

Nickel(macrocycle) Complexes Immobilized within Montmorillonite and MCM-41 as Catalysts for Epoxidation of Olefins

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(Received: 10 August 2004; in final form: 24 February 2005)

Key words: epoxidation, macrocycle ligand, MCM-41, montmorillonite, nickel complex, olefins

Abstract

In this study, we have investigated the role of immobilized Ni(II) complexes with macrocyclic ligands of 1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane (L) and 1,8-dibenzyl-1,3,6,8,10,13-hexaazacyclotetradecane (L') within montmorillonite and MCM-41 as catalysts for epoxidation of cyclohexene, cyclopentene, norbornene, styrene and α -methylstyrene with tert-butylhydroperoxide (TBHP). The yield of epoxide in a given period depends mainly on the reaction rate of the complex with TBHP which is greatly affected by the alkene structure, ligand type and solid support. No desorption was observed during the course of reaction. Some mechanistic points will be presented in this article.

Introduction

The search for finding the new epoxidation catalysts of olefins has been the subject of much research during the last few decades [1]. Metalloporphyrins are well known for their ability to catalyze selective oxidation processes with a variety of oxygen donors [2–5]. It was found that transfer of oxygen atoms to organic substrates would be catalyzed by nonporphyrin transition metal complexes. These complexes have attracted considerable attention as model system for nonheme enzymatic oxidation reactions [5–10].

A few investigations have been focused on nickel compounds as alkenes oxidation catalysts [11, 12]. Mononuclear nickel complexes as oxidation catalysts have been developed by Koola and Kochi [7], Burrows and co-workers [13] and others [14–17]. Recently Feringa and his co-workers have studied the effect of dinuclear Ni(II) complexes in the epoxidation of unsubstituted alkenes [19]. Mitra and his collaborators also have studied the role of schiff-base complexes of Mn and Ni in the epoxidation of olefins [18]. Epoxidation of β -methyl styrene has been promoted with various Ni(II) multiaza macrocycle complexes as well [10].

Immobilization of porphyrin within a solid support has recently been reported as innovation in catalytic properties of such compounds. It was anticipated that immobilization would make the catalyst to be handled

and separated easily from medium as well as possibly stabilizing or modifying the catalytic performance by influencing chemoselectivity, regioselectivity and shapeselectivity of the reaction [19].

In order to heterogenize homogeneous catalysts in this study, we have investigated the role of immobilization of Ni(II) complexes with macrocyclic ligands of 1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane(L) and 1,8-dibenzyl-1,3,6,8,10,13-hexaazacyclotetradecane (L') between silicate layers of montmorillonite and nanoreactors of MCM-41 in the epoxidation of olefins.

Experimental

All the chemicals were obtained from Merk and Fluka. The products were analyzed by GC and GC-Mass using an Agilent 6890 series, with FID detector, HP-5.5% phenylsiloxane capillary column and Agilent 5973 network, mass selective detector HP-5, MS 6890 network GC system, respectively. Cyclic voltammograms were studied by 746VA trace Analyzer Metrohm linked 747 VA stand Metrohm. X-ray diffraction (XRD) data were recorded by with Rigaku D/Max-2550 PC diffractometer (Japan) with nickel filter and CuK(α) radiation at 40 kV and 30 mA. UV–visible spectra of sample solutions were recorded in the range of 200–800 nm with a Philips UV-visible spectrophotometer Pu 8800. FT-IR spectra were recorded on a Bruker Tensor 27 spectrophotometer.

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Immobilization of Ni(macrocycle)²⁺/montmorillonite

Nickel complex with ligand (1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane) and (1,8-dibenzyl-1,3,6,8,10,13-hexaazacyclotetradecane) were prepared according to the reported procedure [20]. Therefore 4.4 g of Ni(macrocycle)(ClO₄)₂ in hot methanol (100 ml) was slowly added to 6 g of montmorillonite in 100 ml methanol. The resultant mixture was refluxed for 24 h under N₂ atmosphere. The hot mixture was filtered and solid was washed with hot methanol. It was then Soxhlet extracted with a mixture of 1:1 chloroform and methanol in order to remove unreacted NiL complex. The AAS determination showed that the percentage of Ni in two solids were 0.28% and 27%, respectively.

