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Synthesis, characterization and catalytic oxidation of cyclohexene with molecular oxygen over host (montmorillonite-K10)/guest (nickel(II) complexes of 12- and 13-membered diaza dioxa Schiff-base macrocyclic ligand) nanocatalyst (HGN)

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Abstract

Nickel(II) complexes of 12- and 13-membered diaza dioxa Schiff-base macrocyclic ligand, 1,4-diaza-7,10-dioxacyclododeca-1,3-diene, $H_2[12]1,3$-dieneN$_2$O$_2$; 2,3-dimethyl-1,4-diaza-7,10-dioxacyclododeca-1,3-diene, $(CH_3)_2[12]1,3$-dieneN$_2$O$_2$; 2,3-diphenyl-1,4-diaza-7,10-dioxacyclododeca-1,3-diene, $(C_6H_5)_2[12]1,3$-dieneN$_2$O$_2$; 2,4-dimethyl-1,5-diaza-8,11-dioxacyclotrideca-1,4-diene, $(CH_3)_2[13]1,4$-dieneN$_2$O$_2$; 2,4-diphenyl-1,5-diaza-8,11-dioxacyclotrideca-1,4-diene, $(C_6H_5)_2[13]1,4$-dieneN$_2$O$_2$ were entrapped into an montmorillonite-K10 (denoted as K10) by simultaneous/pillaring encapsulation method. In this method the simultaneous encapsulation also occurred but the complex, also dissolved in methanol, was added to the clay dispersion. All materials were characterised by FT-IR, DRS, UV–vis and atomic absorption spectroscopy (AAS). In all cases the nickel(II) 12- and 13-membered diaza dioxa Schiff-base complex is mainly physically entrapped within the matrix, although some host–guest interactions with the matrix could be present. The host–guest nanocatalyst; HGN; ($[Ni(R_2[12]1,3$-dieneN$_2$O$_2)]^{2+}$@K10, $[Ni(R_2[13]1,4$-dieneN$_2$O$_2)]^{2+}$@K10; R = H, Me and Ph) is catalytically very efficient as compared to other neat complexes for oxidation of cyclohexene with molecular oxygen as oxidant in the absence of solvent at 70 °C, affording 2-cyclohexene-1-ol and 2-cyclohexene-1-one.
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1. Introduction

Metallomacrocycles in homogeneous solution or immobilized in solid supports are capable of carrying out redox catalysis under ambient conditions [1–8]. In general, heterogeneous rather than homogeneous catalyst metallomacrocycles are desirable for stabilizing the complexes against deactivating dimerization and other destructive processes under oxidizing conditions. We have reported the use of zeolite, and alumina as inorganic matrices for immobilizing copper, nickel, and manganese complex [2–8]. We found that the immobilization processes have been efficient

for improving the catalytic activity of the metallomacrocycles studied. In most cases, the selectivity of a desirable product was lowered. However, we believe that the preparation of a particular product can be modulated by the combination of the support and the metallomacrocycles. On the other hand, immobilization of the macrocycles by electrostatic interactions is a limited process because only few charged macrocycles are known.

It was observed that this water-soluble metallomacrocycles are poor catalyst for oxidation reactions. This behavior can be explained by the absence of halogen atoms in the ring macrocycle periphery that would provide high stability of intermediate catalytic active species. Another factor, in our opinion, is the poor solubility of these metallomacrocycles in good non-coordinate solvents, like CH_2Cl_2, which are frequently used in this kind of reaction. Because of this second reason, it is necessary to perform homogeneous catalysis in solvents like methanol, which cannot lead to high catalytic activity, probably

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because such a process is not favorable to the formation of effective active catalytic species [3]. For this purpose the immobilization of the catalyst on a solid support could be away to overcome operational difficulties. Montmorillonite is an interesting support for the immobilization of charged complexes [1]. There are solvent and matrix cooperative effects arising from the clay interlayer environment and from the clay surface that would be interesting to the catalytic point of view. Montmorillonite is a clay mineral belonging to the group of the smectites. Chemically speaking, it is a hydrated aluminosilicate of idealized formulation $Al_2Si_4O_{10}(OH)_2$ (mineral pyrophyllite) and its crystalline structure are generated by the encapsulation of a gibbsite layer (polymorph of $Al(OH)_3$) with two silica layers [9,10].

