

# Immobilized copper(II) complexes on montmorillonite and MCM-41 as selective catalysts for epoxidation of alkenes

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## Abstract

Copper(II) complexes with 2,2'-bipyridine(bpy) and 1,8-dibenzyl-1,3,6,8,10,13-hexaazacyclotetradecane (macrocycle) immobilized between silicate layers of montmorillonite and nanoreactors of MCM-41 successfully catalyze the epoxidation of norbornene and *trans*-2-hexene-1-ol with good to excellent reactivity and 48–100% selectivity toward the formation of the corresponding epoxides.

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**Keywords:** Cu(II) complexes; Alkenes; Epoxidation; Montmorillonite; MCM-41

## 1. Introduction

The search for finding the new oxidation catalysts of olefins has been the subject of many researches during the last few decades [1–4]. Although dioxygen (O<sub>2</sub>) as the main source of oxygen atoms is ideal in biomimetic oxygenation of organic substrates, in most cases, however, the successful developed model catalysts require alternative oxidants, e.g. hydrogen peroxide, organic peroxides or iodobenzene [5–10].

Epoxides are one of the most important groups of intermediates for the synthesis of oxygen-containing organic compounds both in industry and in academic laboratories. Many different solid catalysts such as supported oxides [11], mixed oxides [12,13], framework substituted redox molecular sieve silicates [14,15], zeolites [16,17], aluminophosphates [18], layered type materials [19], heterogenized homogeneous catalysts, mixed metal exchanged zeolites and resins [20], polymerized chiral ligands [21], tethered or grafted complexes and encapsulated complexes have been used in liquid phase epoxidation of olefins [22].

Metal complexes with nitrogen containing molecules are widely used as model compounds for mimicking the catalytic properties of mono-oxygenases. Recently, Corma and co-workers have used metallophthalocyanines (MPC) on MCM-41 and zeolite Y for oxidation of some organic compounds [23].

In our attempts to develop new catalysis systems, we selected the copper ion as the main metal center present inside the solid supports such as montmorillonite and MCM-41. Selection of the copper ion was based on its higher reduction potential with respect to other transition metals like Fe(II), Mn(II), Ni(II) and Co(II) [24]. Epoxidation of alkenes by Cu<sup>2+</sup>-perchlorophthalocyanine and Cu(Salen) immobilized on MCM-41 has been reported recently [25,26]. In this article, we report the oxidation of olefins in the presence of immobilized complexes of Cu(II) bipyridine and macrocycle ligands on montmorillonite and nanoreactor of MCM-41 with TBHP.

## 2. Experimental

### 2.1. Materials

All the materials were of commercial reagent grade. TBHP (80% in di-*t*-butyl ether) and 2,2'-bipyridine(bpy)

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were prepared from Merk Chemical Company; montmorillonite was obtained from Fluka. All alkenes were distilled under nitrogen before using.

## 2.2. Physical measurements

FT-IR spectra were recorded on Bruker Tensor 27 Spectrophotometer. Atomic absorption spectra (AAS) were recorded on a Perkin-Elmer 4100-1319 Spectrophotometer using a flame approach. The products were analyzed by GC and GC-MASS using an Agilent 6890 series, FID detector, HP-5% 5-phenyl siloxane capillary and Agilent 5973 Network, Mass selective detector, HP-5MS 6890 Network GC system, respectively.

## 2.3. Preparation of materials

### 2.3.1. Preparation of [Cu(macrocycle)]<sup>2+</sup>/montmorillonite

Cu(macrocycle)(ClO<sub>4</sub>)<sub>2</sub> was prepared according to the reported procedure [27]. 0.7 g of Cu(macrocycle)(ClO<sub>4</sub>)<sub>2</sub> 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 Soxhlet extracted with a mixture of 1:1 methanol and chloroform in order to remove unreacted Cu(macrocycle)<sup>2+</sup> complex. The AAS determination showed that the percentage of Cu was 4.38%.

FT-IR (KBr) for [Cu(macrocycle)]<sup>2+</sup>/montmorillonite: 1531, 1496, 1457 and 760 cm<sup>-1</sup>.