Immobilization of Ni(macrocycle) complex within MCM-41

MCM-41 was prepared according to the procedure described previously [21]. 0.1 g of Ni(macrocycle)(ClO₄)₂ in 10 ml methanol was slowly added to 1 g of MCM-41 in 10 ml methanol. The resultant mixture was refluxed for 24 h. The mixture was then filtered and washed with solvent. AAS determination showed that the percentage of Ni in two solids were 0.49% and 0.45%, respectively.

Oxidation of cyclohexene, general procedure

A mixture of 0.3 g catalyst Ni²⁺/mont. and 25 mmol of olefin was stirred under N₂ at 40 °C for 30 min in 5 ml CH₂Cl₂ under reflux condition, then 16 mmol TBHP was slowly added (in 5 min) to the reaction mixture and then it was refluxed for 6 h. After filtration, the solid was washed with CH₂Cl₂. The filtrate was then subjected to GC and GC-MASS for analysis.

Results and Discussion

Effect of Ni(L)²⁺ complexes immobilized between silicate layers of montmorillonite in the epoxidation of cyclohexene is shown in Table 1 and Figure 1. We have included the effect of Ni²⁺/mont. in this Table in order to make the comparison more convenient. Inspection of

Table 1. Oxidation of cyclohexene with TBHP catalyzed by immobilized Ni²⁺ and Ni(macrocycle) complexes between silicate layers of montmorillonite

Run	Type of catalyst	Conversion (%)	Product distribution		TON ^b
			Epoxy (%)	Others ^a (%)	
1	Ni ²⁺ /mont.	4	33	67	15
2	[Ni(L)] ²⁺ /mont.	32	47	53	350
3	[Ni(L')] ²⁺ /mont.	35	77	23	394

Reaction conditions: cyclohexene: 25 mmol, TBHP: 16 mmol, solvent: CH₂Cl₂: 5 ml, time: 6 h, under reflux.^a Others: Alcohol, ketone and alkyl peroxide. ^b TON is mmol of products /mmol of Ni in catalyst.

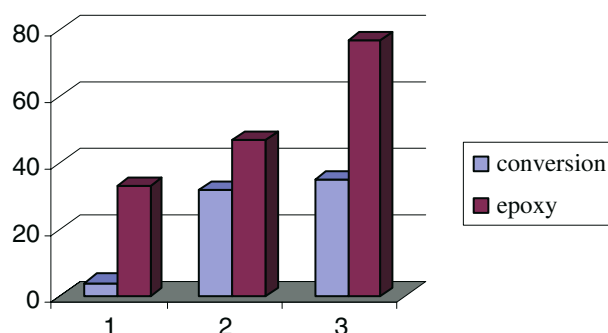


Figure 1. Oxidation products of cyclohexene with TBHP in the presence of immobilized Ni²⁺(macrocycle) complexes.

Table 1 reveals that compared to Ni²⁺/mont. the conversion percentages have increased by a factor of 8 to 9. The allylic site oxidation has taken place simultaneously with the formation of 2-cyclohexene-1-ol, 2-cyclohexene-1-one and 1-tert-butylperoxy-2-cyclohexene as by products.

The role of solvents on yields and products distribution are shown in Table 2 and Figure 2. Solvent has an important effect on the reaction rate and selectivity. In fact, the search for finding the best solvent is a superiority of heterogeneous catalysis systems over the homogenous media which cannot be easily handled in a desirable solvent.

Table 3 and Figure 3 present the oxidation results of different olefins with TBHP as oxidant in CH₂Cl₂ in the presence of NiL²⁺/mont. as catalyst. It is evident that

Table 2. Effect of solvent on the oxidation of cyclohexene with TBHP catalyzed by NiL²⁺/mont.

Run	Solvent	Conversion (%)	Product Distribution		TON
			Epoxy (%)	Others (%)	
4	CCl ₄	5	50	50	25
5	CHCl ₃	8	100	–	88
6	CH ₂ Cl ₂	32	50	50	350
7	CH ₃ CN	32	41	59	350
8	C ₆ H ₁₀	24	46	54	257

Reaction conditions are similar to Table 1.

