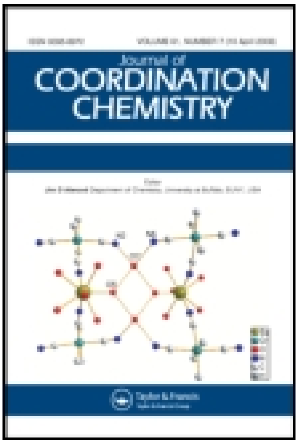
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:20
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis, characterization, and immobilization of nickel(II) tetradentate Schiff-base complexes on clay as heterogeneous catalysts for the oxidation of cyclooctene

Abolfazl Bezaatpour [a] , Mandana Amiri [b] & Vahdat Jahed [c]

[a] Department of Chemistry, Faculty of Basic Science , University of Mohaghegh Ardabili 179 , Ardabil, Iran

[b] Department of Chemistry , Payame Noor University (PNU) , Ardabil, Iran

[c] Department of Chemistry , Semnan University , Semnan, Iran

Published online: 25 May 2011.

To cite this article: Abolfazl Bezaatpour , Mandana Amiri & Vahdat Jahed (2011) Synthesis, characterization, and immobilization of nickel(II) tetradentate Schiff-base complexes on clay as heterogeneous catalysts for the oxidation of cyclooctene, Journal of Coordination Chemistry, 64:10, 1837-1847, DOI: 10.1080/00958972.2011.582582

To link to this article: http://dx.doi.org/10.1080/00958972.2011.582582

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing,

Journal of Coordination Chemistry
Vol. 64, No. 10, 20 May 2011, 1837–1847

Synthesis, characterization, and immobilization of nickel(II) tetradentate Schiff-base complexes on clay as heterogeneous catalysts for the oxidation of cyclooctene

ABOLFAZL BEZAATPOUR*†, MANDANA AMIRI‡ and VAHDAT JAHED§

†Department of Chemistry, Faculty of Basic Science, University of Mohaghegh Ardabili 179, Ardabil, Iran
‡Department of Chemistry, Payame Noor University (PNU), Ardabil, Iran
§Department of Chemistry, Semnan University, Semnan, Iran

(*Received 20 February 2011; in final form 24 March 2011*)

Nickel(II) tetradentate Schiff-base complexes of N,N′-(bis(pyridin-2-yl)formylidene) ethane-1,2-diamine (L1), N,N′-(bis(pyridin-2-yl)formylidene)cyclohexane-1,2-diamine (L2), N,N′-(bis(pyridin-2-yl)formylidene)benzene-1,2-diamine (L3), N,N′-(bis(pyridin-2-yl)formylidene)*meso*-stilben-1,2-diamine (L4), and N,N′-(bis(pyridin-2-yl)formylidene)propane-1,3-diamine (L5) were synthesized, characterized, and immobilized on sodium montmorillonite. The complexes were characterized by IR spectroscopy, diffuse reflectance spectra (DRS), and atomic absorption spectroscopy (AAS). IR and DRS data of the heterogeneous catalysts show that the Ni(II) complexes were physically entrapped within the sodium montmorillonite clay. The supported complexes show good catalytic activity for the epoxidation of cyclooctene using *tert*-butylhydroperoxide (TBHP) as oxygen source in acetonitrile. The Ni-catalyzed oxidation proceeds with 62.3% selectivity for epoxidation with 69% conversion for supported [*Ni*(*L5*)].

Keywords: Immobilization; Heterogeneous catalyst; Ni(II) Schiff-base complex; Oxidation; Montmorillonite

1. Introduction

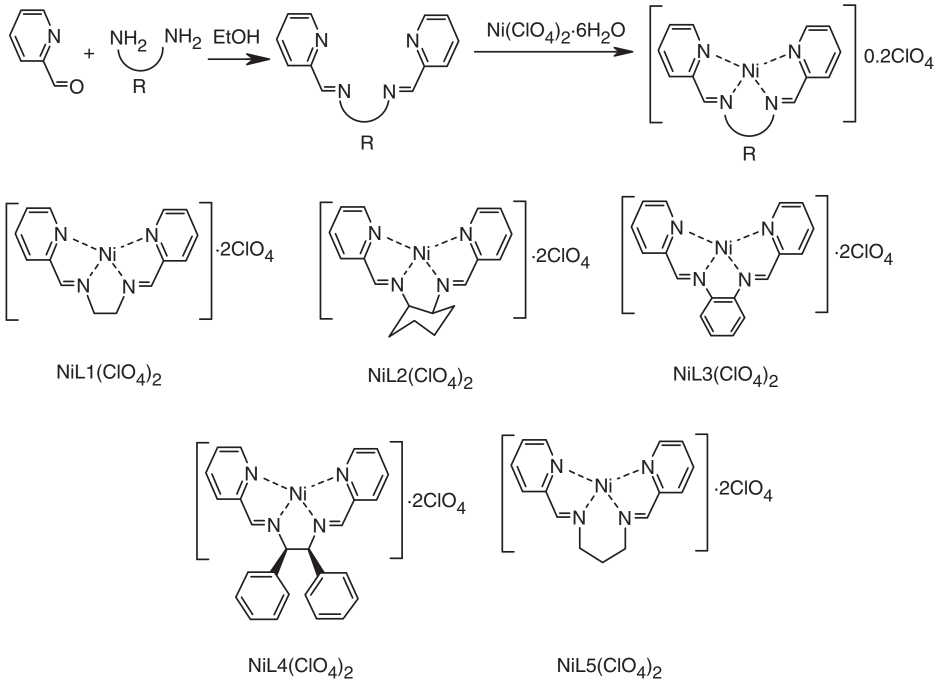
Transition metal complexes are powerful homogeneous catalysts in the oxidation of organic compounds by various oxygen donors such as NaClO, H_2O_2, *tert*-butylhydroperoxide (TBHP), and PhIO [1–3]. Catalytic oxidation of olefins is important for the synthesis of fine chemicals. Epoxides have value in synthetic organic chemistry and chemical technology [4–7]. Schiff-base complexes have been used as homogeneous catalysts in epoxidation of olefins, oxidation of alkanes, alcohols and thiols, electrochemical investigations, amine oxidation, and biological studies [8–11]. Biological and catalytic reactivity investigations of Ni(II) complexes of chelating ligands incorporating pyridine, imidazole, and imine donors have increased [12].