In this presentation, we have attempted to use montmorillonite as the host material for immobilization of nickel(II) complexes of 12- and 13-membered diaza dioxa Schiff-base macrocyclic ligand, 1,4-diaza-7,10-dioxacyclododeca-1,3-diene, $H_2[12]1,3$-dieneN$_2$O$_2$; 2,3-dimethyl-1,4-diaza-7,10-dioxacyclododeca-1,3-diene, $(CH_3)_2[12]1,3$-dieneN$_2$O$_2$; 2,3-diphenyl-1,4-diaza-7,10-dioxacyclododeca-1,3-diene, $(C_6H_5)_2$[12]1,3-dieneN$_2$O$_2$; 2,4-dimethyl-1,5-diaza-8,11-dioxacyclotrideca-1,4-diene, $(CH_3)_2[13]1,4$-dieneN$_2$O$_2$; 2,4-diphenyl-1,5-diaza-8,11-dioxacyclotrideca-1,4-diene, $(C_6H_5)_2$[13]1,4-dieneN$_2$O$_2$ (Scheme 1). To continue we report here the oxidation of cyclohexene catalyzed by [Ni(R$_2$[12]1,3-dieneN$_2$O$_2$)]$^{2+}$@K10 and [Ni(R$_2$[13]1,4-dieneN$_2$O$_2$)]$^{2+}$@K10. The reaction was performed in the presence of the atmospheric pressure of molecular oxygen in the absence of solvent at 70 °C, without the use of any special oxidant or conductant. Under these reaction conditions, 2-cyclohexene-1-ol and 2-cyclohexene-1-one were

product. The effect of temperature and the amount of catalyst used on the reactivity and product selectivity were discussed.

