and heterogeneous Schiff base complexes were developed for oxidation reaction and, in particular, epoxidation of alkenes. Although great attentions were paid on the epoxidation of alkenes using Mn(III) salen complex [2–9], a few investigations have been reported that nickel complexes are found to be good catalysts

for epoxidation of alkenes [10–12]. Ni (II) complexes play an important role in various homogeneous catalytic reactions, such as asymmetric aldol reaction [13], tetralin oxidation [14], alkene epoxidation [15], Mannich-type and Michael reactions [16], and can also exhibit interesting magnetic properties [17, 18]. Some nickel compounds can also act as catalysts toward the Henry reaction under different conditions, namely in homogeneous systems [19], under solvent free microwave conditions [16] or in ionic liquids [20], and high activities (more than 90% yields) are found in a few cases [21]. Immobilization of Ni (II) complexes on a solid support has recently been reported as innovation in catalytic properties of such compounds [22–29].

On the other hand, graphene oxide (GO), a monolayer carbon material, containing plentiful functional groups, including carboxyl, carbonyl, epoxy and hydroxyl groups, shows great potential as an efficient catalyst support [30]. GO shows high activity in the selective catalytic oxidation of various alkynes, alcohols and alkenes to ketones, aldehydes and acids, respectively [31]. It is reported that the increase in hydrophobicity of supports may facilitate the absorption of phenol ring to enhance the catalytic activity of catalysts in the titled reaction [32]. In continuation to our earlier communications on heterogeneous catalyst [33–38], we are reporting here design and characterization of the covalent attachment of homogeneous Ni (II) complex onto GO and its catalytic properties in the epoxidation of olefines using *t*-BuOOH as an oxidant (Scheme 1).
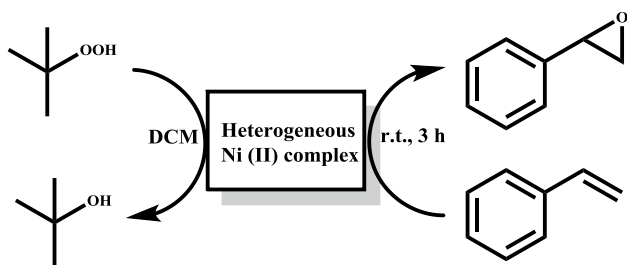
Experimental

Materials

Graphite powder was obtained from Aldrich Company. Tetraethoxysilane (TEOS), 4-chlorostyrene, styrene,

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Scheme 1 Schematic illustration for the epoxidation of alkenes

Fig. 1 Schematic illustration in preparation of heterogeneous catalyst

$Ni(O_2CCH_3)_2 \cdot 4H_2O$, NaOH, cyclohexene, indene, α-methyl styrene, m-chloroperbenzoic acid (m-CPBA), *cis* and *trans* stilbene, ethanol (EtOH), ethyl acetate (EtOAC), dichloromethane (DCM), $NaIO_4$, H_2O_2, tert-butyl hydroperoxide (*t*-BuOOH), NH_4OAC, $PhI(OAC)_2$ and oxone were purchased from Merck Company and used without purification. The resulting GO and heterogeneous Ni (II) complex (A) were characterized by different techniques. The TEM measurements were obtained using the Philips CM10 instrument. The FT-IR experiments were carried out on a Bruker Vector-22 FT-IR spectrometer (AVATR-370) in a KBr pellet. The XRD measurements were carried out using a Bruker D_8-advance X-ray diffractometer with Cu K_α radiation ($k = 1.5406$ A°). The surface area was carried out by N_2 adsorption using Quanta chrome (Chem. Bet-3000). TGA analysis was performed by heating the samples in an Argon flow at a rate of 100 mL min^{-1} using a PerkinElmer Diamond TG/DTA thermal analyzer with a heating rate of 10 °C min^{-1}. The Ni content of the catalysts was determined by Shimadzu AA-6300 atomic absorption spectroscopy (AAS). The yields were determined by Shimadzu GC-17A gas chromatograph (GC) equipped with a flame ionization detector with a capillary column (CBP-5, 30 m × 0.25 mm × 0.25 μm), using helium as a carrier gas.