Heterogenization of homogeneous catalysts onto solid supports has advantages such as long catalytic life, easy separation, thermal stability, high selectivity, and easy

---

*Corresponding author. Email: bezaatpour@uma.ac.ir

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2011.582582



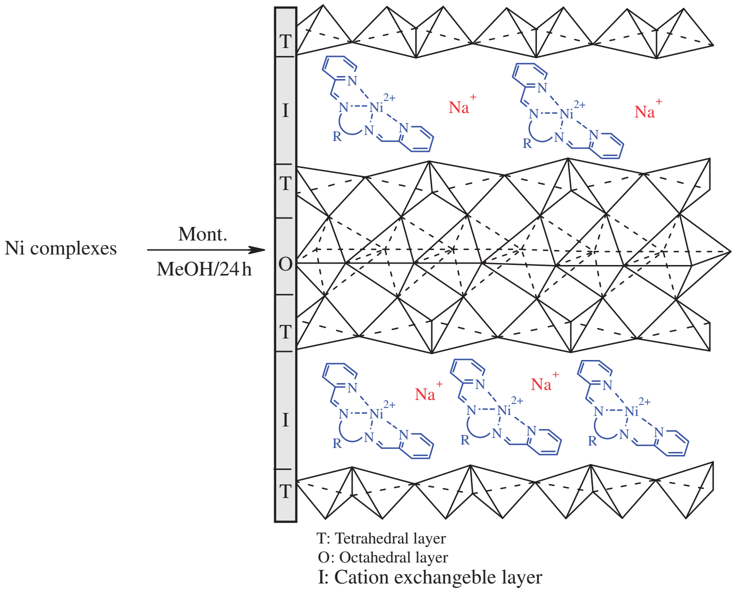
Scheme 1. Nickel(II) Schiff base complexes.

recyclability [13, 14]. The efficiency of heterogenized catalysts has been found to be high in comparison to unsupported catalysts because the aggregation of catalysts reduces efficiency [15].

A general strategy for converting a homogeneous process into a heterogeneous one is to anchor the soluble catalyst on to large surface inorganic supports [16, 17]. Many different solid supports such as metal oxide [18], zeolite [19], and aluminophosphate [20] have been used. Mixed metal exchanged zeolites, ion exchanged resins [21], and polymerized complexes [22] have been applied in liquid phase epoxidation of olefins [23]. Recent immobilization of catalysts on clay-based materials such as montmorillonite, zeolites, and bentonite appear to be a fantastic method of hetrogenising homogeneous catalysts [24]. Montmorillonite has attached the most interest and is a widely used adsorbent for organic and inorganic compounds. A large variety of metal complexes are intercalated by exchange procedure [25].

We have reported the synthesis, characterization, and catalytic reactivity of vanadium(IV) and Cu(II) Schiff base complexes in our earlier work [6, 26].

In this manuscript, montmorillonite is used as the host for immobilization of several Ni(II) complexes with N,N′-(bis(pyridin-2-yl)formylidene)ethane-1,2-diamine (L1), N,N′-(bis(pyridin-2-yl)formylidene)propane-1,2-diamine (L2), N,N′-(bis(pyridin-2-yl) formylidene)benzene-1,2-diamine (L3), N,N′-(bis(pyridin-2-yl)formylidene)cycohexane-1,2-diamine (L4), and N,N′-(bis(pyridin-2-yl)formylidene)*meso*-stilben-1,2-diamine (L5) (schemes 1 and 2). The resulting materials have been characterized using different techniques and been tested for the selective epoxidation of cyclooctene using TBHP as oxidant.



Scheme 2. Preparation of heterogeneous catalysts.