2. Experimental

2.1. Materials and physical measurements

All the materials were of commercial reagent grade. Bifunctional diketone (glyoxal, 2,3-buthanedione, 2,4-pentanedione, 1,3-diphenyl-1,3-propanedione, benzil) and 1,8-diamino-3,6-dioxaoctane were prepared from Merk Chemical Company; montmorillonite-K10 was obtained from Fluka. Cyclohexene was distilled under nitrogen before using. After completely destroying the framework of clay supported with hot and concentrated H_2SO_4, sodium, aluminum and nickel were analyzed by atomic absorption spectrophotometer (AAS, Perkin-Elmer 4100–1319), and SiO_2 was determined by gravimetric analysis. FT-IR spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. The electronic spectra of the neat complexes were taken on a Shimadzu UV-Vis scanning spectrometer (Model 2101 PC). Diffuse reflectance spectra (DRS) were registered on a Shimadzu UV/3101 PC spectrophotometer the range 1500–2000 nm, using MgO as reference. The elemental analysis (carbon, hydrogen and nitrogen) of the materials was obtained from Carlo ERBA Model EA 1108 analyzer. The stability of the supported catalyst was checked after the reaction by UV–vis and possible leaching of the complex was investigated by UV–vis in the reaction solution after filtration of the montmorillonite. [Ni(1,8-diamino-3,6-dioxaoctane)](ClO_4)$_2$ was obtained by the reaction of 1,8-
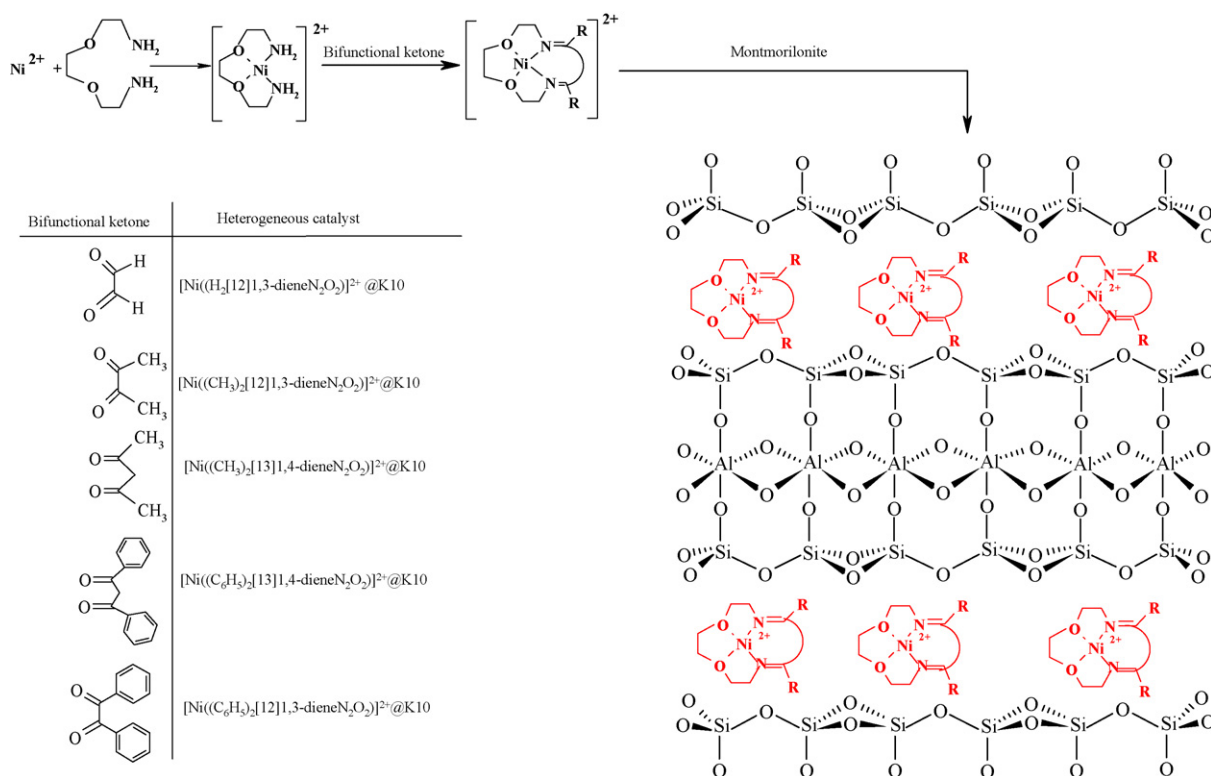
Scheme 1.

diamino-3,6-dioxaoctane with $Ni(ClO_4)_2 \cdot 6H_2O$ in methanol and recrystallized from water [11]. The products then subjected to GC and GC-mass analysis using a Philips pu-4400 chromatograph (1.5 m, 3% OV-17 column), varian 3400 chromatograph (2.5 m, DB-5 column) coupled with a QP finnigan MATINCOF 50, 19 eV, respectively.

2.2. Preparation of $[Ni(R_2[12]1,3\text{-}dieneN_2O_2)](ClO_4)_2$ and $[Ni(R_2[13]1,4\text{-}dieneN_2O_2)](ClO_4)_2$ complexes

