

Immobilization of Cu(II)-Histidine Complex on Al-MCM-41 as Catalyst for Epoxidation of Alkenes

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Abstract

Cu(II) complex with L-histidine (His) ligand, immobilized within Al-MCM-41, designated as Cu(His)₂/Al-MCM-41 was prepared and characterized by powder X-ray diffraction (XRD), nitrogen adsorption desorption, FTIR, UV-Vis and chemical analysis techniques. The surface area and pore volume were found to decrease after immobilization of Cu(II) complex on Al-MCM-41. It was found that Cu(His)₂/Al-MCM-41 catalyze the oxidation of some alkenes such as norbornene and *trans*-stilbene with tert-butylhydroperoxide (TBHP) with high activity and selectivity to the corresponding epoxides. It was concluded that the Al-MCM-41 nanoreactors is a suitable support for immobilization of biomimetic molecules. Particularly significant is that no desorption was observed during the course of reactions.

Keywords: Histidine; Copper complex; Epoxidation; Al-MCM-41

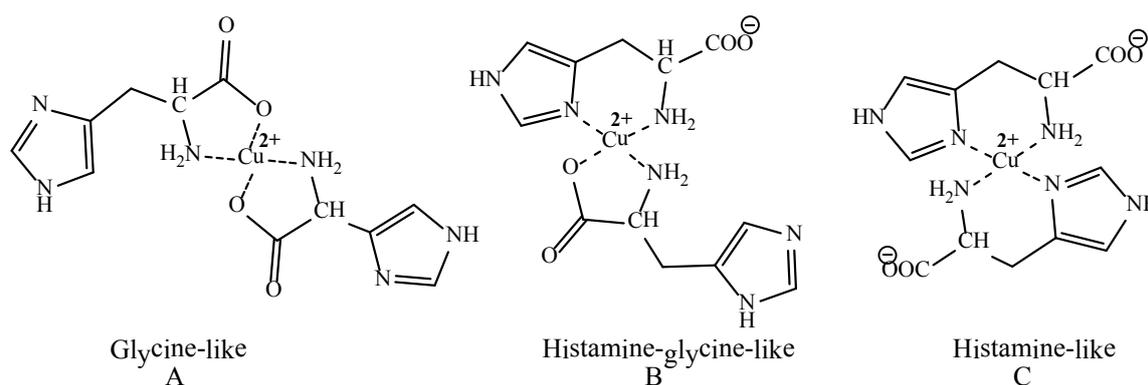
Introduction

Catalytic oxidation is an important technology that finds applications in each kind of chemical industry. It is well known that common oxidation processes have been accomplished using transition metal species as catalysts either supported or not, and stabilized by variety of ligands [1-2]. Enzymes with the properties of ideal catalysts, operate at ambient condition and combine high activity [3-5]. A disadvantage, however is their limited thermal stability and chemical resistance. Many catalyst researches try to design catalyst that matches the performance and properties of an enzyme. Cu is one of the most abundant transition metals present in living systems, and Cu⁺² ions are well-known to play a key role in the working mechanism of several

important metalloenzymes, such as galactose oxidase and superoxidedismutase [6]. A driving force in the activity of these enzymes is the folding of a peptide, which consists of amino acid side chains, around the Cu⁺² cations. Histidine moieties are known to be of major importance in this process because this type of N-coordinating ligand forms fairly stable complexes with the Cu cations. To unravel the formation processes of these types of enzymes and to find the exact coordination geometry of the Cu/His moieties, many research has been conducted in this area, much of which has been summarized in recent reviews[7-9].

Another important motivation to study this amino acid complex is their expected role in the development of manmade enzymes via functionalization of inorganic hosts such as zeolites and clay minerals with these types

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Scheme I. Three different possibility for coordination of L-histidine to the copper ions.

of complexes[10-13].

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 complexes with nitrogen containing molecules are widely used as model compounds for mimicking the catalytic properties of mono-oxygenases [14-15].

In this study, attempt has also been made to encapsulate the copper complex with His in nanoreactors of Al-MCM-41. This novel encapsulation procedure, involves budding a mesoporous (host) around a preformed and structurally defined amino acid copper complex (guest), generating a catalysis system, in order to investigate catalytic behavior of prepared catalysts for epoxidation of alkenes.

Materials and Methods

All the materials of commercial reagent grade were purchased from Merck Chemical Company and used without further purification.

Physical Measurements

BET surface areas and pore size distributions of the initially degassed samples at 373 K for 90–120 min were calculated from nitrogen adsorption–desorption isotherms obtained at 77 K with a Belsorp Mini-II instrument. The UV–Vis measurements were performed on a double beam UV–Vis Perkin Elmer Lambda 35 spectrophotometer. X-ray diffraction patterns were obtained by a Siefert 3003 PTS diffractometer using Cu K_{α} radiation ($\lambda = 1.5406 \text{ \AA}$). FTIR spectra were recorded on a Bruker Tensor 27 IR spectrometer in KBr pellets over the range of 4000–400 cm^{-1} under the atmospheric conditions. The amount of copper in complex was

determined by atomic absorption spectroscopy (AAS) with a GBC spectrophotometer using flame approach. Oxidation products were analyzed by GC and GC Mass using Agilent 6890 Series with FID detector, HP-5% phenylmethylsiloxane capillary and Agilent 5973 Network, mass selective detector, HP-5MS 6989 Network GC system, respectively.

