

Efficient and Selective Oxidation of Hydrocarbons with *tert*-Butyl Hydroperoxide Catalyzed by Copper(II) Unsymmetrical Schiff Base Complex Immobilized into Mesoporous MCM-41

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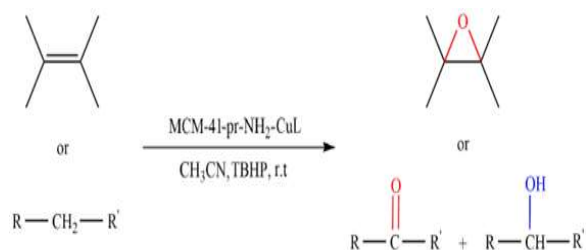
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Abstract: In this study, we investigated the effectiveness of a copper(II) unsymmetrical Schiff base complex (CuL where H₂L = salicylideneiminoethyliminopentane-2-one) immobilized into mesoporous silica MCM-41 in the hydroxylation of alkanes and epoxidation of alkenes through *tert*-butyl hydroperoxide (TBHP) as oxidant. This heterogeneous MCM-41-pr-NH₂-CuL catalyst exhibited remarkable activity and selectivity in alkene epoxidation and alkane hydroxylation, producing high to excellent yields at room temperature. The catalyst could be recovered quickly through simple filtration and reused four times without considerable loss in its catalytic efficiency.

Furthermore, upon analyzing the Fourier transform infrared (FT-IR) spectrum of the recovered catalyst and comparing it with the fresh one, it was found that the structure of the catalyst remained unchanged even after the recovery process.



Keywords: Cu(II) complex, Unsymmetrical Schiff base, MCM-41, Alkene epoxidation, Alkane hydroxylation

1. INTRODUCTION

The oxidation of hydrocarbons, especially alkene epoxidation and alkane hydroxylation, is an essential transformation in organic chemistry, mainly in the production of fine chemicals, and has attracted a considerable deal of researchers' attention.^{1,2} The traditional approach for hydrocarbon oxidation is to use stoichiometric amounts of peracids and peroxides. However, these methods are not selective towards epoxidation and can lead to the formation of unwanted products.³ To overcome this, researchers have developed several methods utilizing homogeneous and heterogeneous transition metal complexes as catalysts for alkane hydroxylation and alkene epoxidation.⁴⁻¹⁰

Transition metal Schiff base complexes have become increasingly popular in the catalysis process owing to their more accessible synthesis circumstances and versatile coordination structures.¹¹⁻¹⁵ Though, homogeneous complexes have their drawbacks, including product separation, poor catalyst recovery, and catalyst deactivation by forming dimeric oxo- and peroxy-bridged species.^{16,17} To address these issues, researchers have been exploring the immobilization of homogeneous catalysts on solid support as an excellent strategy to overcome these problems.¹⁸ As such, many groups have been

experimenting with immobilizing Schiff base complexes on various supports.

Mesoporous materials are very effective in adsorbing molecules owing to their high surface area and large pore size.¹⁹ They are also commonly used as either heterogeneous supports or catalysts. In the case of heterogeneous catalysis, the catalyst's surface area is crucial as it defines the catalytic availability sites for reactants.^{20,21} Therefore, mesoporous silica-supported catalysts are highly effective owing to their large area and more effectiveness in organic heterogeneous catalyzed reactions.^{22,23} Among the mesoporous silica, MCM-41 (mobile crystalline material number 41) has several advantages such as a high concentration of hydroxyl groups used as active sites for homogeneous catalyst attachment on the surface, high surface area, and large pore volume. In addition, MCM-41 has well defined hexagonal mesoporous structure, which promotes the active site to react with reactant molecules.²⁴

Previously, we have presented the synthesis, characterization, and use of an immobilized copper(II) unsymmetrical salen-type Schiff base complex into mesoporous silica MCM-41 in the selective oxidation of alcohols.²⁵ In this work, we explored the potential of MCM-41-pr-NH₂-CuL in the hydroxylation of alkanes

and epoxidation of alkenes with *tert*-butyl hydroperoxide under mild reaction conditions. This research also looked at the stability and reusability of the included catalyst.