To a solution of (1,8-diamino-3,6-dioxaoctane) nickel(II) percholorate (5 mmol); [Ni(1,8-diamino-3,6-dioxaoctane)] $(ClO_4)_2$; in MeOH (100 cm^3), solution of bifunctional diketone (glyoxal, 2,3-butanedione, 2,4-pentanedione, 1,3-diphenyl-1,3-propanedione, benzil; 5 mmol) in MeOH (50 cm^3) was added and the resulting mixture was stirred for *ca.* 26 h at reflux. The solid product was filtered off, washed with CH_3Cl and dried over fused $CaCl_2$ in desiccators. The product was crystallized from hot MeOH. Anal. Calcd. for [Ni(H$_2$[12]1,3-dieneN$_2$O$_2$)](ClO$_4$)$_2$: C, 22.46; H, 3.30; N, 6.55; C/N, 3.43; Ni, 13.71. Found: C, 22.24; H, 3.17; N, 6.71; C/N, 3.31; Ni, 13.50%; Yield: ~60%; νC=N, 1610 cm^{-1}; d $\leftrightarrow$ d, 493 nm (in MeOH solution); μ_B, −0.008 BM; Λ_M, 254 (Ω^{-1} cm^{-1} M^{-1}). Anal. Calcd. for [Ni((CH$_3$)$_2$[12]1,3-dieneN$_2$O$_2$)](ClO$_4$)$_2$: C, 26.34; H, 3.98; N, 6.14; C/N, 4.29; Ni, 12.87. Found: C, 26.17; H, 3.79; N, 6.29; C/N, 4.16; Ni, 12.66%; Yield: ~61%; νC=N, 1608 cm^{-1}; d $\leftrightarrow$ d, 494 nm (in MeOH solution); μ_B, −0.009 BM; Λ_M, 250 (Ω^{-1} cm^{-1} M^{-1}). Anal. Calcd. for [Ni((C$_6$H$_5$)$_2$[12]1,3-dieneN$_2$O$_2$)](ClO$_4$)$_2$: C, 41.41; H, 3.82; N, 4.83; C/N, 8.57; Ni, 10.12. Found: C, 41.26; H, 3.67; N, 4.94; C/N, 8.35; Ni, 10.01%; Yield: ~46%; νC=N, 1614 cm^{-1}; d $\leftrightarrow$ d, 488 nm (in MeOH solution); μ_B, −0.011.75 BM; Λ_M, 248 (Ω^{-1} cm^{-1} M^{-1}). Anal. Calcd. for [Ni((CH$_3$)$_2$[13]1,4-dieneN$_2$O$_2$)](ClO$_4$)$_2$: C, 28.11; H, 4.29; N, 5.96; C/N, 4.72; Ni, 12.49. Found: C, 27.90; H, 4.08; N, 6.10; C/N, 4.57; Ni, 12.27%; Yield: ~53%; νC=N, 1607 cm^{-1}; d $\leftrightarrow$ d, 495 nm (in MeOH solution); μ_B, −0.012 BM; Λ_M, 245 (Ω^{-1} cm^{-1} M^{-1}). Anal. Calcd. for [Ni((C$_6$H$_5$)$_2$[13]1,4-dieneN$_2$O$_2$)](ClO$_4$)$_2$: C, 42.45; H, 4.07; N, 4.72; C/N, 9.00; Ni, 9.88. Found: C, 42.21; H, 3.92; N, 4.87; C/N, 8.67; Ni, 9.69%; Yield: ~42%; νC=N, 1612 cm^{-1}; d $\leftrightarrow$ d, 480 nm (in MeOH solution); μ_B, −0.018 BM; Λ_M, 240 (Ω^{-1} cm^{-1} M^{-1}).

2.3. Preparation of $[Ni(R_2[12]1,3\text{-}dieneN_2O_2)]^{2+}@K10$ and $[Ni(R_2[13]1,4\text{-}dieneN_2O_2)]^{2+}@K10$ (R = H, Me and Ph)

About 0.7 g of $[Ni(R_2[12]1,3\text{-}dieneN_2O_2)](ClO_4)_2$ or $[Ni(R_2[13]1,4\text{-}dieneN_2O_2)](ClO_4)_2$ in hot methanol (10 ml) was slowly added to 1 g of montmorillonite-K10 in 10 ml methanol. The resultant mixture was refluxed for 24 h under nitrogen atmosphere. The hot mixture was filtered and washed with hot methanol. It was then soxhelet extracted with a mixture of 1:1 methanol and chloroform in order to remove unreacted [Ni(1,8-diamino-3,6-dioxaoctane)]$^{2+}$ complex. The blue solid was filtered, washed with methanol and dried at 70 °C under vacuum. The amount of nickel(II)