2. Experimental

2.1. *Materials and physical measurements*

All materials were commercial reagent grade with highest purity and were applied as received. Solvents were purified using known procedures. In this study, 1,2-Ethylenediamine, 1,3-propanediamine, 1,2-cyclohexanediamine, 1,2-diaminobenzene, and 2-pyridine carbaldehyde were purchased from Merck chemical company. Sodium montmorillonite was obtained from Fluka. Cyclooctene and cyclooctene epoxide were purchased from Aldrich Chemical Company. ^{1}H-NMR spectra were recorded using a Bruker FT NMR 500 (500 MHz) spectrophotometer ($CDCl_3$ and $(CD_3)_2SO$). Elemental analyses (carbon, hydrogen, and nitrogen) were performed using a Heraeus Elemental Analyzer CHN-O-Rapid (Elementar-Analysesysteme, GmbH). Atomic absorption analysis was carried out on a Shimadzu 120 spectrophotometer. The purity of the solvents, cyclooctene, and analysis of the oxidation products determined with a Shimadzu GC-170A gas chromatograph (GC) with a capillary column and flame ionization detector (FID). Column temperature was programmed between 180°C and 200°C ($2°C\,min^{-1}$). Nitrogen was used as carrier gas ($40\,mL\,min^{-1}$) at injection temperature. FT-IR spectra were obtained with a Shimadzu 8400S spectrophotometer in KBr pellets. The UV-Vis spectra were recorded using a Shimadzu UV-2101PC spectrophotometer. Diffuse reflectance spectra (DRS) were taken by a Scinco 4100 from 200 to 1100 nm using $BaSO_4$ as reference.

2.2. *Synthesis of Schiff bases*

The Schiff bases were prepared by the reaction of meso-1,2-diphenyl-1,2-ethylenediamine [27], 1,2-ethylenediamine, 1,3-propanediamine, 1,2-orthophenylenediamine, and

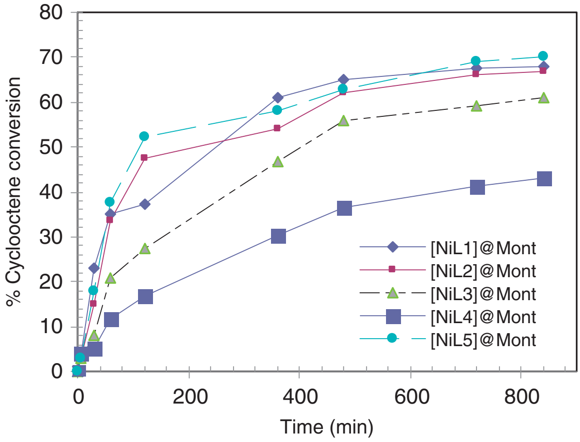


Figure 1. Effect of reaction time on catalytic oxidation of cyclooctene [cyclooctene] : [TBHP] = 1 : 1 at 2 mol L^{-1} and 80°C.

1,2-cyclohexanediamine (2 mmol) with two equivalents of pyridine-2-carboxaldehyde (4 mmol) in ethanol according to literature procedures [28, 29]. Analytical data were in good agreement with literature data. For preparation of N,N′-(bis(pyridin-2-yl)formylidene)*meso*-stilben-1,2-diamine (L5), meso-1,2-diphenyl-1,2-ethylenediamine (0.424 g, 2 mmol) and pyridine-2-carboxaldehyde (0.428 g, 4 mmol) were mixed, stirred, and refluxed in 45-mL absolute ethanol for 6 h. Then, the mixture was cooled and the yellow precipitate collected by filtration, washed with ethanol, and dried in a desiccator. Yield: 0.42 g (76%). Anal. Calcd for $C_{26}H_{22}N_4$: C, 79.97; H, 5.68; and N, 14.35. Found: C, 79.87; H, 5.65; and N, 14.27. IR (KBr, cm^{-1}): 1653 [ν(C=N)]. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.5 (s, 2H, PyCH=N), 7.5–8 (m, 8H, Py), and 7–7.5 (m, 10H, Ar), (scheme 1).

2.3. *Synthesis of [Ni(L1-5)](ClO$_4$)$_2$*

All the complexes were prepared by the reaction of L1, L2, L3, L4, and L5 with an equivalent amount of $Ni(ClO_4)_2{\cdot}6H_2O$ in methanol. *Caution!* Although no problems were encountered in this study, perchlorate salts containing organic ligands are potentially explosive. Only a small amount of the material should be prepared and it should be handled with care.

[Ni(L1)](ClO$_4$)$_2$. To a hot ethanolic solution (50 mL) of $Ni(ClO_4)_2{\cdot}6H_2O$ (1.094 g, 3 mmol) N,N′-(bis(pyridin-2-yl)formylidene)ethane-1,2-diamine (L1) (0.714 g, 3 mmol) was added, and the mixture was vigorously stirred for 80 min under reflux. The resulting green precipitate was collected by filtration, washed with ethanol and ether, and dried in air. Yield of [Ni(L1)](ClO$_4$)$_2$: 1.092 g (73.5%). Anal. Calcd for $C_{14}H_{14}N_4Cl_2O_8Ni$ (%): C, 33.94; H, 2.83; N, 11.31; and C/N, 3.00. Found: C, 33.83; H, 2.73; N, 11.21; and C/N, 3.01. %Ni (atomic absorption) Found (Calcd): 11.63 (11.86). IR (KBr, cm^{-1}): 1651 [ν(C=N)], 1107 [ν(ClO$_4$)], [d → d]: 430 nm.

[Ni(L2)](ClO$_4$)$_2$. [Ni(L2)](ClO$_4$)$_2$ was prepared following the same procedure described for [Ni(L1)](ClO$_4$)$_2$ except that L2 was used instead of L1. Yield: 1.17 g

(71%). Anal. Calcd for $C_{18}H_{20}N_4Cl_2O_8Ni$: C, 39.41; H, 3.64; N, 10.21; and C/N, 3.86. Found: C, 39.23; H, 3.51; N, 10.1; and C/N, 3.88. %Ni (atomic absorption) Found (Calcd): 10.48 (10.71) IR (KBr, cm^{-1}): 1648 [ν(C=N)], 1098 [$\nu(ClO_4)$], and [d → d]: 463 nm.