Synthesis of Ni(II) complex immobilized on CPGO

GO and 3-chloropropyltrimethoxysilane functioned GO (CPGO) were prepared as described in the literature [34, 39, 40]. *N*, *N'*-Bis (2,4-di-hydroxybenzaldehyde)-1,2-cyclohexanediamine [41] and Ni(II) salen complex [42] were synthesized as described in the literature. The synthesized Ni (II) complex has been covalently anchored to the CPGO using a procedure described in Fig. 1. Initially, CPGO (2 g) was dispersed in ethanol (100 mL) for 20 min followed by addition of homogeneous Ni (II) complex (0.6 g). The resulting mixture was refluxed for 12 h under inert atmosphere. The immobilized nano-catalyst was repeatedly extracted on a Soxhlet extractor with methanol and dichloromethane until the washing becomes colorless. The heterogeneous nano-catalyst was dried at 70 °C under vacuum

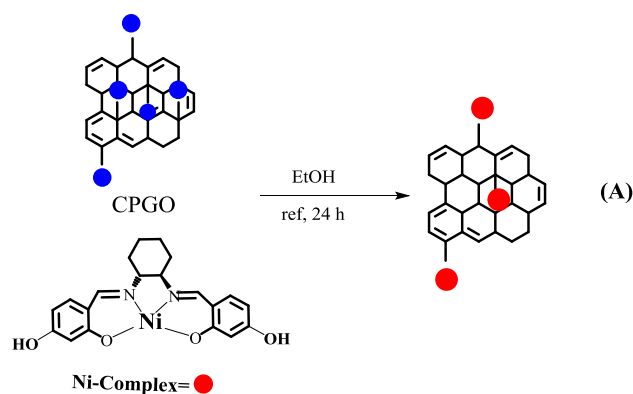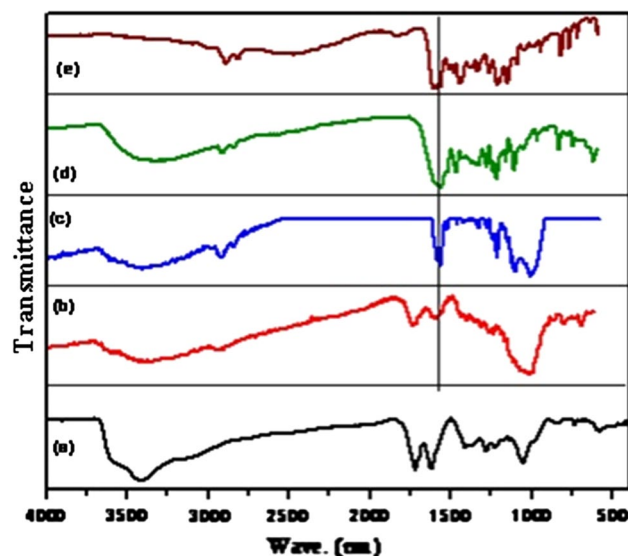**Fig. 2** FT-IR spectra of **a** GO, **b** CPGO, **c** heterogeneous catalyst, **d** Ni (II) complex and **e** salen

for 6 h and characterized by different techniques (XRD, TEM, AAS, FT-IR, TGA and nitrogen adsorption at room temperature).

Catalytic measurements

2 mol% of catalyst (based on Ni element) was dispersed in 3 mL of DCM for 20 min. Then, styrene (1 mmol), toluene (internal standard, 40 μL), *t*-BuOOH (2 mmol) as oxidant are added, respectively. The mixture was stirred for appropriateness of time and the progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated and supernatant was washed with brine (8 mL), dried over $MgSO_4$ and concentrated to 1 mL. Finally, the conversion and selectivity values of products were determined by GC. The catalyst was washed twice with ethanol and reused.

