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Epoxidation of cyclohexene with K10-montmorillonite and Schiff-base macrocyclic copper complexes

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Abstract

Copper(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_2O_2; 2,3-dimethyl-1,4-diaza-7,10-dioxacyclododeca-1,3-diene, $(CH_3)_2$[12]1,3-dieneN_2O_2; 2,3-diphenyl-1,4-diaza-7,10-dioxacyclododeca-1,3-diene, $(C_6H_5)_2$[12]1,3-dieneN_2O_2; 2,4-dimethyl-1,5-diaza-8,11-dioxacyclotrideca-1,4-diene, $(CH_3)_2$[13]1,4-dieneN_2O_2; 2,4-diphenyl-1,5-diaza-8,11-dioxacyclotrideca-1,4-diene, $(C_6H_5)_2$[13]1,4-dieneN_2O_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 characterized by FTIR, DRS, UV–Vis and atomic absorption spectroscopy (AAS). In all cases the copper(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. All new materials show catalytic activity in the epoxidation of cyclohexene using *tert*-butylhydroperoxide (TBHP) as oxygen source in solvent. The solids presented high cyclohexene epoxide selectivity and were reused for three times, but a small decrease in the catalytic activity was observed. FTIR spectra of catalysts after the catalytic reactions suggest that during the reaction no structural changes of the K10 took place, but some active phase leaching and deactivation have occurred which are responsible for the decrease in the catalytic activity on reutilisation.

Keywords: Copper(II); Schiff-base macrocycle; Epoxidation; Montmorillonite-K10

1. Introduction

Development of non-porphyrinic transition metal complexes as catalysts for oxidation of organic substrates is a part of our current research interest (Chatterjee et al., 1993, 1994, 1995; Chatterjee, 1997). Recent trends (Bowers and Dutta, 1990; Barloy et al., 1990; Kowlak et al., 1991; Romanovsky and Gabrielov, 1992; Gerrits et al., 1994; Valli and Alper, 1995) in immobilisation of catalyst complexes on insoluble solid support (mainly clay-based materials) appear to be a good way of heterogenising homogeneous catalysis. Such type of heterogenised–homogeneous catalytic systems not only offer the combined advantages of homogeneous (mild conditions) and heterogeneous (easy separation), but also impose extreme shape selectivity in catalytic process. This prompted us to

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initiate a research programme on oxo-transfer reaction catalysed by Schiff-base/macrocyclic complexes of transition metals in heterogenised homogeneous conditions.

Among the inorganic mimics of enzymes, transition metal complexes containing porphyrin, Schiff-base, cyclam, phthalocyanine and other macrocyclic ligands have been investigated as possible alternative catalysts in many oxidation and hydroxylation reactions (Herron, 1986; Raja and Ratnasamy, 1996; Jacob et al., 1998; Armengol et al., 1999). One approach is to stabilize and isolate the transition metal complexes by encapsulation inside the nanodimensional pores of a zeolite or zeolite-like materials (Balkus and Gabrielov, 1995; DeVos et al., 1994, 1998; Salavati-Niasari, 2004a,b,c; Salavati-Niasari, 2005a,b,c; Salavati-Niasari, 2006). The porous inorganic mantle is supposed to provide the right steric configuration of the metal complexes and orient in a way that the access to the active site (the metal center) by the substrate molecule is regulated. Many porous materials have been used to encapsulate or anchor these metal complexes and the most popular systems have been the large pore X and Y zeolites, which have a large α-cage with about ~ 1.2 nm diameter. The bulkier metal complexes which have molecular dimensions of >1.2 nm do not fit easily inside the zeolite cages and are reported to be distorted after encapsulation (Raja and Ratnasamy, 1997). These complexes also tend to adsorb strongly on the external surface of the zeolite. Intercalation of clays is known to transform the unstable clay structures into highly porous and stable structures. The robust oxide particles, which form the pillars in between the clay layers, prevent the collapse of the expanded layers and simultaneously lead to the formation of large pores with dimensions of > 2.0 nm, depending upon the extent of pillaring and the pillared material (Raja and Ratnasamy, 1997; Pinnavaia et al., 1984). The presence of such large pores in montmorillonite-K10 is expected to facilitate the introduction and stabilization of the metal complexes. Montmorillonite is an interesting support for the immobilization of charged complexes (Bedioui, 1995). 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 is generated by the encapsulation of a gibbsite layer (polymorph of $Al(OH)_3$) with two silica layers (Grim, 1953; Russel and Fraser, 1994).