[Ni(L3)](ClO_4)$_2$. [Ni(L3)](ClO_4)$_2$ was prepared following the same procedure except that L3 was used instead of L1. Yield: 1.00 g (~61.7%). Anal. Calcd for $C_{18}H_{14}N_4Cl_2O_8Ni$: C, 39.85; H, 2.58; N, 10.33; and C/N, 3.86. Found: C, 39.68; H, 2.35; N, 10.53; and C/N, 3.77. %Ni (atomic absorption) Found (Calcd): 10.51 (10.83). IR (KBr, cm^{-1}): 1651 [ν(C=N)], 1108 [$\nu(ClO_4)$], and [d → d]: 420 nm.

[Ni(L4)](ClO_4)$_2$. [Ni(L4)](ClO_4)$_2$ was prepared following the same procedure except that L4 was used instead of L1. Yield: 1.538 g (79%). Anal. Calcd for $C_{26}H_{22}N_4Cl_2O_8Ni$: C, 48.18; H, 3.4; N, 8.65; and C/N, 5.57. Found: C, 47.95; H, 3.27; N, 8.82; and C/N, 5.44. %Ni (atomic absorption) Found (Calcd): 8.83 (9.06) IR (KBr, cm^{-1}): 1645 [ν(C=N)], 1103 [$\nu(ClO_4)$], and [d → d]: 480 nm.

[Ni(L5)](ClO_4)$_2$. [Ni(L5)](ClO_4)$_2$ was prepared following the same procedure except that L5 was used instead of L1. Yield: 1.156 g (~75.6%). Anal. Calcd for $C_{15}H_{16}N_4Cl_2O_8Ni$: C, 35.32; H, 3.14; N, 10.99; and C/N, 3.21. Found: C, 35.01; H, 3.23; N, 11.23; and C/N, 3.12. %Ni (atomic absorption) Found (Calcd): 11.33 (11.51) IR (KBr, cm^{-1}): 1643 [ν(C=N)], 1097 [$\nu(ClO_4)$], and [d → d]: 434 nm.

2.4. *Preparation of heterogeneous catalysts: [Ni(L1)]@Mont, [Ni(L2)]@Mont, [Ni(L3)]@Mont, [Ni(L4)]@Mont and [Ni(L5)]@Mont*

Ni(II) Schiff-base complex (0.85 g) was dissolved in 15 mL hot methanol and slowly added to 1 g of sodium montmorillonite in 10 mL methanol. The mixture was heated and stirred for 48 h under inert atmosphere. The resultant hot mixture was filtered, washed with hot methanol, and then Soxhlet extracted with a mixture of 1 : 1 methanol and acetone to remove unreacted Ni(II) complex. The resultant solid was filtered, washed with hot methanol, and dried at 60°C under vacuum. [Ni(L1)]@Mont; Anal. Found: C, 5.07; H, 7.47; N, 1.72; and C/N, 2.94; %Ni (atomic absorption): 1.83; IR (KBr, cm^{-1}): 1649 [ν(C=N)], and d → d: 431 nm. [Ni(L2)]@Mont; Anal. Found: C, 6.62; H, 7.17; N, 1.68; and C/N, 3.94; %Ni (atomic absorption): 1.78; IR (KBr, cm^{-1}): 1647 [ν(C=N)], d → d: 461 nm. [Ni(L3)]@Mont; Anal. Found: C, 7.22; H, 6.84; N, 1.88; C/N, and 3.84; %Ni (atomic absorption): 1.91; IR (KBr, cm^{-1}): 1649 [ν(C=N)], d → d: 418 nm. [Ni(L4)]@Mont; Anal. Found: C, 7.76; H, 7.35; N, 1.43; and C/N, 5.42; %Ni (atomic absorption): 1.43; IR (KBr, cm^{-1}): 1643 [ν(C=N)], d → d: 479 nm. [Ni(L5)]@Mont; Anal. Found: C, 5.34; H, 9.44; N, 1.75; and C/N, 3.05; %Ni (atomic absorption): 1.73; IR (KBr, cm^{-1}): 1641 [ν(C=N)], d → d: 435 nm.

2.5. *Catalytic oxidation of cyclooctene*

Oxidation of cyclooctene using various homogeneous and heterogeneous catalysts was carried out in a 25 mL Schlenk tube. All glassware was oven-dried prior to use. The system was purged with argon. In a typical experiment, a mixture of catalyst (1.34×10^{-4} mol), freshly distilled acetonitrile (10 mL), 20 mmol freshly distilled cyclooctene, and 20 mmol of TBHP was refluxed for 8 h. After filtration (heterogeneous catalysts), the solid was washed with acetonitrile. The filtrate was then subjected to GC analysis.