molecules intercalated into the montmorillonite-K10 was calculated by nitrogen elemental analysis and was found to be ~92 mg/1 g of montmorillonite-K10. Anal. Found for [Ni(H$_2$[12]1,3-dieneN$_2$O$_2$)]$^{2+}$@K10: C, 2.45; N, 0.76; Ni, 1.73; C/N, 3.24; νC=N, 1608 cm^{-1}; d $\leftrightarrow$ d, 491 nm. Anal. Found for [Ni((CH$_3$)$_2$[12]1,3-dieneN$_2$O$_2$)]$^{2+}$@K10: C, 2.97; N, 0.74; Ni, 1.67; C/N, 4.03; νC=N, 1607 cm^{-1}; d $\leftrightarrow$ d, 492 nm. Anal. Found for [Ni((C$_6$H$_5$)$_2$[12]1,3-dieneN$_2$O$_2$)]$^{2+}$@K10: C, 5.95; N, 0.73; Ni, 1.63; C/N, 8.16; νC=N, 1610 cm^{-1}; d $\leftrightarrow$ d, 486 nm. Anal. Found for [Ni((CH$_3$)$_2$[13]1,4-dieneN$_2$O$_2$)]$^{2+}$@K10: C, 3.18; N, 0.74; Ni, 1.64; C/N, 4.29; νC=N, 1606 cm^{-1}; d $\leftrightarrow$ d, 494 nm. Anal. Found for [Ni((C$_6$H$_5$)$_2$[13]1,4-dieneN$_2$O$_2$)]$^{2+}$@K10: C, 6.06; N, 0.72; Ni, 1.61; C/N, 8.40; νC=N, 1610 cm^{-1}; d $\leftrightarrow$ d, 474 nm.

2.4. Oxidation of cyclohexene, general procedure

Generally, 10 cm^3 of cyclohexene and 3.45×10^{-6} mol of heterogeneous catalyst were added to a glass reactor with a gas inlet tube connected to a gas burette and an oxygen storage bottle. The mixture was heated to 70 °C in water bath and stirred with a magnetic stirring bar. The oxidation reactions were performed under atmospheric pressure of molecular oxygen in the absence of solvent, giving 2-cyclohexene-1-ol and 2-cyclohexene-1-one as the major products.

3. Results and discussion

The mononuclear diaza dioxa Schiff-base complexes (Scheme 1) were readily prepared as the main product by the reaction of the (1,8-diamino-3,6-dioxaoctane)nickel(II) with bifunctional diketone in a 1:1 molar ratio. The mononuclear complex can be readily isolated by fractional recrystallization of the product from *ca.* 0.05 M HClO$_4$ aqueous solutions. The molar conductance values of neat complexes (~250 Ω^{-1} mol^{-1} cm^2) were measured in water correspond to 1:2 electrolytes. The overall geometries of macrocyclic complexes have been deduced on the basis of the observed values of the magnetic moments (~−0.008 μ_B) and the band positions in the electronic spectra. The molecular formulae of the complexes have been assigned on the basis of the results of their elemental analyses. A preliminary identification of the metal complexes was made on the basis of their IR spectra, which exhibited no bands characteristic of free primary amine, thus supporting the proposed macrocyclic skeleton (Scheme 1). The nickel contents of the catalysts were estimated by dissolving known amounts of the catalyst in conc. H$_2$SO$_4$ and from these solutions, the nickel contents were estimated using AAS. The chemical compositions confirmed the purity and stoichiometry of the neat and entrapped complexes. 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 complex indicates Ni:C:N molar ratios almost close to those calculated for the mononuclear structure.