In this presentation, we have attempted to use montmorillonite-K10 as the host material for immobilization of copper(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_2O_2; 2,3-dimethyl-1,4-diaza-7,10-dioxacyclododeca-1,3-diene, $(CH_3)_2$[12]1,3-dieneN_2O_2; 2,3-diphenyl-1,4-diaza-7,10-dioxacyclododeca-1,3-diene, $(C_6H_5)_2$[12]1,3-dieneN_2O_2; 2,4-dimethyl-1,5-diaza-8,11-dioxacyclotrideca-1,4-diene, $(CH_3)_2$[13]1,4-dieneN_2O_2; 2,4-diphenyl-1,5-diaza-8,11-dioxacyclotrideca-1,4-diene, $(C_6H_5)_2$[13]1,4-dieneN_2O_2 (Scheme 1). The resulting materials are characterized by different techniques and tested for selective epoxidation of cyclohexene using *tert*-butylhydroperoxide (TBHP) as oxidant.

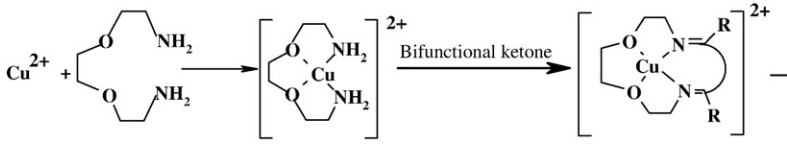
2. Experimental

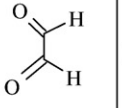
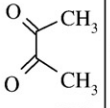
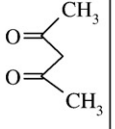
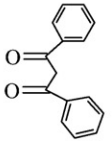
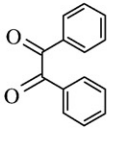
2.1. Materials and physical measurements

All the materials were of commercial reagent grade. TBHP (80% in di-*t*-butyl ether), 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 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 copper 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 1500–200 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. [Cu(1,8-diamino-3,6-dioxaoctane)]$(ClO_4)_2$ was obtained by the reaction of 1,8-diamino-3,6-dioxaoctane with $Cu(ClO_4)_2 \cdot 6H_2O$ in methanol and recrystallized from water (Salavati-Niasari and Bazarganipour, 2006). The products were 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 [Cu(R_2[12]1,3-dieneN_2O_2]$(ClO_4)_2$ and [Cu(R_2[13]1,4-dieneN_2O_2)]$(ClO_4)_2$ complexes

To a solution of (1,8-diamino-3,6-dioxaoctane)copper(II) perchlorate (5 mmol); [Cu(1,8-diamino-3,6-dioxaoctane)]$(ClO_4)_2$; in MeOH (100 cm^3), solution of bifunctional diketone



Bifunctional ketone	Heterogeneous catalyst
	$[Cu((H_2[12]1,3\text{-diene}N_2O_2)]^{2+}$ @K10
	$[Cu((CH_3)_2[12]1,3\text{-diene}N_2O_2)]^{2+}$@K10
	$[Cu((CH_3)_2[13]1,4\text{-diene}N_2O_2)]^{2+}$@K10
	$[Cu((C_6H_5)_2[13]1,4\text{-diene}N_2O_2)]^{2+}$@K10
	$[Cu((C_6H_5)_2[12]1,3\text{-diene}N_2O_2)]^{2+}$@K10

Scheme 1.