### 2.3.2. Preparation of [Cu(bpy)<sub>2</sub>]<sup>2+</sup>/montmorillonite

Two millimole of bipyridine in methanol was slowly added to 1 mmol of CuCl<sub>2</sub>·2H<sub>2</sub>O in hot methanol. The resultant mixture was refluxed for 2 h. The mixture was then cooled and filtered. The solid was washed with methanol and dried. Then 0.2 g of [Cu(bpy)<sub>2</sub>]Cl<sub>2</sub> in 10 ml methanol was added to 1 g of montmorillonite in 10 ml methanol. The resultant mixture was refluxed for 24 h. The mixture was then filtered and washed with methanol. The AAS determination showed that the percentage of Cu was 1.52%.

FT-IR (KBr) for [Cu(bpy)<sub>2</sub>]<sup>2+</sup>/montmorillonite: 1496, 1474, 1446 and 770 cm<sup>-1</sup>.

### 2.3.3. Preparation of MCM-41

MCM-41 was prepared according to the procedure described previously [28]. The XRD of prepared MCM-41 was consistent with that reported before.

### 2.3.4. Immobilization of Cu(bpy)<sub>2</sub> complex within MCM-41

0.2 g of [Cu(bpy)<sub>2</sub>]Cl<sub>2</sub> in 10 ml methanol was added to 1 g MCM-41 in 10 ml methanol. The resultant mixture was refluxed for 24 h. The mixture was then filtered and washed with methanol. The percentage of Cu was determined to be 0.53% by AAS.

FT-IR (KBr) for Cu(bpy)<sub>2</sub> complex/MCM-41: 3423, 1495, 1475, 1446, 730 and 559 cm<sup>-1</sup>.

### 2.3.5. Immobilization of Cu(macrocycle) complex within MCM-41

The preparation method was similar to Section 2.3.4. 0.2 g of [Cu(macrocycle)](ClO<sub>4</sub>)<sub>2</sub> in 10 ml methanol was slowly added to 1 g MCM-41 in 10 ml methanol and stirred for 24 h. The resultant mixture was filtered and washed with methanol. The Cu percentage was determined to be 0.847%.

FT-IR (KBr) for Cu(macrocycle) complex/MCM-41: 3447, 1636, 1457, 1083, 800 and 630 cm<sup>-1</sup>.

## 2.4. Oxidation of cyclohexene, general procedure

A mixture of 0.2 g of catalyst and 20 mmol of cyclohexene in 5 ml CH<sub>2</sub>Cl<sub>2</sub> was stirred under nitrogen at 40 °C for 30 min. Then 24 mmol of TBHP was added and the mixture was refluxed for 6 h. After filtration, the solid was washed with methylene chloride. The filtrate was then subjected to GC analysis.

## 3. Results and discussion

The effect of some copper(II) complexes of [Cu(macrocycle)]<sup>2+</sup> and [Cu(bpy)<sub>2</sub>]<sup>2+</sup> immobilized between the montmorillonite silicate layers in the oxidation of cyclohexene, norbornene and *trans*-2-hexene-1-ol are shown in Table 1

Table 1  
Effect of Cu(macrocycle)<sup>2+</sup>/montmorillonite and [Cu(bpy)<sub>2</sub>]<sup>2+</sup>/montmorillonite catalysts in the oxidation of alkenes

Catalyst	Substrate	Conversion (mol%)	Product distribution				TON
			Epoxy	One	Ol	Others	
Cu(macrocycle) <sup>2+</sup> /montmorillonite	Cyclohexene	48	48	10	22	20	69
	Norbornene	92	100	–	–	–	133
	<i>trans</i> -2-Hexene-1-ol	92	100	–	–	–	130
[Cu(bpy) <sub>2</sub> ] <sup>2+</sup> /montmorillonite	Cyclohexene	26	15	28	18	39	35
	Norbornene	43	100	–	–	–	430
	<i>trans</i> -2-Hexene-1-ol	90	100	–	–	–	160

Conditions: alkenes, 20 mmol; TBHP, 24 mmol; time, 6 h; solvent, CH<sub>2</sub>Cl<sub>2</sub> 5 ml.