Results and discussion

Characterization of the heterogeneous Ni (II) complex

FT-IR analysis

Figure 2a shows the FT-IR spectrum of GO. A broad peak appeared at 3440 cm^{-1}, assigned to the stretching mode of an O–H bond, reveals the abundance of hydroxyl groups in GO. The functional groups C=O, C=C, C–OH and C–O (epoxy) revealed the strong band at 1714, 1617, 1222 and 1057 cm^{-1}, respectively. In FT-IR spectrum of CPGO which is shown in Fig. 2b an obvious decrease are shown in intensities of peaks such as 3440, 1725 and 1395 cm^{-1} which are corresponding to the OH, C=O stretching vibration and O–H deformation peak, respectively. Also, the presence of aliphatic C–H bonds is confirmed by the bands at 2880 and 2920 cm^{-1}. The strong band at 1610 cm^{-1} is shown in the IR spectra of Salem legend which is assigned to stretching vibration of the C=N group (Fig. 2e). The coordination of Ni through C=N functional groups shifts this band in the lower position (25 cm^{-1}) in heterogeneous Ni (II) complex (Fig. 2d). The new stretching, vibration bonds at 2928, 2880, 1584 and 1192 cm^{-1} suggest the grafting of homogeneous Ni (II) complex on the CPGO (Fig. 2c) [43].

XRD analysis

The XRD patterns of GO, CPGO and heterogeneous nano-catalyst are shown in Fig. 4 [43–45]. Upon oxidation of graphite, the basal reflection (002) peak is appeared at $2\theta = 11.79^0$ (d spacing = 0.79 nm) [42] (Fig. 3a). Immobilization of 3-chloropropyltrimethoxysilane on the GO appears a broad peak at $2\theta = 15$–$27\circ$ which is depending on amorphous silica (Fig. 3b) and decreased the intensity of the 002 reflection peak of GO. By immobilization of homogeneous Ni (II) complex was completely disappeared the 002 reflections peak of GO (Fig. 3c).

Thermogravimetric analysis

Figure 4 shows the TG curve of pure GO, CPGO and heterogeneous nano-catalyst [44, 45]. A small mass losses (2.5 wt%) at ca. 100 °C is observed on the TG curve of GO which is attributable to the loss of adsorbed water (Fig. 4a). Second degradation steps were observed at 165–250 °C which is due to the loss of hydroxyl, epoxy functional groups and remaining water molecules, and the third degradation step (450–650 °C) is depend on the pyrolysis of the remaining oxygen-containing groups as well as the burning of ring carbon. The TG curve of CPGO showed three stepwise weight losses (Fig. 4b). At the first step, 4.5% weight loss is observed at 60–200 °C which is attributed to the loss of the surface or interstitial water. Also,

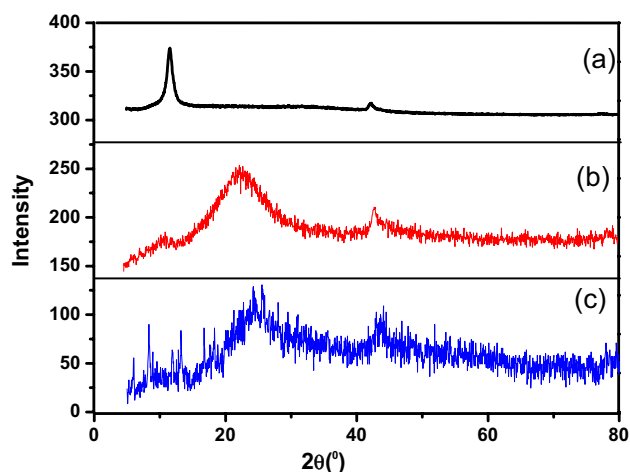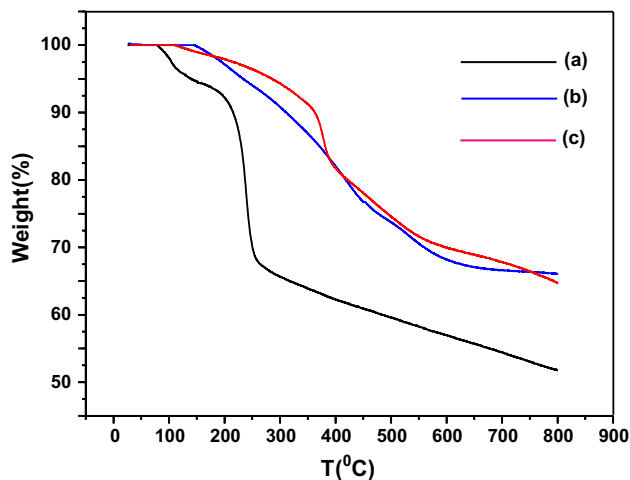**Fig. 3** XRD patterns of **a** GO, **b** CPGO and **c** Ni complex

Fig. 4 TG curve of **a** GO, **b** CPGO and **c** heterogeneous nano-catalyst

31% weight loss was observed in the temperature range 200–600 °C that is corresponding to the decomposition of the appended organic groups. In comparison with 49% weight loss at 650 °C experienced by pure GO, weight losses of 31 and 37% have been noted for CPGO and heterogeneous catalyst, respectively (Fig. 4b,c). According to the TGA curves, the homogeneous Ni (II) complex loading in the heterogeneous nano-catalyst was 0.4 mmol/g based on Ni element.