2. EXPERIMENTAL

Materials and methods

The chemicals used in the experiments were sourced from Merck and Fluka. The used heterogeneous MCM-41-*pr*-NH₂-CuL catalyst was prepared and characterized by FT-IR, XRD, BET, SEM, TGA and ICP techniques as previously described.²⁵ A Thermo SCIENTIFIC NICOLET iS10 spectrometer obtained FT-IR spectra as KBr pellets in the 400-4000 cm⁻¹ wavenumber range. To analyze the metal content of the catalyst, an ICP-SpectroCiros CCD instrument was utilized. A Philips GC-PU 4600 tool was used for gas chromatography (GC), along with a flame ionization detector (FID).

Synthesis of copper(II) Schiff base complex (CuL)

Unsymmetrical tetradentate Schiff base ligand, salicylideneiminoethyliminopentane-2-one (H₂L), was synthesized in good yield based on the procedure described in the literature.²⁶ To prepare copper(II) Schiff base complex (CuL), 1 mmol (0.24 g) of H₂L ligand was dissolved in 25 mL of methanol and 1 mmol (0.19 g) of Cu(OAc)₂·H₂O salt dissolved in 25 mL of methanol was added to this solution. After refluxing the reaction mixture for 2 h, it was allowed to be cooled to room temperature. The resultant solid product was collected and washed several times with methanol and then purified from hot methanol (Yield: 65%). M.p.: 187 °C. Anal. calcd. for CuC₁₄H₁₆N₂O₂ (%): C, 54.59; H, 5.25; N, 9.10. Found: C, 54.08; H, 5.90; N, 8.45. FT-IR data, ν (cm⁻¹): 1630 (s, C=N), 1599 (s, C=N), 1450, 1538 (m, C=C), 1350 (m, C-O). UV-vis (CH₃CN, λ_{max} /nm): 230, 275, 328, 370.

Preparation of MCM-41-*pr*-NH₂-CuL catalyst

First, the mesoporous silica MCM-41 was prepared according to the method reported by Cai et al.²⁷ Then, pure MCM-41 (3 g) was suspended in dry toluene (50 mL), and 3-aminopropyltriethoxysilane (3 g) was added to it. The mixture was stirred and refluxed under N₂ atmosphere for 24 h. The resulting white solid MCM-41-*pr*-NH₂ was filtered, washed with toluene and dichloromethane, respectively, and dried at 100 °C for 4 h. Subsequently, a solution of CuL complex (0.5 g, 1.6 mmol) in methanol (50 mL) was added to a suspension of freshly MCM-41-*pr*-NH₂ (2 g) in methanol (50 mL). The mixture was vigorously stirred under reflux for 24 h. Finally, the obtained green solid MCM-41-*pr*-NH₂-CuL was filtered, washed with methanol using a Soxhlet apparatus, and dried at 80 °C in vacuum for 4 h.²⁵

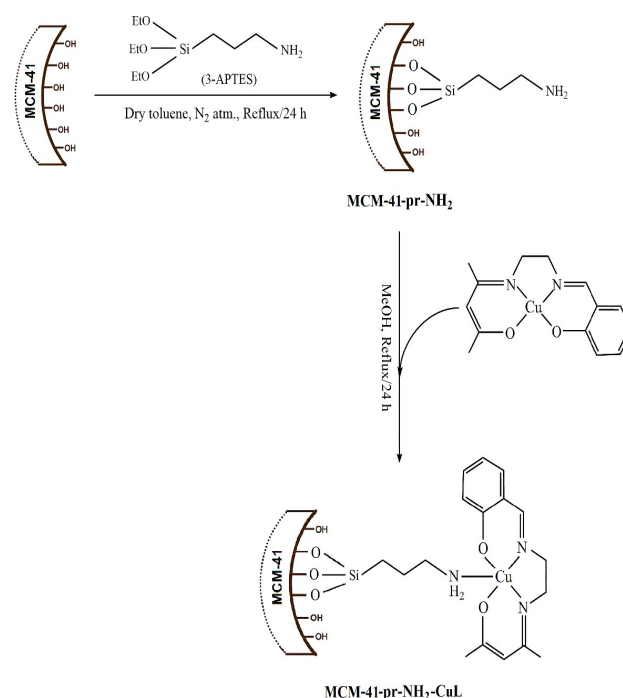
The general method for hydrocarbon oxidation with 30% H₂O₂ catalyzed by MCM-41-*pr*-NH₂-CuL