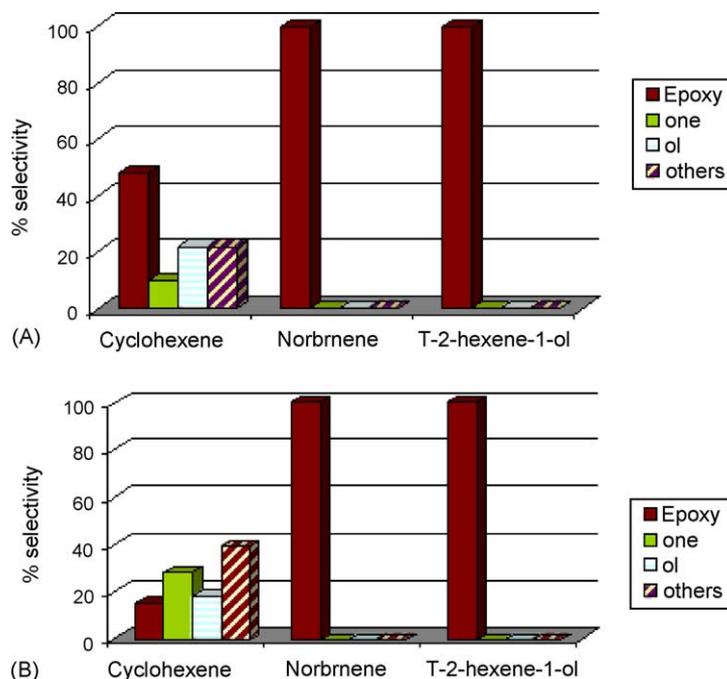


Fig. 1. Comparison between alkenes oxidation using (A)  $\text{Cu}(\text{macrocycle})^{2+}/\text{montmorillonite}$  and (B)  $[\text{Cu}(\text{byp})_2]^{2+}/\text{montmorillonite}$  catalysts.

and Fig. 1. With the exception of cyclohexene, norbornene and *trans*-2-hexene-1-ol have reacted with more than 90% conversion and 100% selectivity toward the formation of the corresponding epoxides. In the case of cyclohexene, the allylic site oxidation has taken place besides the epoxidation with the formation of 2-cyclohexene-1-ol and 2-cyclohexene-1-one as byproducts.

To see the effect of solid supports, we substituted the MCM-41 with montmorillonite. Table 2 and Fig. 2 list the catalytic results of different complexes on MCM-41 in the oxidation of cyclohexene and norbornene. As is seen, different ranges of activities are observed in the results. The remarkable conversions and 100% selectivity toward the epoxidation in the case of  $\text{Cu}(\text{macrocycle})$  complex/MCM-41 was accompanied with approximately 10% desorption. On the other hand, good to fair conversions with  $\text{Cu}(\text{byp})_2$  complex/MCM-41 appear excellent because no desorption was observed during the course of reaction since the filtrate

did not show any activity when the solution was examined in the oxidation reaction.

Table 3 shows the effect of solvents on the oxidation results in the presence of  $\text{Cu}(\text{byp})_2$  complex/MCM-41. It can be seen that changing solvent from  $\text{CH}_3\text{CN}$  to  $\text{CH}_2\text{Cl}_2$  increases the conversion percentage and TON of  $\text{Cu}(\text{byp})_2$  complex/MCM-41 by a factor of 60%. Effect of different solvents showed the trend of  $\text{CH}_3\text{CN} < \text{MeOH} < \text{CHCl}_3 < \text{CH}_2\text{Cl}_2$  which is consistent with solvent polarities reduction. This can be explained by considering the fact that the transition state of  $\text{Cu}(\text{I})$  has a lower charge density than the starting material  $\text{Cu}(\text{II})$ . Therefore, the reaction should be accelerated by changing solvent to a less polar solvent.