(glyoxal, 2,3-buthanedione, 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.

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

0.7 g of $[Cu(R_2[12]1,3\text{-}dieneN_2O_2](ClO_4)_2$ or $[Cu(R_2[13]1,4\text{-}dieneN_2O_2)](ClO_4)_2$ in hot methanol (10 ml) was slowly added to 1 g of montmorillonite 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 $[Cu(1,8\text{-diamino-}3,6\text{-dioxaoctane})]^{2+}$ complex. The blue solid was filtered, washed with methanol and dried at 70 °C under vacuum.

2.4. Oxidation of cyclohexene, general procedure

A mixture of 0.20 g of catalyst and 20 mmol of cyclohexene in 5 ml CH_2Cl_2 was stirred under nitrogen at reflux for 30 min. Then 24 mmol of TBHP was added and the mixture was refluxed for 8 h. After filtration, the solid was washed with CH_2Cl_2. The filtrate was then subjected to GC analysis.

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) copper(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 (~ 265 Ω^{-1} mol^{-1} cm^2) were measured in water correspond to 1:2 electrolytes (Table 1). The overall geometries of macrocyclic complexes have been deduced on the basis of the observed values of the magnetic moments (~ 1.73 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 copper contents of the catalysts were estimated by dissolving known amounts of the catalyst in conc. H_2SO_4 and from these solutions, the copper 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 Cu:C:N molar ratios almost close to those calculated for the mononuclear structure (Table 1).

The IR spectrum of K10 shows intense and large bands due to the clay structure: in the region 3700–

Table 1
Chemical composition, UV–Vis, DRS absorption and IR stretching frequencies (as KBr pellets) of neat and montmorillonite-entrapped copper(II) complexes[a]

Catalyst	C (%)	H (%)	N (%)	C/N	Cu (%)	Yield (%)	$\upsilon_{(C=N)}$, (cm^{-1})	d↔d, (nm)	μ_B, (B.M.)	Λ_M, (Ω^{-1} cm^{-1} M^{-1})[b]
$[Cu((H_2[12]1,3\text{-}dieneN_2O_2)](ClO_4)_2$	22.20 (21.96)	3.26 (3.13)	6.47 (6.59)	3.43 (3.33)	14.68 (14.51)	56	1612	580[b]	1.74	267
$[Cu((H_2[12]1,3\text{-}dieneN_2O_2)]^{2+}$@K10	2.64	8.65	0.82	3.21	1.87	–	1610	578	–	–
$[Cu((CH_3)_2[12]1,3\text{-}dieneN_2O_2)](ClO_4)_2$	26.06 (25.88)	3.94 (3.78)	6.08 (6.24)	4.29 (4.15)	13.79 (13.58)	53	1609	582[b]	1.73	264
$[Cu((CH_3)_2[12]1,3\text{-}dieneN_2O_2)]^{2+}$@K10	3.22	8.70	0.80	4.03	1.81	–	1607	579		–
$[Cu((C_6H_5)_2[12]1,3\text{-}dieneN_2O_2)](ClO_4)_2$	41.07 (40.88)	3.79 (3.60)	4.79 (4.91)	8.57 (8.32)	10.86 (10.69)	40	1618	576[b]	1.75	257
$[Cu((C_6H_5)_2[12]1,3\text{-}dieneN_2O_2)]^{2+}$@K10	6.43	8.76	0.78	8.24	1.76	–	1614	574	–	–
$[Cu((CH_3)_2[13]1,4\text{-}dieneN_2O_2)](ClO_4)_2$	27.82 (27.61)	4.25 (4.10)	5.90 (6.04)	4.72 (4.57)	13.38 (13.23)	55	1607	583[b]	1.74	253
$[Cu((CH_3)_2[13]1,4\text{-}dieneN_2O_2)]^{2+}$@K10	3.43	8.73	0.78	4.41	1.78	–	1603	582	–	–
$[Cu((C_6H_5)_2[13]1,4\text{-}dieneN_2O_2)](ClO_4)_2$	42.11 (41.93)	4.04 (3.90)	4.68 (4.82)	9.00 (8.70)	10.61 (10.49)	39	1616	577[b]	1.73	284
$[Cu((C_6H_5)_2[13]1,4\text{-}dieneN_2O_2)]^{2+}$@K10	6.56	8.79	0.76	8.63	1.74	–	1609	573	–	–

[a]Estimated values are given in parentheses.
[b]In MeOH solution.
[c]Recovered catalyst.