3. Results and discussion

3.1. *Characterization of catalysts*

Tetradentate N_4-type Schiff bases were obtained by the reaction of meso-1,2-diphenyl-1,2-ethylenediamine, 1,2-ethylenediamine, 1,3-propanediamine, 1,2-orthophenylenediamine, and 1,2-cyclohexanediamine (2 mmol) with two equivalents of pyridine-2-carboxaldehyde. IR spectra of the ligands show C=N stretch at 1641–1651 cm^{-1}. The Ni(II) complexes have C=N stretches centered at $1655 \pm 5\,cm^{-1}$ which shift approximately 8–10 cm^{-1} to lower wavenumber upon coordination. The absorbance at 1100 cm^{-1} is assigned for the perchlorate of complexes. IR spectra of heterogeneous catalysts at 1641–1649 cm^{-1} are assigned to C=N stretch [30–32]. The C=N stretch of heterogeneous catalysts with slightly different wavenumbers show that the complexes are physically entrapped within the clay. The overall geometries of the Ni(II) complexes have been deduced from band positions in electronic spectra [32]. Electronic absorptions of Ni(II) complexes at 420–480 nm can be attributed to d–d transitions, in agreement with square-planar Ni(II) complexes [33]. Comparison of DRS of the heterogeneous Ni(complex)@mont catalysts and electronic absorption bands of the Ni(II) complexes show that the Ni(II) complexes are physically entrapped within the sodium montmorillonite clay. The immobilization process was confirmed by the color change of the clays from light cream to light green. The suspended materials were filtered, washed with methanol, and dried in air. The heterogeneous catalysts were stable in solvents such as methanol, dichloromethane, acetonitrile, and water as they released no Ni(II) complexes even after stirring in these solvents for several days.

The molecular formulas of the complexes have been assigned from their elemental analyses. The chemical compositions confirmed the purity and stoichiometry of the neat and entrapped complexes. The nickel contents of the heterogeneous catalyst and complexes were estimated using atomic absorption spectroscopy (AAS). The chemical analyses of the samples reveal the presence of organic matter with a C/N ratio roughly similar to that for neat complexes. The analytical data of each heterogeneous catalyst show C : N : Ni molar ratios almost close to those calculated for the Ni(II) complexes.

3.2. *The catalytic activity of heterogeneous catalysts for the oxidation of cyclooctene by TBHP*

Ni(II) heterogeneous catalysts were tested for oxidation of cyclooctene. The conversion increases with increasing reaction time but levels off after 8 h (figure 1). The percent conversion increases with increasing molar ratio of [cyclooctene] : [TBHP] from 0.5 to 1.0 and decreasing from 1.0 to 2.0. The conversion of cyclooctene was maximum at 1 : 1 molar ratio of [cyclooctene] : [TBHP] (figure 2). The effect of reaction temperature on conversion of cyclooctene was studied by varying the temperature in 10 mL

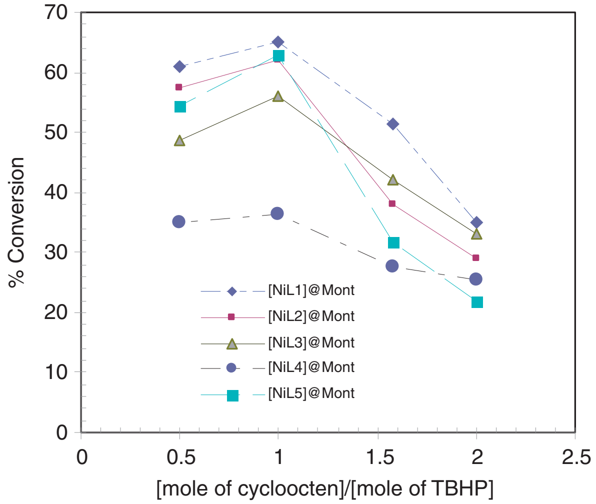


Figure 2. Effect of [cyclooctene] : [TBHP] ratio on cyclooctene conversion at 80°C.

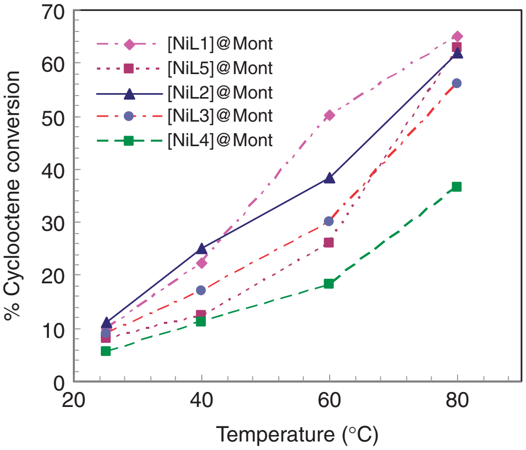


Figure 3. The effect of reaction temperature on conversion of cyclooctene at $2\,\mathrm{mol\,L^{-1}}$ and [cyclooctene] : [TBHP] = 1 : 1.

acetonitrile at $2\,\mathrm{mol\,L^{-1}}$ [cyclooctene] and [TBHP] and 1.34×10^{-4} mol catalyst. The conversion increases with increasing temperature from 25°C to 80°C (figure 3). Typical catalytic reaction conditions involve acetonitrile (10 mL) solutions at 78 ± 2°C, cyclooctene (20 mmol), TBHP (20 mmol), and catalyst (1.34×10^{-4} mol) stirred for 8 h. The final solution exhibited no color and no presence of metal was detected in the solution, confirmed by AAS. Under these conditions, cyclooctene was oxidized to a mixture of epoxide, ketone, alcohol, and peroxide. The product distributions in the oxidation of cyclooctene by homogeneous and heterogeneous catalysts are shown in tables 1 and 2. Homogeneous complexes form oxo and peroxo dimeric and other polymeric species that deactivate catalysts. This is solved by immobilizing of the metal complexes the solid supports, where dimeric and polymeric species will not form.