To see the effect of time on product distribution, we examined the reaction times of 2, 4, 6 and 8 h. The results are shown in Table 4 and Fig. 3. It can be seen that at 6 h maximum conversion takes place and going beyond that has no

Table 2  
Catalytic results of different complexes on MCM-41 for epoxidation of norbornene and cyclohexene in acetonitrile

Catalyst	Substrate	Conversion (mol%)	Product distribution (mol%)			TON
			Epoxy	One	Ol	
MCM-41	Norbornene	7	100	–	–	–
Cu/MCM-41		91	100	–	–	2541
$\text{Cu}(\text{macrocycle})/\text{MCM-41}$		80	100	–	–	598
$\text{Cu}(\text{byp})_2/\text{MCM-41}$		50	100	–	–	603
MCM-41	Cyclohexene	<2	–	–	–	–
Cu/MCM-41		58	25	66	9	1614
$\text{Cu}(\text{macrocycle})/\text{MCM-41}$		73	39	37	29	549
$\text{Cu}(\text{byp})_2/\text{MCM-41}$		28	–	67	33	338

Conditions: alkenes, 20 mmol; TBHP, 24 mmol; solvent, 5 ml; time, 6 h.

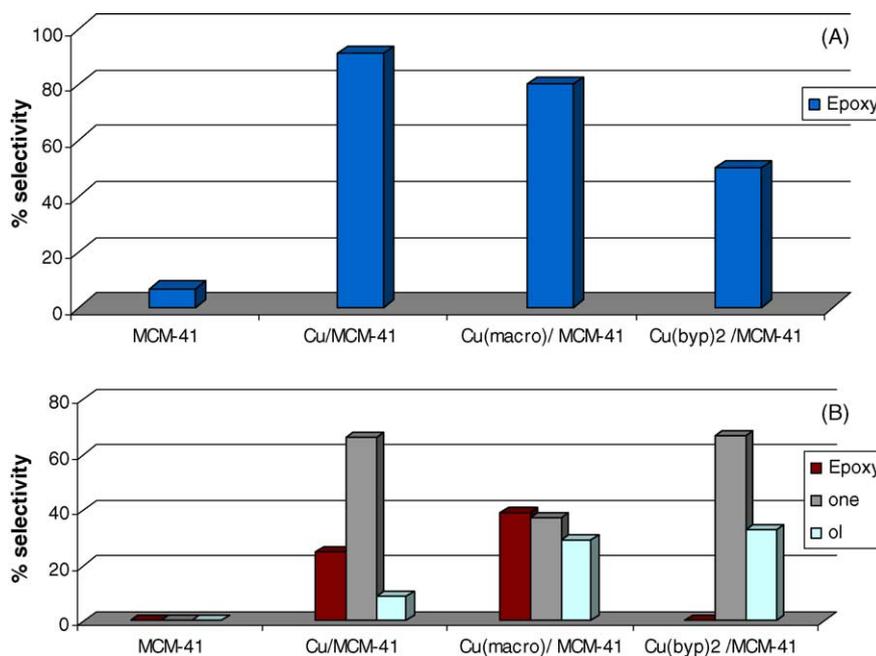


Fig. 2. Catalytic results of different complexes on MCM-41 for epoxidation of (A) norbornene and (B) cyclohexene in acetonitrile.

effect on reactivity. The observation of a plateau after 6 h is not unexpected because no considerable norbornene is then available to show tangible activity.

The key step in the oxidation mechanism is reduction of Cu(II) to Cu(I). This process would simultaneously decomposes TBHP to *t*-BuOO radical and proton. The latter would balance the charge deficiency of Cu(II) to Cu(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. Due to the stability of cyclohexene radical and instability of norbornene radical whose formation violates the Bredt's rule [29], cyclohexene yields a mixture of products while norbornene winds up exclusively to norbornene epoxide. In the case of *trans*-2-hexene-1-ol, we believe that a concerted oxidation mechanism has been involved in the reaction via simultaneous complexation of hydroxyalkene and TBHP to the copper ion prior to the oxidation step.