Table 2
Oxidation of cyclohexene with TBHP catalyzed by copper(II) complexes in MeOH=10 ml; catalyst=1.02×10^{-5} mol; duration=8 h, at reflux; cyclohexene=20 mmol; TBHP=24 mmol

Catalyst	Conversion (%)	Selectivity (%)			
		Peroxy[d]	Alcohol[c]	Ketone[b]	Epoxy[a]
$[Cu((C_6H_5)_2[13]1,4\text{-dieneN}_2O_2)](ClO_4)_2$	40.6	2.3	29.8	11.2	56.7
$[Cu((C_6H_5)_2[13]1,4\text{-dieneN}_2O_2)](ClO_4)_2$[e]	32.8	2.5	31.6	10.7	55.2
$[Cu((C_6H_5)_2[13]1,4\text{-dieneN}_2O_2)](ClO_4)_2$[f]	42.7	5.6	27.4	13.5	53.5
$[Cu((C_6H_5)_2[13]1,4\text{-dieneN}_2O_2)](ClO_4)_2$[g]	45.3	6.6	24.5	16.8	52.1
$[Cu((C_6H_5)_2[12]1,3\text{-dieneN}_2O_2)](ClO_4)_2$	38.6	4.6	27.6	13.5	54.3
$[Cu((H_2[12]1,3\text{-dieneN}_2O_2)](ClO_4)_2$	35.1	4.9	28.5	10.2	56.4
$[Cu((CH_3)_2[12]1,3\text{-dieneN}_2O_2)](ClO_4)_2$	30.4	1.2	29.3	9.7	59.8
$[Cu((CH_3)_2[13]1,4\text{-dieneN}_2O_2)](ClO_4)_2$	30.1	0.5	29.8	8.5	61.2
$Cu(ClO_4)_2$	16.7	8.6	30.6	52.3	8.5

[a]Cyclohexene epoxide.
[b]2-cyclohexene-1-one.
[c]2-cyclohexene-1-ol.
[d]1-(*tert*-butylperoxy)-2-cyclohexene.
[e]Catalyst=0.5×10^{-5} mol.
[f]Catalyst=2.04×10^{-5} mol.
[g]Catalyst=4.08×10^{-5} mol.

3300 cm^{-1}, which are assigned to the surface hydroxyl groups from the acidic Al–OH group (Coudurier and Lefebvre, 1994; Flego et al., 1998; Salerno et al., 2001), at 1630 cm^{-1} and in the range 1300–400 cm^{-1}, from lattice vibrations (Coudurier and Lefebvre, 1994) (asymmetric stretching vibrations of SiO_2 tetrahedra) (Flego et al., 1998). 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 copper(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 copper(II) complexes is physically entrapped within the K10 structure, but probably slightly distorted as a consequence of the constraints imposed by the matrix; some host–guest interactions between the K10 framework and the complex cannot be ruled out. The absorption bands in the ~ 570 nm can be attributed to ligand–field transitions. This behavior is compatible with that observed for square-planar copper(II) complexes with two nitrogen and two oxygen donors (Hause, 1972; Palombi et al., 1999; Farzaneh et al., 1999; Salavati-Niasari et al., 2002; Salavati-Niasari and Najafian, 2003; Salavati-Niasari, 2004a,b,c; Salavati-Niasari, 2005a,b,c; Salavati-Niasari and Amiri, 2006; Salavati-Niasari and Davar, 2006; Salavati-Niasari and Bazarganipour, 2006). The results are attributed to the electronic properties of the substituent group and are supported by similar observations with similar copper(II) N_2O_2 macrocycles (Hause, 1972; Palombi et al., 1999; Farzaneh et al., 1999; Salavati-Niasari et al., 2002; Salavati-Niasari and Najafian, 2003; Salavati-Niasari, 2004a,b,c; Salavati-Niasari and Amiri, 2005a,b,c; Salavati-Niasari and Amiri, 2006; Salavati-Niasari and Davar, 2006; Salavati-Niasari and Bazarganipour, 2006).