The IR spectrum of K10 shows intense and large bands due to the clay structure: in the region 3700–3300 cm^{-1}, which are assigned to the surface hydroxyl groups from the acidic Al–OH

Table 1
Oxidation of cyclohexene with molecular oxygen catalyzed by nickel(II) complexes (reaction condition: 1 atm of O_2; time 8 h; temperature 70 °C; cyclohexene 10 cm^3)

Catalyst	Amount of catalyst (mol)	Conversion (%)	Selectivity (%)	
			2-Cyclohexene-1-ol	2-Cyclohexene-1-one
[Ni(H$_2$[12]1,3-dieneN$_2$O$_2$)](ClO$_4$)$_2$	3.45×10^{-6}	50.4	53.0	47.0
[Ni((CH$_3$)$_2$[12]1,3-dieneN$_2$O$_2$)](ClO$_4$)$_2$	3.45×10^{-6}	45.7	57.8	42.2
[Ni((C$_6$H$_5$)$_2$[12]1,3-dieneN$_2$O$_2$)](ClO$_4$)$_2$	3.45×10^{-6}	58.6	61.4	38.6
[Ni((C$_6$H$_5$)$_2$[12]1,3-dieneN$_2$O$_2$)](ClO$_4$)$_2$	1.72×10^{-6}	47.2	55.1	44.9
[Ni((C$_6$H$_5$)$_2$[12]1,3-dieneN$_2$O$_2$)](ClO$_4$)$_2$	5.17×10^{-6}	56.5	64.5	35.5
[Ni((C$_6$H$_5$)$_2$[12]1,3-dieneN$_2$O$_2$)](ClO$_4$)$_2$	8.62×10^{-6}	40.2	66.9	33.1
[Ni((CH$_3$)$_2$[13]1,4-dieneN$_2$O$_2$)](ClO$_4$)$_2$	3.45×10^{-6}	43.1	54.5	45.5
[Ni((C$_6$H$_5$)$_2$[13]1,4-dieneN$_2$O$_2$)](ClO$_4$)$_2$	3.45×10^{-6}	56.3	60.7	39.3
Ni(ClO$_4$)$_2$·6H$_2$O	3.45×10^{-6}	25.8	43.7	56.3

group [12–14], at 1630 cm^{-1} and in the range 1300–4000 cm^{-1}, from lattice vibrations [12] (asymmetric stretching vibrations of SiO$_2$ tetrahedra) [13]. In addition to these strong bands, the spectra of the new materials obtained also show low intense bands in the 1600–1200 cm^{-1} region, where K10 matrix does not absorb, that are attributed to the nickel(II) complexes. These bands are slightly broader but their wave numbers are almost the same as those of free complex (the differences in their wave numbers are not higher than 4 cm^{-1}). These results suggest that the nickel(II) complexes is physically entrapped within the K10. The absorption bands in the ~570 nm can be attributed to ligand-field transitions. This behavior is compatible with that observed for square-planar nickel(II) complexes with two nitrogen and two oxygen donors [15–19]. The results are attributed to the electronic properties of the substituent group and are supported by similar observations with similar nickel(II) N$_2$O$_2$ macrocycles [15–19].

The immobilization process was characterized by the color change of the clays. In the case of [Ni(R$_2$[12]1,3-dieneN$_2$O$_2$)]$^{2+}$@K10 the change was from light yellow to light blue, with a final color of deep blue in the case of and [Ni(R$_2$[13]1,4-dieneN$_2$O$_2$)]$^{2+}$@K10. The end of the immobilization process was characterized by the disappearance of the characteristic metallo complex solution color by UV–vis analysis.

The solid materials obtained after filtration of the reaction suspension were washed thoroughly with CH$_2$Cl$_2$, CH$_3$OH, and CH$_3$CN and dried at 70 °C. They were found to be very stable in CH$_2$Cl$_2$, CH$_3$OH, CH$_3$CN, cyclohexane, and water as they released no nickel(II) complexes even after stirring in these solvents for several days. FT-IR spectra for heterogeneous catalysts recorded after the third re-use showed band broadening in the 1620–1200 cm^{-1} region, which corresponds to the frequency range where bands due to the complex occur. Contrary, the bands typical for K10 matrix do not show significant changes after the catalytic reaction. These observations suggest that no structural changes of the K10 matrix took place during the consecutive catalytic cycles.