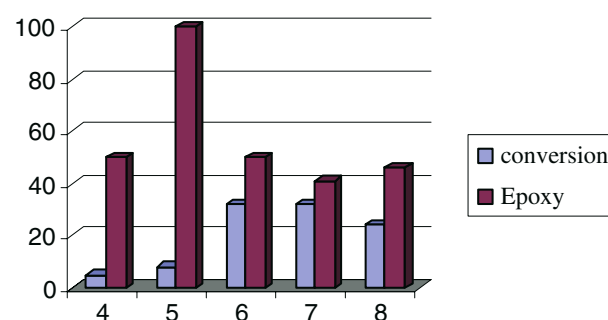


Figure 2. Effect of solvent on cyclohexene oxidation products distribution.

Table 3. Oxidation of olefins with TBHP catalyzed by $\text{NiL}^{2+}/\text{mont.}$ in CH_2Cl_2

Run	Substrate	Conversion (%)	Product distribution		TON
			Epoxy (%)	Others (%)	
9	Cyclohexene	32	50	50	350
10	Cyclopentane	33	50	50	350
11	norbornene	58	100	–	634
12	Styrene	17	100	–	207
13	α -methylstyrene	19	100	–	186

Reaction conditions are similar to Table 1.

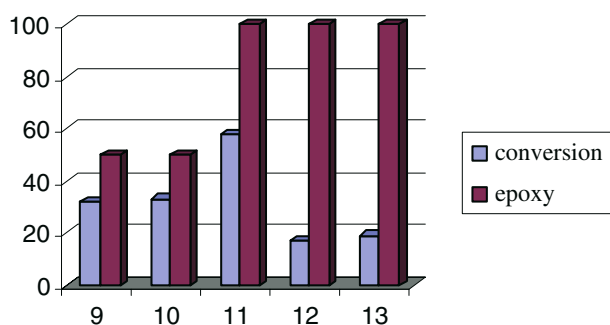


Figure 3. Oxidation of olefins with TBHP catalyzed by $\text{NiL}^{2+}/\text{mont.}$ in CH_2Cl_2 .

while norbornene shows the most reactivity and selectivity toward the epoxidation, cyclopentene and cyclohexene take part in two competing reactions either through double bond and formation of the corresponding epoxides or via allylic positions and resulting in the relevant alcohol, ketone and peroxide. Although the rate of styrene and α -methylstyrene have increased partially, the formation of the corresponding epoxides as the sole products seem interesting since in similar reactions, some other oxidation by-products are generated [22].

When we used Ni^{2+} complexes with macrocycle ligand 1,8-dibenzyl-1,3,6,8,10,13-hexaazacyclotetradecane (L') and studied its effect on the epoxidation of norbornene, we observed an abrupt enhancement in conversion percentage from 58 to 80 percent with simultaneous formation of norbornene oxide in 100 percent (Figure 4, Table 4).

Effect of time on the reaction results were studied by running the norbornene reaction in 2, 4, 6, and 8 h. As we can see in Table 5 and Figure 5, increasing time from 2 to 8 h has increased the conversion percentages from 1 to 58. No conversion enhancement was observed beyond 8 h.

To see the effect of solid support on the oxidation, we substituted the montmorillonite with MCM-41. Table 6 and Figure 6 exhibit the oxidation results. It is evident that compared to montmorillonite, the reactivity and TON's of norbornene and cyclohexene have increased by a factor of 1.5 to 3. Effect of time for epoxidation of norbornene with immobilized Ni

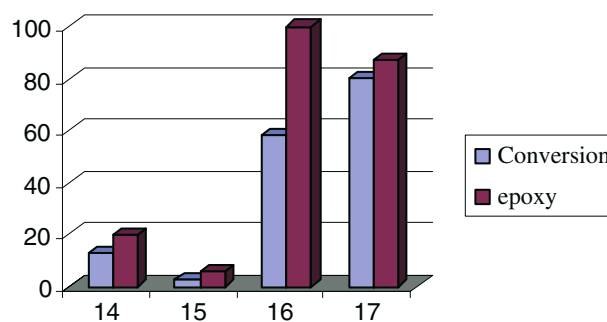


Figure 4. Oxidation products of norbornene with TBHP catalyzed by montmorillonite immobilized $\text{Ni}^{2+}/\text{mont.}$ and $\text{Ni}^{2+}(\text{macrocycle})/\text{mont.}$ complexes.