The immobilization process was characterized by the color change of the clays. In the case of $[Cu(R_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10 the change was from light yellow to light blue, with a final color of deep blue in the case of and $[Cu(R_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10. The end of the immobilization process was characterized by the disappearance of the characteristic metallo complex solution color by UV–visible analysis.

The solid materials obtained after filtration of the reaction suspension were washed thoroughly with CH_2Cl_2, CH_3OH, and CH_3CN and dried at reflux. They were found to be very stable in CH_2Cl_2, CH_3OH, CH_3CN, cyclohexane, and water as they released no copper(II) complexes even after stirring in these solvents for several days. FTIR spectra for heterogeneous catalysts recorded after the third reuse 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 copper(II) complexes from each other by entrapped within montmorillonite. Since the formation of these bulky dimeric and polymeric species is 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 2 and 3 support the above hypothesis. As mentioned earlier, the neat complexes could not be recycled even once as they lost their catalytic activity after use. By contrast, the entrapped, solid catalysts could be filtered, washed with a solvent and reused without major loss in activity.

Table 3 shows the effect of solvents on the oxidation results in the presence of $[Cu((C_6H_5)_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10. It can be seen that changing solvent from acetonitrile to dichloromethane increases the conversion percentage of $[Cu((C_6H_5)_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10 by a factor of 1.42. Effect of different solvents showed the trend of $CH_3CN < MeOH < CHCl_3 < CH_2Cl_2$ which is consistent with solvent polarities reduction. This can be explained by considering the fact that the transition state of Cu(I) has a lower charge density than the starting material Cu(II). Therefore, the reaction should be accelerated by changing solvent to a less polar solvent.

At the end of the reaction, the catalyst was separated by filtration, thoroughly washed with solvent and reused under similar conditions. Although the analysis of the recovered catalysts by AAS showed no reduction in the amount of metal ions, they showed a slightly lower catalytic activity (Table 3). The recovered catalysts show a slight decrease of copper content, but this decrease is not very significant given the adsorption of organic products, as shown by the higher carbon content; however, the N/Cu ratio remains constant. As observed with the clays with low content of complex, the copper in the recovered catalysts is much less active as shown by the lower conversion.

To see the effect of time on product distribution, we examined the reaction times of 2, 4, 6, 8 and 10 h. The results are shown in Table 3. It can be seen that at 8 h maximum conversion takes place and going beyond that has no effect on reactivity. The observation of a plateau after 10 h is not unexpected because no considerable cyclohexene is then available to show tangible activity.

The key step in the oxidation mechanism is reduction of copper(II) to copper(I). This process would simultaneously decompose TBHP to *t*-$BuOO^{\bullet}$ radical

Table 3
Oxidation of cyclohexene with TBHP catalyzed by copper(II) complexes (solvent = 10 ml; catalyst = 1.02×10^{-5} mol; duration = 8 h, at reflux; cyclohexene = 20 mmol; TBHP = 24 mmol)