TEM analysis

A TEM image of a GO exhibits a completely disordered and amorphous structure (Fig. 5) [44, 45]. The nanoscopic features of the heterogeneous Ni (II) complex by amorphous nature are shown in Fig. 6.
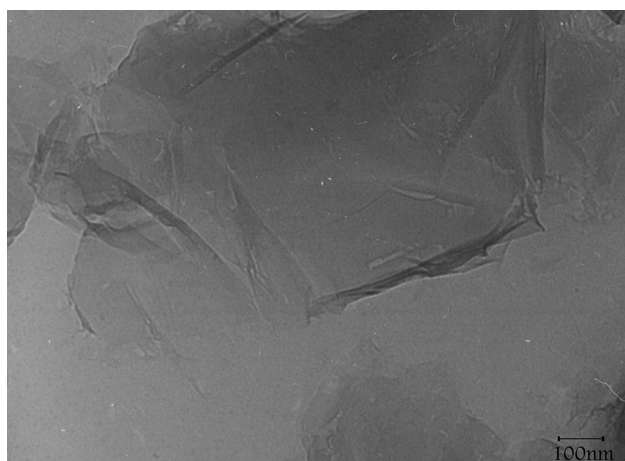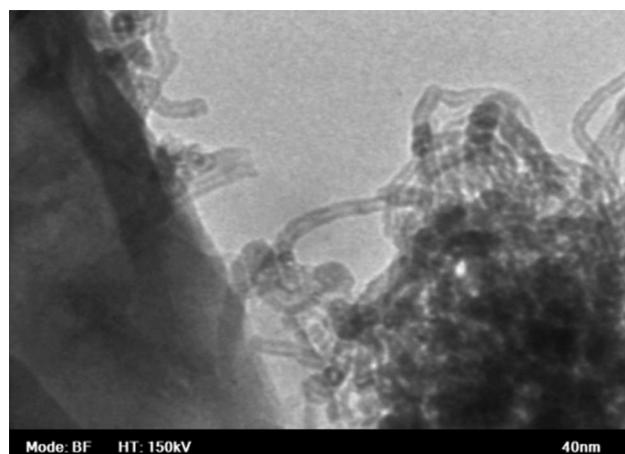
Fig. 5 TEM image of GO nano-sheets

Fig. 6 TEM image of heterogeneous nano-catalyst

The BET specific surface area of the heterogeneous nano-catalyst was 19.5 m²/g, which is determined at room temperature by nitrogen physisorption. The loading of homogeneous Ni (II) complex in the heterogeneous catalyst was 0.4 mmol/g based on Ni element analysis by AAS.

Catalyst activity

The oxidation of terminal olefin was studied using *t*-BuOOH as oxidative systems in the presence of heterogeneous Ni (II) complex at room temperature. To investigate the activity of heterogeneous Ni (II) complex, styrene was chosen as model substrate. The model reaction was performed in the presence of different amount of heterogeneous Ni (II) complex (0.5–3 mol% based on Ni element) to optimize the amount of catalyst. As the amount of Ni (II) complex was increased, the yield is significantly enhanced up to 95% (Table 1, entries 1–5). For comparison, the

Table 1 Optimization of the amount of heterogeneous Ni (II) complex

Entry	Catalyst mol%	Time (h)	Yield[a] (%)
1	0.5	2.5	30
2	1	2.5	58
3	1.5	2.5	75
4	2	2.5	91
5	2.5	2.5	93
7	No catalyst	2.5	8

Reaction conditions: styrene (1 mmol), *t*-BuOOH (2 mmol), DCM (3 mL)

[a] Determined by GC with a CBP1 column (Shimadzu 30 m × 0.32 mm × 0.25 mm)