Table 1. Results of catalytic oxidation of cyclooctene with TBHP catalyzed by Ni(II) complexes in 10 mL acetonitrile, with 1.34×10^{-4} mol catalyst for 8 h at reflux with cyclooctene and TBHP = 20 mmol.

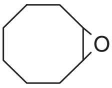
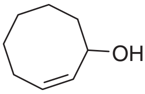
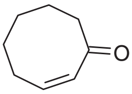
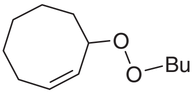
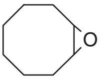
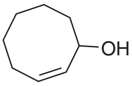
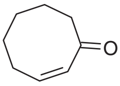
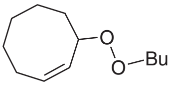
		Selectivity (%)			
Catalyst	Conversion (%)				
$[Ni(L1)](ClO_4)_2$	47	63.5	19.9	9.1	7.5
$[Ni(L2)](ClO_4)_2$	41	48.8	24.5	21.8	4.9
$[Ni(L3)](ClO_4)_2$	32	55.4	20.7	19.3	4.6
$[Ni(L4)](ClO_4)_2$	37	59.7	17.6	14.7	8
$[Ni(L5)](ClO_4)_2$	45	53.8	21.8	17.9	6.5
$Ni(ClO_4)_2$	14	19.4	26.5	46.3	7.8

Table 2. Catalytic oxidation of cyclooctene with TBHP catalyzed by heterogeneous Ni(II) complexes in 10 mL acetonitrile, with 1.34×10^{-4} mol catalyst for 8 and 12 h at reflux with cyclooctene and TBHP = 20 mmol.

			Selectivity (%)			
Catalyst	Time (h)	Conversion (%)				
[Ni(L1)]@Mont[a]	8	65	62.5	27.3	5.2	5
[Ni(L1)]@Mont	12	67.6	65	23.6	4.6	6.8
[Ni(L1)]@Mont[b]	8	62	63	29	3.5	4.5
[Ni(L1)]@Mont[c]	8	60	62.2	29.6	3.1	5.1
[Ni(L2)]@Mont[a]	8	62.1	55	27	11	7
[Ni(L2)]@Mont	12	66	53	25.5	15	6.5
[Ni(L2)]@Mont[b]	8	60.1	52.9	29.6	10.8	6.7
[Ni(L2)]@Mont[c]	8	58.2	53.6	26.8	11.5	8.1
[Ni(L3)]@Mont[a]	8	56	57	18	19	6
[Ni(L3)]@Mont	12	59	51	26.9	14	8.1
[Ni(L3)]@Mont[b]	8	54.2	54.7	20.4	17.6	7.3
[Ni(L3)]@Mont[c]	8	53.2	53.2	19.8	16.9	10.1
[Ni(L4)]@Mont[a]	8	36.5	70	15.9	11.2	2.9
[Ni(L4)]@Mont	12	41.2	64	21.2	14.8	–
[Ni(L4)]@Mont[b]	8	34.3	69	14.4	12.5	4.1
[Ni(L4)]@Mont[c]	8	33.8	68.2	15.3	10.8	5.7
[NI(L5)]@Mont[a]	8	63	66	19	9.9	5.1
[Ni(L5)]@Mont	12	69	62.3	22.3	12.5	2.9
[Ni(L5)]@Mont[b]	8	61.5	65.1	18.1	10.5	6.3
[Ni(L5)]@Mont[c]	8	60.3	64	16.2	15	4.8

[a]First reuse; [b]Second reuse; [c]Third reuse

Comparison of tables 1 and 2 shows that heterogeneous catalysts gave higher percent conversion of cyclooctene than their corresponding metal complexes. The Ni-catalyzed oxidation proceeds with 62.3% selectivity for epoxidation with 69% conversion for [Ni(L5)]@Mont (table 2). The product selectivity for the oxidation of cyclooctene catalyzed by heterogeneous Ni(II) complexes is shown in figure 4. Catalytic reactions are not affected by light. In the absence of catalysts or neat clay, (15–20%) oxidation occurs with low conversion.

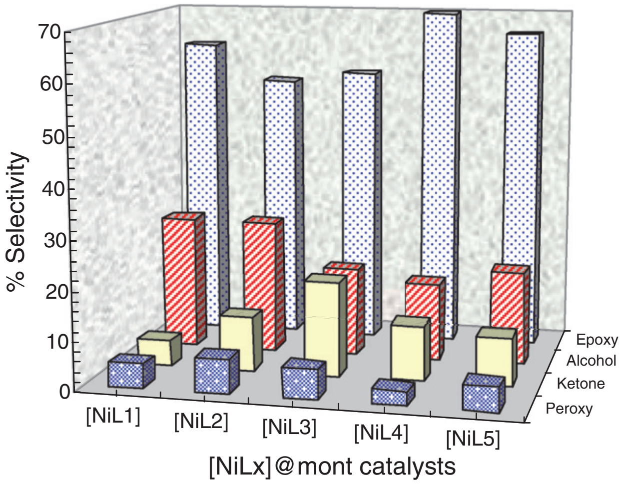


Figure 4. Product selectivity for oxidation of cyclooctene catalyzed by heterogeneous Ni(II) complexes at 2 mol L^{-1}, 80°C and [cyclooctene] : [TBHP] = 1 : 1.