All oxidation reactions were conducted in a test tube with a magnetic stirring bar at room temperature. Alkene or alkane (1 mmol) and MCM-41-*pr*-NH₂-CuL (100 mg, 0.011 mmol) were mixed in CH₃CN (4 mL) and added 2 mmol of *tert*-BuOOH (TBHP) as oxidant. The mixture was stirred appropriately while gas chromatography (GC) monitored the reaction progress. By completing the reaction, dilution of the reaction mixture was performed with CH₂Cl₂ (20 mL), and separated the catalyst by

simple filtration. Then, the catalyst was rinsed with CH₂Cl₂, and purified the combined washings on a silica-gel column to obtain the pure product.

3. RESULTS AND DISCUSSION

The supported MCM-41-*pr*-NH₂-CuL catalyst was created by attaching the copper(II) unsymmetrical Schiff base complex to the amino-modified MCM-41 by coordinating the copper atoms to the terminal NH₂ groups on the support (Scheme 1). The bonding between the MCM-41 support and the Cu(II) Schiff base complex is so robust that CuL is not eluted from the support with usual solvents. The amount of copper anchored on 1.0 g of the supported catalyst was defined as 0.11 mmol using the inductively coupled plasma (ICP) technique.



Scheme 1. Synthetic route for MCM-41-*pr*-NH₂-CuL catalyst²⁵

Catalytic oxidation of hydrocarbons

After examining the impressive catalytic activity of MCM-41-*pr*-NH₂-CuL in the selective oxidation of alcohols,²⁵ we were intrigued to explore the potential of this supported catalyst in oxidizing hydrocarbons like alkanes and alkenes. To investigate the MCM-41-*pr*-NH₂-CuL ability in the oxidation of alkenes, we focused on oxidizing cyclooctene as a model substrate, and different parameters, including the amount of catalyst, kind of solvent, and type of oxidant were examined.

To find an appropriate solvent for the oxidation of cyclooctene in the existence of MCM-41-*pr*-NH₂-CuL, various solvents such as methanol, ethanol, acetonitrile, acetone, chloroform, and carbon tetrachloride were tested, and the results showed that the best cyclooctene

conversion and epoxide yield was achieved in acetonitrile at room temperature (Table 1). It appears that increasing the solvent polarity is likely to lead to an increase in epoxide yield and conversion.

Table 1. The solvents effect on the epoxidation of cyclooctene with *tert*-BuOOH catalyzed by MCM-41-pr-NH₂-CuL at room temperature^a

Entry	Solvent	Dipole moment (D)	Time (h)	Epoxide yield (%)
1	CH ₃ OH	1.70	4	35
2	C ₂ H ₅ OH	1.69	4	42
3	CH ₃ COCH ₃	2.88	4	53
4	CH ₃ CN	3.92	4	90
5	CHCl ₃	1.15	4	27
6	CCl ₄	0	4	12

^aReaction conditions: cyclooctene (1 mmol), *tert*-BuOOH (2 mmol), catalyst (100 mg), solvent (4 mL).







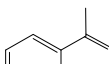

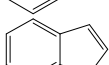





After conducting several tests, it was found that the optimal amount of MCM-41-pr-NH₂-CuL catalyst for the epoxidation of cyclooctene with *tert*-BuOOH is 100 mg (0.011 mmol of Cu). The higher amount of catalyst did not show any significant impact on the epoxide yield (Table 2). Note that when MCM-41 and MCM-41-pr-NH₂ (without CuL complex) were used as catalysts, the results were similar to the reaction in the absence of catalyst (Table 2, entries 7 and 8).