One of the major drawbacks of homogeneous metal complexes as catalysts is their irreversible deactivation due to formation of μ-oxo and μ-peroxo dimeric and other polymeric species especially when using oxidant. This problem may be avoided by isolating the nickel(II) complexes from each other by entrapped within montmorillonite. The conversion increased by several orders of magnitude when the nickel(II) complexes are isolated from each other by entrapped within the interlayer of the montmorillonite (Scheme 1). Since the formation of these bulky dimeric and polymeric species are sterically impossible when the monomeric complex is entrapped and physically confined within the layers of montmorillonite, it was anticipated that entrapped catalysts would be more rugged and can be recycled for use. The data in Tables 1 and 2 support the above hypothesis.

Results of Table 1 and Fig. 1 show the catalytic activity of homogeneous catalysts. Comparing between neat and montmorillonite entrapped complexes (Table 2 and Fig. 2) as catalyst evidence that K10-entrapped catalysts gave higher conversion of cyclohexene than their corresponding neat complexes. The higher activity of entrapped complexes is because of site isolation of the complexes.

The selectivity and activity of this K10-entrapped catalyst on the oxidation of cyclohexene with O$_2$ are given in Table 2 and Fig. 2. At the end of reaction, the catalyst was separated by filtrations, thoroughly washed with solvent and reused under similar conditions by atomic absorption spectroscopy showed no reduction in the amount of nickel; they exhibited slightly lower catalytic activities (0.80%).

To investigate the effect of temperature on the reactivity and product selectivity of catalyst, the oxidations were car-
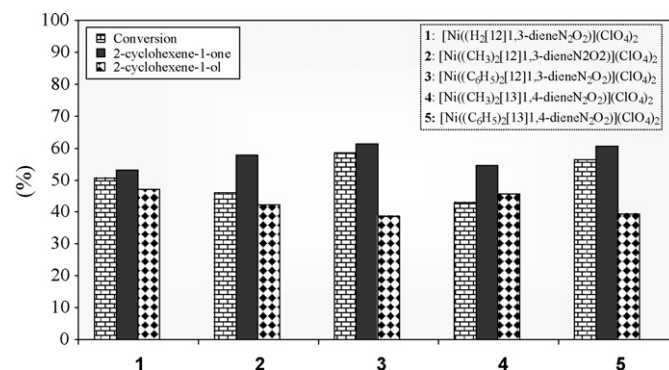

Fig. 1. Conversion and oxidation products distribution of cyclohexene with molecular oxygen over [Ni(R$_2$[12]1,3-dieneN$_2$O$_2$)](ClO$_4$)$_2$ and [Ni(R$_2$[13]1,4-dieneN$_2$O$_2$)](ClO$_4$)$_2$ as catalyst.

Table 2
Oxidation of cyclohexene with molecular oxygen catalyzed by montmorillonite entrapped nickel(II) complexes (reaction condition: 1 atm of O_2; time 8 h; temperature 70 °C; cyclohexene 10 cm^3)

Catalyst	Amount of catalyst (mol)	Temperature (°C)	Conversion (%)	Selectivity (%)	
				2-Cyclohexene-1-ol	2-Cyclohexene-1-one
$[Ni(H_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10	3.45×10^{-6}	70	59.4	38.8	61.2
$[Ni((CH_3)_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10	3.45×10^{-6}	70	53.5	45.5	54.5
$[Ni((C_6H_5)_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10	3.45×10^{-6}	70	70.3	34.6	65.4
$[Ni((C_6H_5)_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10[a]	3.45×10^{-6}	70	69.5	35.5	64.5
$[Ni((C_6H_5)_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10[b]	3.45×10^{-6}	70	68.7	35.9	64.1
$[Ni((C_6H_5)_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10[c]	3.45×10^{-6}	70	67.2	37.0	63.0
$[Ni((C_6H_5)_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10	3.45×10^{-6}	50	10.6	69.3	30.7
$[Ni((C_6H_5)_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10	3.45×10^{-6}	60	18.5	58.2	41.8
$[Ni((C_6H_5)_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10	3.45×10^{-6}	80	34.6	32.6	67.4
$[Ni((CH_3)_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10	3.45×10^{-6}	70	50.2	47.7	52.3
$[Ni((C_6H_5)_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10	3.45×10^{-6}	70	67.5	42.6	57.4
Ni(II)@K10	3.45×10^{-6}	70	23.7	40.8	59.2