Table 4. Oxidation of norbornene with TBHP catalyzed by $\text{NiL}^{2+}/\text{mont.}$ and $\text{NiL}^{2+}/\text{mont.}$ in CH_2Cl_2

Run	Type of catalyst	Conversion (%)	Product distribution		TON
			Epoxy (%)	Others (%)	
14	mont.	13	20	80	–
15	$\text{Ni}^{2+}/\text{mont.}$	3	6	94	3.3
16	$[\text{Ni}(\text{L})]^{2+}/\text{mont.}$	58	100	–	635
17	$[\text{Ni}(\text{L})]^{2+}/\text{mont.}$	80	87	13	915

Reaction conditions: norbornene: 2 mmol, catalyst: 0.3 g, oxidant: TBHP: 2 mmol, solvent: CH_2Cl_2 : 5 ml, under reflux.

Table 5. Effect of time on products distribution in the oxidation of norbornene catalysed by $\text{NiL}^{2+}/\text{mont.}$

Run	Time	Conversion (%)	Product distribution	TON
			Epoxy (%)	
18	2	1	100	22
19	4	5	100	55
20	6	33	100	361
21	8	58	100	635
22	10	58	100	635

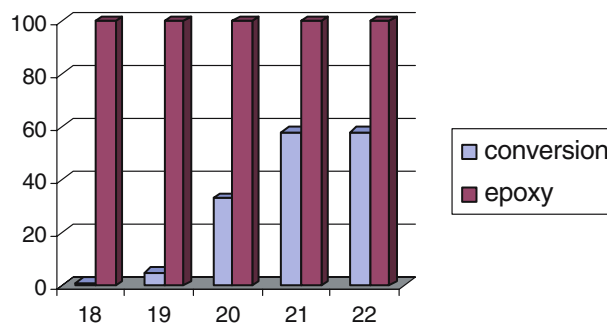


Figure 5. Effect of time on products distribution in the oxidation of norbornene catalysed by $\text{NiL}^{2+}/\text{mont.}$

Table 6. Effect of Ni macrocycle complex/MCM-41 in the epoxidation of norbornene and cyclohexene

Run	Catalyst	Substrate	Conversion (%)	Epoxide (%)	TON
23	MCM-41	Norbornene*	7	100	–
24	Ni ²⁺ /MCM-41		43	96	24
25	NiL/MCM-41		85	100	1201
26	NiL'/MCM-41		90	100	1246
27	MCM-41	Cyclohexene	4	23	–
28	Ni-MCM-41		23	34	12.5
29	NiL/MCM-41		65	29	975
30	NiL'/MCM-41		75	41	975

Reaction conditions: Catalyst: 0.2 g, Solvent: CH₃CN (5 ml), under reflux TBHP: 24 mmol; Substrate: 20 mmol; TON = mmol products/mmole Ni complex.

*Other products for cyclohexene: alcohol, ketone, alkyl peroxide.

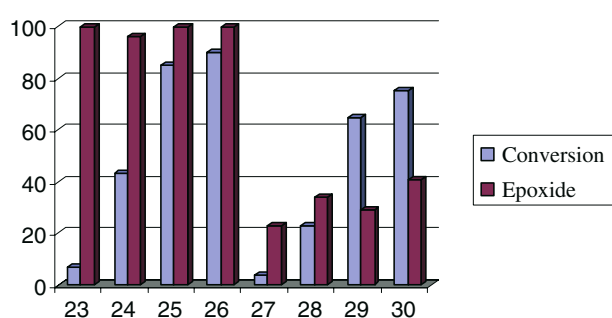


Figure 6. Epoxidation of norbornene by immobilized Ni macrocycle complexes/MCM-41.

Table 7. Effect of time in the epoxidation of norbornene in the presence of NiL' complex/MCM-41

Run	Time (h)	Conversion (%)	Epoxide (%)	TON
31	2	5	100	71
32	4	20	100	283
33	6	85	100	1201
34	8	90	100	1262

Reaction conditions: Norbornene: 20 mmol, TBHP: 24 mmol, Solvent: CH₃CN (5 ml), Under reflux.