Table 2. The effect of catalyst amount on the epoxidation of cyclooctene with *tert*-BuOOH catalyzed by MCM-41-pr-NH₂-CuL at room temperature^a

Entry	catalyst amount (mg)	Time (h)	Epoxide yield (%)
1	0	4	10
2	25	4	35
3	50	4	52
4	75	4	73
5	100	4	90
6	125	4	92
7	MCM-41 (100 mg)	4	10
8	MCM-41-pr-NH ₂ (100 mg)	4	12

^aReaction conditions: cyclooctene (1 mmol), *tert*-BuOOH (2 mmol), catalyst, CH₃CN (4 mL).

Table 4. Epoxidation of various alkenes with *tert*-BuOOH catalyzed by MCM-41-pr-NH₂-CuL at room temperature^a

Entry	Alkene	Product	Conversion (%)	Epoxide yield (%)	Time (h)
1			90	90	4
2			85 ^b	80	4
3			90 ^c	83	4
4			83 ^d	75	4
5			82	82	4
6			73	73	4.5
7			57	57	4.5

^aReaction conditions: alkene (1 mmol), *tert*-BuOOH (2 mmol), catalyst (100 mg, 0.011 mmol), CH₃CN (4 mL). ^bThe by-product is 2-cyclohexene-1-one (5%). ^cThe by-product is benzaldehyde (7%). ^dThe by-product is acetophenone (8%).

According to Table 3, *tert*-BuOOH is the most effective oxidant for the epoxidation of cyclooctene when compared to other oxidants, such as 30% H₂O₂, urea/H₂O₂ (UHP), and NaIO₄. It is worth noting that in the absence of oxidant, no epoxide was obtained.

Table 3. The epoxidation of cyclooctene catalyzed by MCM-41-pr-NH₂-CuL with various oxidants at room temperature^a

Entry	Oxidant	Time (h)	Epoxide yield (%)
1	30% H ₂ O ₂	4	57
2	H ₂ O ₂ /urea	4	33
3	<i>tert</i> -BuOOH	4	90
5	NaIO ₄	4	8
6	No oxidant	4	No reaction

^aReaction conditions: cyclooctene (1 mmol), oxidant (2 mmol), catalyst (100 mg), CH₃CN (4 mL).

Table 4 presents the findings of the oxidation of different alkenes utilizing *tert*-BuOOH and the MCM-41-pr-NH₂-CuL catalyst at room temperature under optimal reaction circumstances. Experimentally, this heterogenized catalytic system is highly effective in the epoxidation of different types of alkenes. Styrene and α -methyl styrene were converted to their respective epoxides with high selectivity, and only 7% of benzaldehyde and 8% of acetophenone were created as minor products, respectively. Cyclooctene was transformed to its epoxide with an impressive yield of 90% after 4 h. Cyclohexene oxidation resulted in cyclohexene oxide as the major product (80%), with only a minor amount (5%) of 2-cyclohexene-1-one. Indene was transformed to its equivalent epoxide with selectivity of 100% and yield of 82%, while linear alkenes like 1-dodecene and 1-octene produced their respective epoxides with high yields and selectivity. These results proved that this catalytic system has great potential for producing various epoxides.

In organic chemistry, the oxidation of saturated hydrocarbons has always been a challenging problem. So, the catalytic activity of MCM-41-pr-NH₂-CuL was examined in the oxidation of alkanes. The findings showed that this catalytic system can convert various alkanes into corresponding alcohols and ketones under mild reaction conditions. According to Table 5, cyclohexane and cyclooctane were oxidized to their respective alcohols and ketones with good yields.

However, the results for ethylbenzene, propylbenzene, and tetralin were moderate and only the corresponding ketones were produced.

After analyzing the performance of MCM-41-pr-NH₂-CuL for epoxidation using *tert*-BuOOH, it was found that this method offers several benefits compared to previously reported data (Table 6). The protocol demonstrated high TON and TOF, short reaction times and mild reaction conditions.