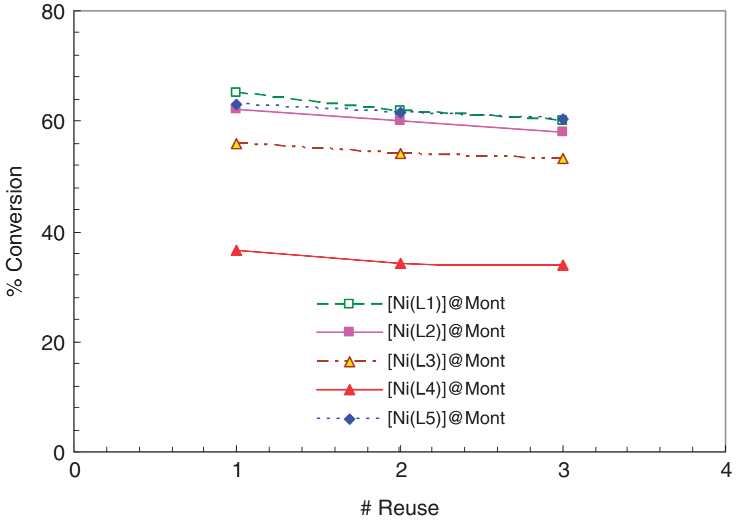


Figure 5. Conversion *vs.* reuse of heterogeneous Ni(II) catalysts.

The most important advantage of these heterogeneous Ni(II) catalysts is the increase of complex stability in reaction media and easy reuse of the catalyst after simple filtration. The catalytic activity and selectivity of immobilized Ni(II) complexes do not change after three times of reuse (figure 5). The catalysts can be reused after washing with CH_2Cl_2 and drying under vacuum at 80°C.

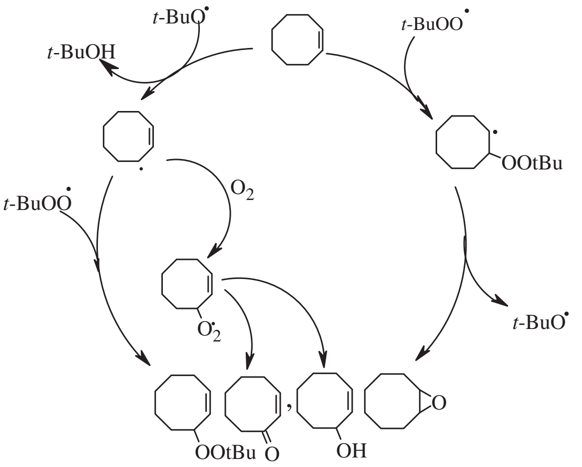
The transition metal-catalyzed oxidation of alkenes in the presence of TBHP can proceed via two mechanisms, one involving high valent metal oxo/peroxo species and the other involving free radical intermediates [34]. For the present catalyst systems, Ni(II) is reduced to Ni(I) by decomposition of TBHP to *t*-BuOO$^{\bullet}$ and proton.

$$\mathit{mont}\text{-LNi}^{2+} + t\text{-BuOOH} \longrightarrow \mathit{mont}\text{-LNi}^{+} + t\text{-BuO}\dot{\text{O}} + \text{H}^{+}$$

$$\mathit{mont}\text{-LNi}^{+} + t\text{-BuOOH} \longrightarrow \mathit{mont}\text{-LNi}^{2+} + t\text{-BuO}^{\bullet} + \text{OH}^{-}$$

$$2t\text{-BuOOH} \longrightarrow t\text{-BuO}\dot{\text{O}} + t\text{-Bu}\dot{\text{O}} + \text{H}_2\text{O}$$

$$2t\text{-BuOO}^{\bullet} \longrightarrow 2t\text{-Bu}\dot{\text{O}} + \text{O}_2$$



Scheme 3. Suggested mechanism for catalytic oxidation of cyclooctene by TBHP.

The proton would balance the charge deficiency of Ni(II)/Ni(I) conversion, while *t*-BuOO• subsequently adds to cyclooctene and leads to the corresponding epoxide, alcohol, ketone, and peroxide. A suggested mechanism for catalytic oxidation of cyclooctene by heterogeneous catalyst in the presence of TBHP is shown in scheme 3.

4. Conclusion

We report the synthesis and characterization of five new heterogeneous catalysts prepared by the immobilization of tetradentate N_4 type Ni(II) Schiff-base complexes into pillared sodium montmorillonite clay matrix. The DRS and IR data show that these complexes are physically supported in the matrix. These catalysts are heterogeneous and efficient chemoselective catalysts for the epoxidation of cyclooctene with TBHP as oxygen source in acetonitrile. These catalysts can be reused three times without significant decrease in catalytic activity.

Acknowledgment

The authors are grateful to the Research Council of Mohaghegh-e-Ardabili University for their financial support.