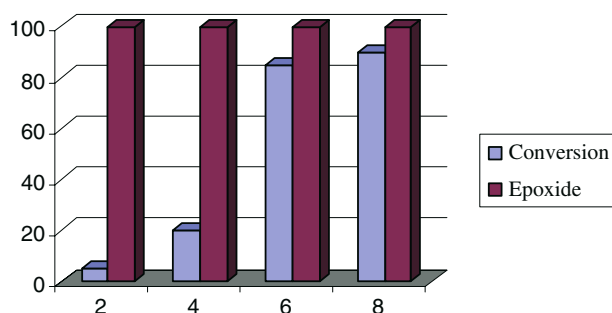


Figure 7. Effect of time in epoxidation of norbornene by immobilized NiL' complex/MCM-41.

macrocycle complexes in MCM-41 are also given in Table 7 and Figure 7.

In order to make insight into the reaction mechanism, we examined the following steps:

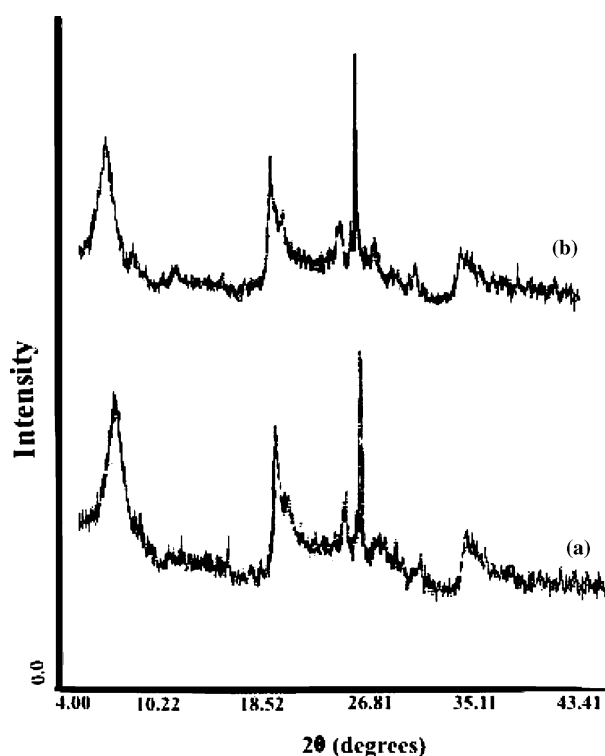


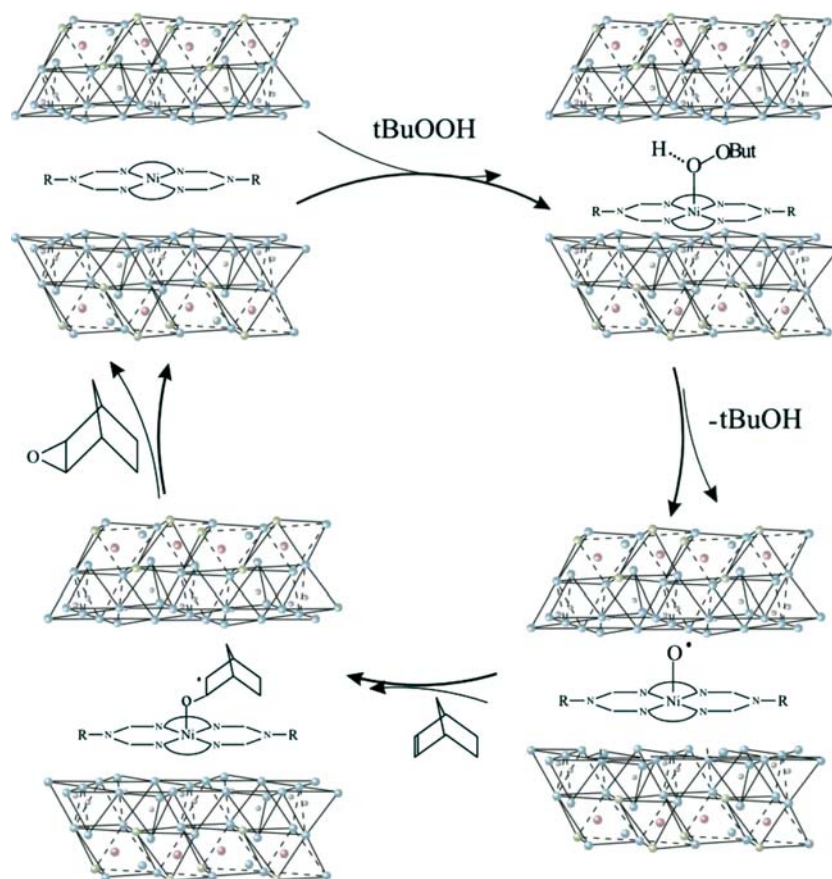
Figure 8. X-ray powder diffraction patterns of (a) montmorillonite and (b) Ni(L)²⁺/montmorillonite.