Proposed reaction mechanism


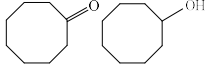

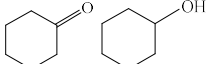
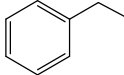
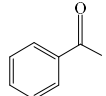
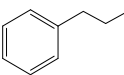
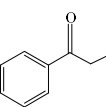
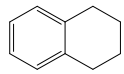
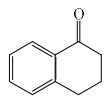
In order to study the mechanism of epoxidation reaction, cyclooctene oxidation was carried out in the presence of Ph₂NH as an efficient radical scavenger. It was found that the addition of Ph₂NH inhibits the cyclooctene oxidation and the reaction proceeds via a radical mechanism. So, it seems that decomposition of *tert*-BuOOH to *tert*-butoxyl and *tert*-butylperoxyl radicals is catalyzed by Cu²⁺ in one-

electron transfer processes.³³ According to the radical mechanism operation, the main reason for different product selectivity in the oxidation of cyclic alkenes is due to competition between oxidation of the double bond and the allylic site.³⁴ In this catalytic system (Scheme 2), the sole product of cyclooctene oxidation is cyclooctene epoxide. The high selectivity of the epoxide reveals that only the double bond undergoes oxidation. In the case of cyclohexene, both epoxidation and allylic oxidation occurred, and cyclohexene epoxide was formed as the main product and 2-cyclohexen-1-one as a side product. On the other hand, styrene oxidation gives styrene epoxide and benzaldehyde. In this reaction, styrene epoxide is firstly formed and production of benzaldehyde may be due to the ring opening of styrene epoxide followed by cleavage of C-C bond.³⁵

Catalyst reuse and stability

The reusability of the MCM-41-pr-NH₂-CuL catalyst was explored in the oxidation of cyclooctene with *tert*-BuOOH. The catalyst was carefully washed with CH₂Cl₂, dried in the oven at 90 °C after each reaction, and used for the next run under optimal reaction circumstances. The findings indicate that the catalyst can be reused up to four times without experiencing a significant loss of its initial activity and selectivity. Furthermore, atomic absorption spectroscopy (AAS) was used to analyze the filtrates

Table 5. Hydroxylation of alkanes with *tert*-BuOOH catalyzed by MCM-41-pr-NH₂-CuL at ambient temperature^a

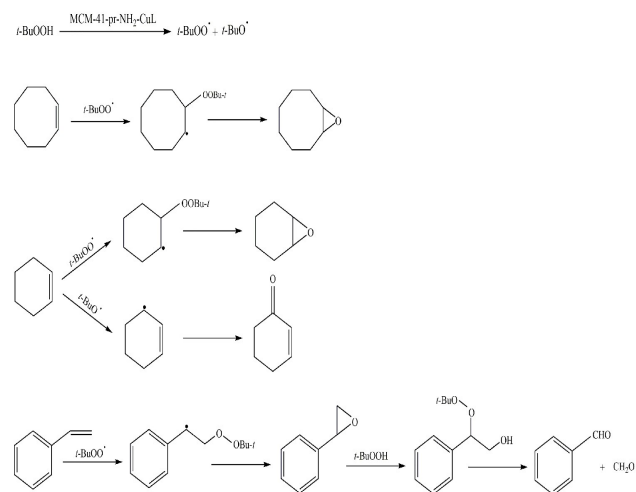
Entry	Alkane	Product	Conversion (%)	Ketone (%)	Alcohol (%)	Time (h)
1			82	57	25	4
2			72	64	8	4
3			62 ^b	62	-	4
4			54 ^c	54	-	4
5			65 ^d	65	-	4

^aReaction conditions: alkane (1 mmol), *tert*-BuOOH (2 mmol), catalyst (100 mg, 0.011 mmol), CH₃CN (4 mL). ^bThe product is acetophenone. ^cThe product is ethyl phenyl ketone. ^dThe product is 1-tetralone.