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

ried out only at temperatures >50 °C. The results are shown in Table 2. At temperatures ranging from 50 °C to 80 °C, the reactivity and product selectivity of the complex vary with the temperature. At 70 °C the conversion is 70.3% and the selectivity to 2-cyclohexene-1-ol and 2-cyclohexene-1-one is 34.6% and 65.4%, respectively, while at 50 °C the conversion is 10.6% and the selectivity to 2-cyclohexen-1-ol and 2-cyclohexen-1-one is 69.3% and 30.7%, respectively. The typical trend shows that reactivity and the selectivity to 2-cyclohexen-1-one are increased with the temperature in the range of 50–70 °C.

To investigate the effect of catalyst used on the reaction, the oxidation was carried out at 70 °C by varying the amount of catalyst; $[Ni((C_6H_5)_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10; while holding the amount of cyclohexene constant. The results are shown in Table 2. The catalytic conversion was found to be related to the amount of catalyst used is 3.45×10^{-6} mol in 10 cm^3 cyclohexene. Although the amount of catalyst used obviously influenced the reactivity of the catalyst, it showed a relatively small effect on the product distribution. The activity of cyclohexene oxidation decreases in the series $[Ni((C_6H_5)_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10 > $[Ni((C_6H_5)_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10 > $[Ni((H_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10 > $[Ni((CH_3)_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10 > $[Ni((CH_3)_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10. The results clearly suggest that $[Ni((C_6H_5)_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10 efficiently catalyses conversion of cyclohexene to 2-cyclohexene-1-one with 70.3% selectivity. The more activity of $R_2[12]1,3\text{-dieneN}_2O_2$ system has clearly arisen from the existence of electron donating ligand which facilitate the electron transfer rate, a process that has previously observed by us in other oxidation reactions [16,20–24]. All conversion efficiency with high selectivity obtained in this study is significantly higher than that obtained using metal containing porous and non-porous materials [16,20,25].

4. Conclusions

These new heterogeneous catalysts have been prepared by simultaneous pillaring/encapsulation of $[Ni(R_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10 and $[Ni(R_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10 complexes into pillared clay matrix. The nickel(II) complexes are mainly physically entrapped throughout the matrix and distorted due to physical constrains imposed by the matrix and/or owing to host–guest interactions. These interactions can play an important role in the retention of the complex. The new materials behave as catalysts in the heterogeneous oxidation of cyclohexene using molecular oxygen as oxygen source, but after three reuses, some decrease in their catalytic activity was observed.
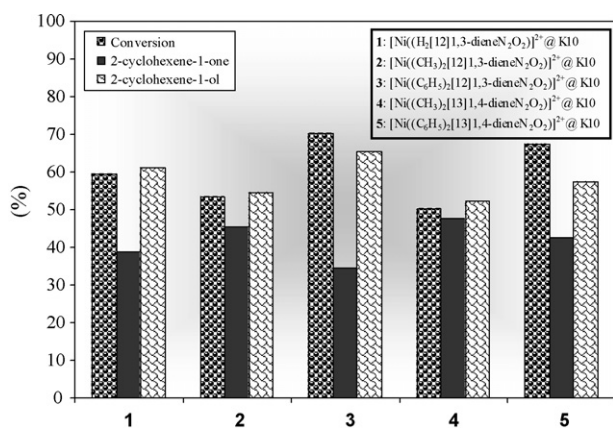
Acknowledgment

Fig. 2. Conversion and oxidation products distribution with molecular oxygen catalyzed by montmorillonite entrapped nickel(II) complexes ($[Ni(R_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10 and $[Ni(R_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10).

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