Table 2 Effect of different solvents on the epoxidation of styrene

Entry	Solvent	Time (h)	Yield[a] (%)
1	EtOAC	6	80
2	CH₃CN	6	70
3	H₂O	6	20
4	CHCl₃	6	60
5	THF	6	50
6	DCM	6	91

Reaction conditions: styrene (1 mmol)

t-BuOOH (2 mmol) and Catalyst (2 mol% based on Ni) at r.t

[a] Yields refer to GC yield

**Table 3** Effect of different oxidants on the epoxidation of α-methylstyrene
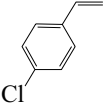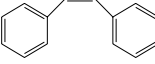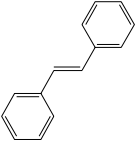
Entry	Oxidant system	Time (h)	Yield[a] (%)
1	m-CPBA	3	91
2	tert-BuOOH	3	91
3	Oxone	3	30
4	NaIO₄	3	35
5	UHP	3	25
6	PhIO	3	57
7	H₂O₂	3	24
8	PhI(OAC)₂	3	45

Reaction conditions: styrene (1 mmol), DCM (3 mL) and catalyst (2 mol% based on Ni)

[a] Yields refer to GC yield

homogeneous Ni (II) complex was also investigated under the same reaction conditions, but shortening the reaction time to 1.5 h. Blank reaction system (in the presence of *t*-BuOOH but in the absence of Ni (II) complex) was also performed and the yield of the products was very low (8%, entry 6).

Table 4 Epoxidation of different olefins catalyzed by heterogeneous Ni (II) complex

Entry	Alkene	Time (h)	Selectivity[a] %	Yield[b] (%)	TON	TOF (h^{-1})
1		3	99	91	45.5	15.16
2		3	98	91	45.5	15.16
3		3	99	91	45.5	15.16
4		3	98	94	47	15.66
5		3	98	93	46.5	15.5
6		3	98	90	45	15
7		3	95	91	45.5	15.16
8		3	95	92	46	15.33
9		3	99	90	45	15

Reaction conditions: substrate (1 mmol), DCM (3 mL), oxidant (2 mmol) and catalyst (2 mol% based on Ni)

[a] Selectivity based on alkenes conversion

[b] Determined by GC with a CBP5 column (Shimadzu 30 m × 0.32 mm × 0.25 mm)

Table 5 Comparison of the efficiency of heterogeneous Ni (II) complex with different catalysts

| Entry	Catalyst	Oxidant	Time	Yield (%)	Ref.
1	Ni–amp-Cl	TBHP	6 h	25	47
2	Ni (macrocycle) @ MCM-41	TBHP	6 h	17	48
3	Ni-AMM	TBHP	24 h	78.2	49
4	Chiral Ni_II. Complex	NaOCl	24 h	83	50
5	Ni (II) Complex	PhIO	5 h	26	51
6	Ni (salen) complex	NaOCl	2 h	42	52
7	Heterogeneous Ni (II) complex	TBHP	3 h	91	This work

Substrate is styrene

Effect of different solvents in the epoxidation of styrene

The effect of different solvents such as EtOAC, CH$_3$CN, THF, CHCl$_3$, DCM and water were examined. The results demonstrated that DCM gave higher yields (Table 2, entry 6).

Effect of different oxidants in the epoxidation of styrene

The effect of various oxidants such as oxone, NaIO$_4$, H$_2$O$_2$, m-CPBA, t-BuOOH, UHP, PhIO and PhI (OAC)$_2$ are investigated in the epoxidation of styrene. As the results are shown, m-CPBA and t-BuOOH gave higher yields and t-BuOOH was the chosen as the best oxygen source for alkenes (Table 3, entries 1 and 2). A good relationship was existed between yields and the concentration of oxidants. Different amounts of oxidant were also tested, and higher catalytic activity was obtained with 2 equivalents of the oxidant. Consequently, the optimum molar ratio of olefin to oxidant is 1:2.