According to our results, epoxidation of norbornene was carried out remarkably with 80% conversion, 100% selectivity and high TON (see Table 3). As compared to the recently published system which worked with isobutylaldehyde and

molecular oxygen [25], and obtained the best epoxidation result in the case of styrene, our system seems simpler and more efficient. Moreover, the high efficiency of norbornene to norbornene epoxide and good to low efficiency of cyclohexene to cyclohexene epoxide especially in the presence of Cu(bpy)<sub>2</sub> complex/MCM-41 clearly supports the intermediacy of alkyl peroxy radical. Because of the instability of norbornene radical, abstraction of hydrogen from norbornene is not possible. Therefore, addition of alkyl peroxy radical to double bond is unavoidable and the reaction finally leads to norbornene 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. The similarity of these results with ours emphasizes the operation of a radical mechanism and involvement of *tert*-butyl peroxy radical in either cases. This radical has been formed from catalytic decomposition of TBHP. Due to its low selectivity in comparison to acyl peroxy radicals, addition to double bond with subsequent epoxide formation occurs by a lesser amount with respect to hydrogen atom abstraction and

Table 3  
Oxidation of Norbornene by Cu(bpy)<sub>2</sub> complex/MCM-41 in various solvents

Solvent	Conversion (%)	Epoxy	TON
CH <sub>3</sub> CN	50	100	603
CH <sub>2</sub> Cl <sub>2</sub>	80	100	956
CHCl <sub>3</sub>	61	100	730
MeOH	59	100	704

Condition: catalyst, 0.2 g; Norbornene, 20 mmol; TBHP, 24 mmol; solvent, 5 ml; time, 6 h.

Table 4  
Effect of time on the oxidation of Norbornene with TBHP in the presence of Cu(bpy)<sub>2</sub> complex /MCM-41 in CH<sub>2</sub>Cl<sub>2</sub>

Time (h)	Conversion (%)	Epoxy	TON
2	21	100	251
4	43	100	515
6	80	100	956
8	80	100	956

Conditions: catalyst, 0.2 g; TBHP, 24 mmol; Norbornene, 20 mmol; solvent, 5 ml at reflux condition.

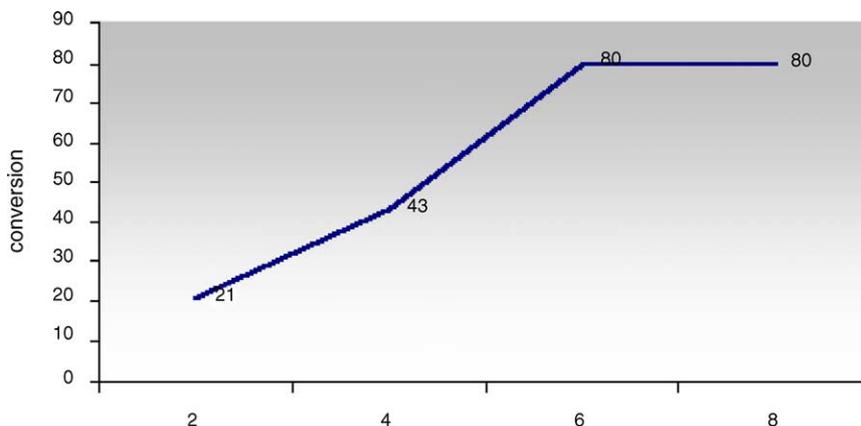


Fig. 3. Effect of time (h) on the oxidation of Norbornene with TBHP in the presence of  $\text{Cu}(\text{bpy})_2$  complex/MCM-41 in  $\text{CH}_2\text{Cl}_2$ .

giving rise to the formation of allylic site products [25]. That styrene has led to the corresponding epoxide with good efficiency under Agashe's conditions arises from the unavailability of allylic hydrogens in this molecule. The formation of about 28% of decene epoxide from 1-decene under the best conditions, something in between styrene and cyclohexene supports our proposal. Although 1-decene behaves much better than cyclohexene, the yield is still too far from styrene and the difference in molecular structures is the existence of allylic hydrogens in 1-decene.

#### 4. Conclusion

It was demonstrated that  $\text{Cu}(\text{bpy})_2$  complex/MCM-41 in combination with clear and inexpensive TBHP is remarkable for the epoxidation of norbornene which is inefficient toward the formation of stable allyl radicals. Since in this reaction and similar processes, the active radical intermediate is *t*-butyl peroxy radical, one cannot expect to obtain epoxides as the main products from alkenes containing allylic hydrogens in their molecular structures [26]. Obtaining epoxides from such alkenes is possible only if the oxo-metal species can be formed under the reaction conditions [25].

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