(1) The oxidation potentials of $E_{\text{Ni(II)/Ni(III)}}^0$, $E_{\text{NiL}^{2+}/\text{NiL}^{3+}}^0$ and $E_{\text{NiL}'^{2+}/\text{NiL}'^{3+}}^0$ were determined to be 1.35, 1.15 and 0.56 V, respectively. It can be seen that the [Ni(L)²⁺]/mont. and NiL'/MCM-41 system with the least oxidation potential provides the most conversion percentage yield (see Tables 1, 4 and 6). These results are consistent with those reported by M. Paik Suh and his coworkers for Ni(II) complexes with macrocyclic ligands[20].

It seems also worthwhile to point out to the XRD pattern of NiL²⁺/mont., which shows the interlayer distance increases from 12.73 Å to 13.13 Å compared to Ni²⁺/mont. (Figure 8). It can be concluded that NiL²⁺ is accommodated between layers as shown in Scheme 1.

(2) The UV-Vis is electronic spectra of NiCl₂·6H₂O, NiL(ClO₄)₂ and NiL'(ClO₄)₂ in acetonitrile are recorded in Figure 9. The spectrum of NiCl₂ in acetonitrile shows typical absorption at 620, 320 and 200 nm attributable to d-d transition (low intensity) and charge transfer with high intensity. By coordination of macrocyclic ligands to Ni(II) ions, the octahedral complexes of Ni(II) species have been changed to square planar complexes because the UV spectra of NiL(ClO₄)₂ and NiL'(ClO₄)₂ are consistent with those reported before [20, 23].

(3) The progress of epoxidation reaction with NiL²⁺ was monitored by UV spectroscopy. The results are presented in Figure 10. It can be seen that compared to original spectrum A, changes to B and finally C occur immediately after addition of a drop of TBHP and then leaving the system under reflux conditions for 6 h respectively. These results might be attributed to the



Scheme 1. Proposed mechanism for the epoxidation of norbornene with Ni(L)²⁺/mont.

rapid coordination of TBHP with Ni(II) ion and subsequent elimination of tert-BuOH and formation of [L(Ni(III)-O•)] intermediate.

On the basis of these results, the reaction mechanism can be formulated as shown in Scheme 1. Reaction of Nickel(macrocycle) with TBHP leads to LNi^{III}-O• intermediate. Subsequent addition of this radical to norbornene generates a second alkyl radical intermediate which finally forms the corresponding epoxide via a reductive elimination reaction. In the case of cyclopentene and cyclohexene, allylic hydrogen abstraction

and formation of the corresponding alcohol, ketone and tert-butyl peroxide compete with the epoxidation process. That the similar competition reaction does not occur in norbornene arises from the instability of norbornene radical and violation of Bredt's rule which we have explained in some details in our recent publication [24].