Table 6. The catalytic activity of MCM-41-pr-NH₂-CuL compared with some other systems reported for epoxidation of cyclooctene

Entry	Catalyst	Conditions	Time (h)	Conversion (%)	Epoxide yield (%)	TON	TOF (h ⁻¹)	Ref.
1	V-MIL-101	CH ₃ CN, TBHP, Reflux	14	35	90	148	10.57	[28]
2	Fe@B-Im-V	C ₂ H ₄ Cl ₂ , TBHP, Reflux	4.5	98	98	43.75	9.72	[29]
3	DVB-AA-Mo	CHCl ₃ , TBHP, 70 °C	4	95	95	19	4.75	[30]
4	[MoO ₂ (acac)-POM]	C ₂ H ₄ Cl ₂ , TBHP, 75 °C	8	100	100	62.48	7.81	[31]
5	[Mn(TPP)Cl]@AP-MWCNT	CH ₃ CN/H ₂ O, NaIO ₄ , r.t.	6	94	94	45.36	7.56	[32]
6	MCM-41-pr-NH ₂ -CuL	CH ₃ CN, TBHP, r.t.	4	90	90	81.82	20.45	This work

collected after each cycle to determine copper leaching, and the results showed no significant copper leaching after the first three runs (Table 7).



Scheme 2. Proposed mechanism for oxidation of cyclooctene, cyclohexene, and styrene with *tert*-BuOOH catalyzed by MCM-41-pr-NH₂-CuL

Table 7. Reusability and stability of MCM-41-pr-NH₂-CuL catalyst in the epoxidation of cyclooctene with *tert*-BuOOH at room temperature^a

Run	Conversion (%)	Epoxide yield (%)	Time (h)	Cu leached (%) ^b
1	90	90	4	2.7
2	87	87	4	1.5
3	85	85	4	1.0
4	85	85	4	0

^aReaction conditions: cyclooctene (1 mmol), *tert*-BuOOH (2 mmol), catalyst (100 mg), CH₃CN (4 mL). ^bDetermined by AAS.

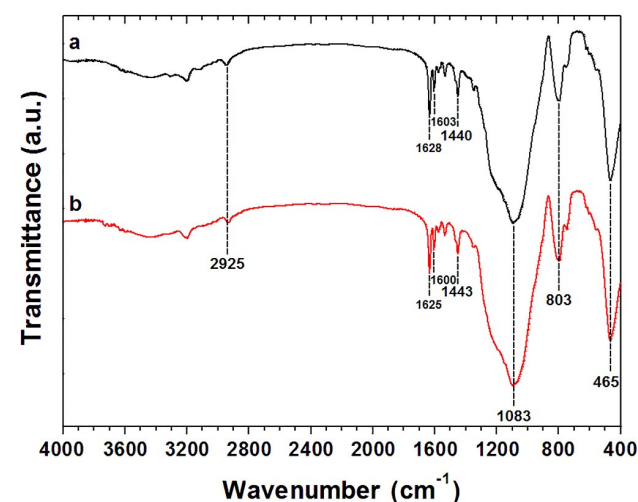


Figure 1. FT-IR spectrum of (a) fresh and (b) recovered MCM-41-pr-NH₂-CuL catalyst.

The FT-IR spectroscopy was also used to characterize the recovered catalyst. The catalyst's FT-IR spectrum after five runs is displayed in Figure 1a. The three bands at 1083, 803, and 465 cm⁻¹ were allocated to the Si-O-Si

asymmetrical stretching, symmetrical stretching, and bending vibrations, respectively. Additionally, the band at 2925 cm⁻¹ was associated with the vibrations of aliphatic CH₂ groups. Two bands at 1625 and 1600 cm⁻¹ were assigned to two different C=N stretching vibrations of the Schiff base ligand, while the band at 1443 cm⁻¹ was ascribed to the C=C stretching vibrations. It is worth noting that all of these IR bands were also observed for the fresh catalyst (Figure 1b), indicating that the structure of the catalyst remained preserved after recovery.

4. CONCLUSIONS

In summary, the MCM-41-pr-NH₂-CuL composite was utilized as a heterogeneous catalyst for the selective oxidation of alkanes and alkenes with *tert*-BuOOH as oxidant at room temperature. This method has several benefits, including short reaction times, good to superior yields, and mild reaction circumstances. Furthermore, it is possible to separate the catalyst from the reaction mixture by simple filtration and reuse it four times without losing effectiveness.

CONFLICTS OF INTEREST

No conflicts of interest are declared.

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