Catalyst	Time (h)	Solvent	Conversion (%)	Selectivity (%)			
				Peroxy[d]	Alcohol[c]	Ketone[b]	Epoxy[a]
$[Cu((C_6H_5)_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10	8	CH_2Cl_2	56.3	13.6	21.6	14.2	50.6
$[Cu((C_6H_5)_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10[e]	8	CH_2Cl_2	54.7	15.7	21.2	14.0	49.1
$[Cu((C_6H_5)_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10[f]	8	CH_2Cl_2	53.2	17.2	20.8	13.7	48.3
$[Cu((C_6H_5)_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10[g]	8	CH_2Cl_2	52.7	18.7	20.6	13.2	47.5
$[Cu((C_6H_5)_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10	2	CH_2Cl_2	18.6	19.6	14.6	3.1	62.7
$[Cu((C_6H_5)_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10	4	CH_2Cl_2	30.2	17.4	18.6	5.7	58.3
$[Cu((C_6H_5)_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10	6	CH_2Cl_2	41.6	14.2	19.8	9.6	56.4
$[Cu((C_6H_5)_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10	10	CH_2Cl_2	57.9	11.9	20.2	20.4	47.5
$[Cu((C_6H_5)_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10	8	$CHCl_3$	51.3	13.9	21.3	16.3	48.5
$[Cu((C_6H_5)_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10	8	CH_3OH	44.5	9.7	28.5	20.6	41.2
$[Cu((C_6H_5)_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10	8	CH_3CN	39.6	6.8	31.3	24.5	37.4
$[Cu((C_6H_5)_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10	8	CH_2Cl_2	51.2	14.2	19.8	16.5	49.5
$[Cu((H_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10	8	CH_2Cl_2	49.5	11.9	23.2	13.2	51.7
$[Cu((CH_3)_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10	8	CH_2Cl_2	47.7	7.7	25.1	12.6	54.6
$[Cu((CH_3)_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10	8	CH_2Cl_2	45.8	6.4	26.4	11.7	55.5
Cu^{2+}@K10	8	CH_2Cl_2	18.5	16.4	24.5	55.7	3.4

[a]Cyclohexene epoxide.
[b]2-cyclohexene-1-one.
[c]2-cyclohexene-1-ol.
[d]1-(*tert*-butylperoxy)-2-cyclohexene.
[e]First reuse.
[f]Second reuse.
[g]Third reuse.

and proton. The latter would balance the charge deficiency of copper(II) to copper(I) conversion while the former subsequently adds either to double bond and leads to the corresponding epoxide or abstracts an allylic hydrogen atom from olefin, resulting in the allylic radical intermediate.

According to our results, epoxidation of cyclohexene was carried out remarkably with 56.3% conversion and 50.6% selectivity (see Table 3). As compared to the recently published system which worked with PhIO and O_2 (Farzaneh et al., 1999) and obtained the best epoxidation result in the case of styrene, our system seems simpler and more efficient. Moreover, the high efficiency of cyclohexene to cyclohexene epoxide in the presence of $[Cu(R_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10 clearly supports the intermediacy of alkyl peroxy radical. Therefore, addition of alkyl peroxy radical to double bond is unavoidable and the reaction finally leads to cyclohexene epoxide. Although Agashe and co-workers in a very recent publication have reported that they obtained maximum 52% epoxide from styrene with TBHP in the presence of Cu/Co-salen immobilized MCM-41, using cyclohexene led to 1.4–3.2% of the corresponding epoxide (Karandikar et al., 2004). The similarity of these results with ours emphasizes the operation of a radical mechanism and involvement of *tert*-butyl peroxide radical in either case. This radical has been formed from catalytic decomposition of TBHP.

4. Conclusions

These new heterogeneous catalysts have been prepared by simultaneous pillaring/encapsulation of $[Cu(R_2[12]1,3\text{-dieneN}_2O_2)]^{2+}$@K10 and $[Cu(R_2[13]1,4\text{-dieneN}_2O_2)]^{2+}$@K10 complexes into pillared clay matrix. The copper(II) complexes are mainly physically entrapped throughout the matrix and distorted due to physical constraints 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 chemoselective catalysts in the heterogeneous epoxidation of cyclohexene at reflux using TBHP as oxygen source in solvent, but after three reuses, some decrease in their catalytic activity was observed.

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