Under optimized conditions, the catalytic activity of heterogeneous Ni (II) complex was investigated for the epoxidation of various terminal olefins using t-BuOOH. As shown in Table 4, heterogeneous Ni (II) complex effectively catalyzes the oxidation of various allergens. Conditions used: injector temperature, 230 °C; detector temperature, 260 °C, injection volume, 0.1 μL; and column, isothermal 90 °C for styrene and 80 °C for α-methyl styrene. Conditions used for the other alkenes: 60 °C (3 min),
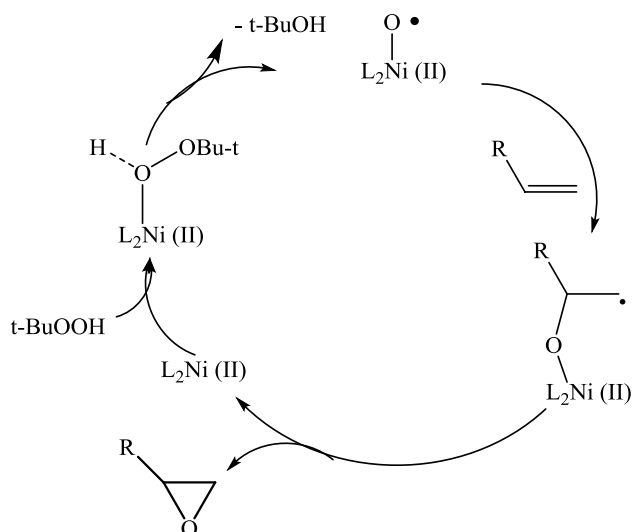
Scheme 2 A proposed mechanism for the epoxidation of styrene with TBHP in the presence of heterogeneous Ni (II) complex

Table 6 Recycling of the heterogeneous nano-catalyst for epoxidation of styrene

Run	T ($^{\circ}$C)	Yield %
1	r.t.	91
2	r.t.	91
3	r.t.	90
4	r.t.	90
5	r.t.	88

Reactions were performed in EtOAC (3 ml) with styrene

(1.0 mmol), catalyst (2 mol% based on Ni), t-BuOOH (2 mmol)

5 °C min^{-1}, 170 °C (2 min), 20 °C min^{-1}, 200 °C (10 min) [46]. The following formula was used for calculation of TON and TOF: TON = mmol of converting alkene/mmol Ni and TOF = TON/time of reaction.

The present study on the catalytic oxidation of alkenes by t-BUOOH in the presence of heterogeneous Ni (II) complex showed that the system with TON (45–47) exhibits high catalytic efficiency. Also, the catalytic activity of heterogeneous Ni (II) complex showed excellent catalytic activity reaching a TOF of 15–15.66 h^{-1} at conversion of 90–94% and selectivity higher than 95% in the epoxidation of terminal alkenes (Table 4).

The efficiency of Ni (II) complex was compared with previously reported results (Table 5) [48–52]. All the reaction which is mentioned in Table 5 have long reaction times and low yields (Table 5, entries 1–6) while our reaction conditions showed a shorter reaction time as well as excellent yield (Table 5, Entry 7).

A proposed mechanism for the epoxidation of styrene was suggested according to the literature [47]. As shown in Scheme 2, the heterogeneous Ni (II) complex, designated as L$_2$Ni (II), takes up TBHP to form L$_2$Ni (II)$^{...}$OOBut adduct which further coordinates to substrate to bring the oxidant and the substrate closer to each other. Now, this intermediate leads to the formation of an epoxide and regeneration of catalyst.

The reusability of the catalyst

To investigate the recyclability of the heterogeneous Ni (II) complex, the heterogeneous nano-catalyst was completely washed with ethanol and dichloromethane and reused in repeated epoxidation reactions with styrene by adding fresh reactants (Table 6). In each run, No nickle was detected in the filtrates by AAS. Therefore, it is obvious that the heterogeneous nano-catalyst worked well for up to five cycles with no considerable decrease in the reactivity (conversion: from 91 to 88%).

Conclusions

Ni (II) salen complex was covalently anchored onto CPGO and characterized by FT-IR, XRD, TGA, TEM and nitrogen adsorption at room temperature. This heterogeneous nano-catalyst showed good catalytic activity and selectivity toward the epoxidation of olefins. Catalytic tests showed that the heterogeneous Ni (II) complex is the most active with t-BUOOH as the oxidant in DCM as the solvent. The catalyst can be recovered and reused five runs without any significant decrease in reactivity.

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