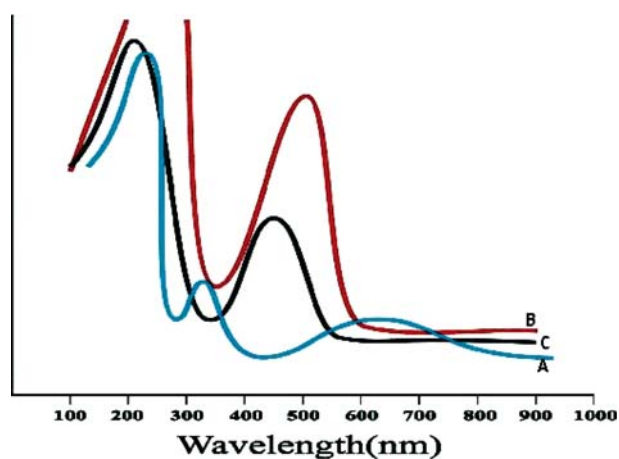


Figure 9. UV-Vis spectra of (A) NiCl₂·6H₂O, (B) NiL(ClO₄)₂, (C) NiL'(ClO₄)₂.

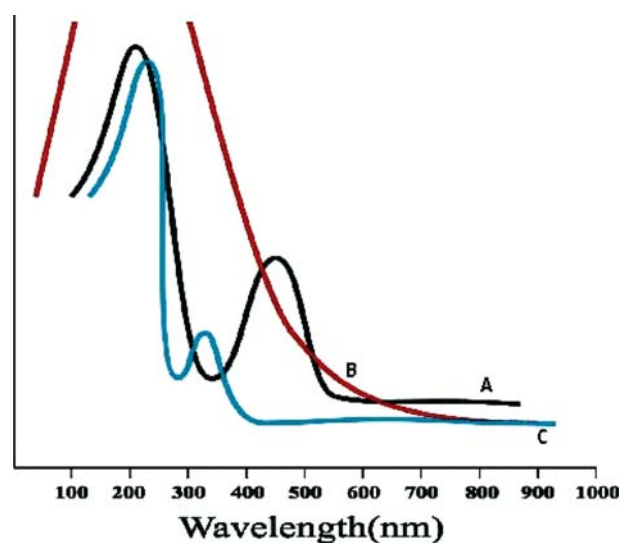


Figure 10. UV-Vis spectra of (A) Ni(L)²⁺, (B) after addition THBP, (C) After 6 h reflux.

The operation of a radical mechanism in the presence of Ni(II) cyclam complexes has been studied brilliantly by Burrows and his co-workers who used different mechanistic techniques including the competition studies of para-substituted styrenes relative to styrene and found the Hammett slope $\rho^+ = -0.82$. The poor correlation with the Hammett parameter σ and the low magnitude of ρ^+ are both consistent with the intermediacy of $\text{RCH}_2^\delta \dots \text{H}^\delta \dots \text{O}^\delta \dots - \text{Ni}^{\text{III}} - \text{L}$ and its polarized mesomeric form $\text{RCH}_2^{\delta+} \dots \text{H}^\delta \dots \text{O} - \text{Ni}^{\text{III}} - \text{L}$ [22]. Although we did not study the reaction rates in our system, but the simultaneous formation of both allylic oxidation and epoxidation products from cyclohexene and cyclopentene unequivocally support the performance of a radical mechanism.

Compared to the reported results using Ni(II) multi-azamacrocyclic complexes as homogenous catalysts for oxidation of trans- β -methyl styrene[25], the TON's of our system which were determined as 975 to 1246 (see Table 3) clearly indicate the higher efficiency of heterogeneous system with respect to the homogenous system and seems promising.

Finally, it should be mentioned that there was no desorption during the course of reaction. This was confirmed by testing the filtrate solution and observing no activity for oxidation reaction.

Conclusion

Based on these results we can conclude that Ni(II) complex with macrocycle ligand of 1,8-dimethyl 1,3,6,8,10,13-hexaaza-cyclotetradecane immobilized between silicate layers and MCM-41 is active as catalyst for epoxidation of olefins. By changing this ligand to 1,8-dibenzyl-1,3,6,8,10,13-hexaazacyclotetradecane, the reactivity of the epoxidation of norbornene was increased to 90%. No desorption was observed in all experiments. We recommend our latter catalysis system for catalyzing the epoxidation of olefins in general and particularly for olefins having no allylic hydrogens available for hydrogen abstraction by radical intermediates.

Acknowledgements

The authors gratefully acknowledge Alzahra University for financial support.

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