References

[1] T. Linker. *Angew. Chem. Int. Ed. Engl.*, **38**, 2060 (1997).
[2] M. Palucki, G.J. McCormick, E.N. Jacobsen. *Tetrahedron Lett.*, **36**, 5457 (1995).
[3] X. Zhou, J. Shearer, S.E. Rokita. *J. Am. Chem. Soc.*, **122**, 9046 (2000).
[4] J. Jiang, R. Li, H. Wang, Y. Zheng, H. Chen, J. Ma. *Catal. Lett.*, **120**, 221 (2008).
[5] A. Puzari, J.B. Baruah. *J. Mol. Catal. A: Chem.*, **187**, 149 (2002).
[6] D.M. Boghaei, A. Bezaatpour, M. Behzad. *J. Mol. Catal. A: Chem.*, **245**, 12 (2006).
[7] J. Jiang, K. Ma, Y. Zheng, S. Cai, R. Li, J. Ma. *Appl. Clay Sci.*, **45**, 117 (2009).
[8] W. Zhang, J.L. Loebach, S.R. Wilson, E.N. Jacobsen. *J. Am. Chem. Soc.*, **112**, 2801 (1990).
[9] S. Shahrokhian, Z. Kamalzadeh, A. Bezaatpour, D.M. Boghaei. *Sens. Actuators B. Chem.*, **109**, 278 (2005).
[10] W. Zhang, E.N. Jacobsen. *J. Org. Chem.*, **56**, 2296 (1991).
[11] E. Tsuchida, K. Oyaizu. *Coord. Chem. Rev.*, **237**, 213 (2003).
[12] (a) S. Chattopadhyay, M.G.B. Drew, A. Ghosh. *Polyhedron,* **26**, 3513 (2007); (b) R.I. Kureshy, N.H. Khan, S.H.R. Abdi, P. Iyer, A.K. Bhatt. *J. Mol. Catal. A: Chem.*, **130**, 41 (1998); (c) J.G. Muller, L.A. Kayser, S.J. Paikoff, V. Duarte, N. Tang, R.J. Perez, S.E. Rokita, C.J. Burrows. *Coord. Chem. Rev.*, **185–186**, 761 (1999).
[13] M. Salavati-Niasari, E. Zamani, M. Bazarganipour. *Appl. Clay Sci.*, **38**, 9 (2007).
[14] (a) Q.H. Fan, Y.M. Li, A.S.C. Chan. *Chem. Rev.*, **102**, 3385 (2002); (b) C.D. Nunes, M. Pillinger, A.A. Valente, A.D. Lopes, I.S. Goncalves. *Inorg. Chem. Commun.*, **6**, 1228 (2003).
[15] (a) C.M. Andersson, K. Karabelas, A. Hallbery. *J. Org. Chem.*, **50**, 3891 (1983); (b) H.A. Dick, R.F. Heck. *J. Org. Chem.*, **40**, 1083 (1975).
[16] C.A. McNamara, M.J. Dixon, M. Bradley. *Chem. Rev.*, **102**, 3275 (2002).
[17] C. Baleizão, B. Gigante, D. Das, M. Álvaro, H. Garcia, A. Corma. *J. Catal.*, **223**, 106 (2004).
[18] S. Imamura, H. Sakai, M. Shono, H. Kanai. *J. Catal.*, **177**, 72 (1998).
[19] J.C. van der Waal, H. van Bekkum. *J. Mol. Catal. A: Chem.*, **124**, 137 (1997).
[20] M.S. Rigutto, H.V. Bekkum. *J. Mol. Catal. A: Chem.*, **81**, 77 (1993).
[21] H. Brunner, A. Stumpf. *Monatsh. Chem.*, **125**, 485 (1994).
[22] K.C. Gupta, H.K. Abdulkadir, S. Chand. *J. Mol. Catal. A: Chem.*, **202**, 253 (2003).
[23] A. Corma, A. Fuerte, M. Iglesias, F. Sanchez. *J. Mol. Catal. A: Chem.*, **107**, 225 (1996).
[24] (a) J. Jiang, K. Ma, Y. Zheng, S. Cai, R. Li, J. Ma. *Appl. Clay Sci.*, **45**, 117 (2009); (b) J. Gao, L. Lu, W. Zhou, G. Gao, M. He. *J. Porous Mater.*, **15**, 127 (2008).
[25] M. Boufatit, H. Ait-Amar, W.R. Mc Whinnie. *Desalination*, **223**, 366 (2008).
[26] D.M. Boghaei, M. Behzad, A. Bezaatpour. *J. Mol. Catal. A: Chem.*, **241**, 1 (2005).
[27] M.N.H. Irving, R.M. Parkins. *J. Inorg. Nucl. Chem.*, **27**, 270 (1965).
[28] M.S. Ray, R. Bhattacharya, S. Chaudhuri, L. Righi, G. Bocelli, G. Mukhopadhyay, A. Ghosh. *Polyhedron*, **22**, 617 (2003).
[29] B. Chiswell. *Inorg. Chim. Acta*, **12**, 195 (1975).
[30] C. Flego, L. Galasso, R. Millini, I. Kiricsi. *Appl. Catal., A*, **168**, 323 (1998).
[31] G. Coudurier, F. Lefebvre. *Catalyst Characterisation Physical Techniques for Solid Materials*, pp. 11–44, Plenum Press, New York (1994).
[32] P. Salerno, M.B. Asenjo, S. Mendiroz. *Thermochim. Acta*, **379**, 101 (2001).
[33] S.H. Rahaman, H.K. Fun, B.K. Ghosh. *Polyhedron*, **24**, 3091 (2005).
[34] U.G. Singh, R.T. Williams, K.R. Hallam, G.C. Allen. *J. Mol. Catal. A: Chem.*, **178**, 3405 (2005).