Preparation of Catalysts

Synthesis of Al-MCM-41

The Al-MCM-41 (Si/Al = 50) with molar composition 1:SiO₂: 1:6 methyl amine: 0.215 hexadecyltrimethylammonium bromide (HDTMABr): 125 H₂O:0.02 Al₂O₃ was prepared according to the reported method [16]. First, methylamine (2.08 mL) was added to distilled H₂O (42 mL) and the mixture was stirred at room temperature for 10 min. The surfactant HDTMABr (1.47 g) was then gradually added to the solution under stirring for 60 min, followed by drop wise addition of tetraethylorthosilicate (TEOS) (2.1 g, 2.25 mL) and aluminum hydroxide (0.06g in 5ml H₂O). The pH of the reaction mixture was adjusted to 8.5 by slow addition of hydrochloric acid solution (1 M). At this stage, a precipitate was formed. After 2 h, under slow stirring, the precipitate was separated by centrifugation. The sample was dried at 45 °C for 12 h. The obtained solid was calcined at 550 °C for 5 h to afford a white powder.

Preparation of Cu(His)₂ Complex

Cu(His)₂ complex was prepared according to the reported procedure.[6]. To L-Histidine (2 mmol in a 5 ml H₂O) was slowly added NaOH (6 M, 0.33 mL). A solution of Cu(NO₃)₂·3H₂O (1 mmol) in H₂O (5 mL) was then added to the basic histidine solution. The precipitate of the complex was formed after stirring for

10 min. The solid product was filtered and washed with acetone for three times. The FTIR(KBr) $\nu_{\text{asCO}_2^-}$ (1601 cm^{-1}), $\nu_{\text{C=N}}$ (1501 cm^{-1}), $\nu_{\text{CO}_2^-}$ (1395 cm^{-1}), $\nu_{\text{Cu-N}^\pi}$ (1272, 1082 cm^{-1}), $\nu_{\text{Cu-N}}$ (454 cm^{-1}) and UV-Vis $\sigma \rightarrow \sigma^*$ (210 nm), $\pi \rightarrow \pi^*$ (245 nm), d-d (636 nm)] were consistent with those reported before [6,17-18].

Immobilization of Cu Complex within Al-MCM-41

Cu(His)₂ complex (0.5 mmol, 0.2 g in 10 mL MeOH) was added to Al-MCM-41 (1g in 10 mL MeOH). The resultant mixture was refluxed for 24 h. The solid was then filtered and washed with MeOH and dried under vacuum for 2 h.

Oxidation of Olefins: General Procedure

All epoxidation reactions of the alkenes (norbornene, cyclohexene, cyclooctene, styrene and *trans*-stilbene) were carried out in a round bottom flask equipped with a magnet stirrer and a water-cooled condenser under atmospheric pressure. Typically, a mixture of catalyst (100 mg) and alkene (20 mmol) dissolved in CH₃CN (5 mL) was added to the reaction flask upon slow stirring. After a few min, TBHP (24 mmol, 80% in di-tertiary butyl peroxide) was added and the mixture was refluxed for 6 h. The solid was then filtered, washed with fresh acetone and the filtrate was subjected to GC and GC mass analysis.

Results and Discussion

Characterization of Cu Complex

The general coordination for a copper complex with two α -amino acids such as L-histidine is the binding of the Cu²⁺ by both amino nitrogens and carboxyl oxygen designated as NNNO coordination or a glycine like bonding (Scheme.IA) [13,19]. For Cu(histidine)₂ in the pH region 4.5-7.5, the two histidine ligands are coordinated to Cu²⁺ ions in the coordination plane by the amino N and the imidazole N, while the carboxylate group in an apical position. However, the carboxylate oxygen of one of the histidine ligands can replace partially by one of the imidazole nitrogens and an equilibrium exists between NNNN and NNNO binding in the coordination plane of bis histidine complexes. In NNNO species one histidine is bound histamine-like and the other glycine like (Scheme.IB) and NNNN coordination are called histamine-like bonds (scheme IC). At physiological pH, one of the imidazole groups of histidine ligand not involved in copper coordination [12,18,19].

Based on previous reports[13,19-20], at pH=7.5, two histidine ligands are coordinated to Cu²⁺, one glycine-like and one histamine-like. In addition, one carboxylate group coordinates in an apical position. If such, the formed complex containing NNNO coordination has a net positive charge of 1. Comparison of the FTIR spectrum of the Cu complex with that reported previously [21], the coordination of the prepared complex should be Histamine-glycine-like (schemeIB) [6]. The peaks observed at regions of 1633 cm^{-1} , 1501, and 454 cm^{-1} are due to the carboxylate group, C=N and Cu-N bindings to the Cu²⁺ ions, respectively.

Characterization of Immobilized Copper Complexes in Nanoreactors of Al-MCM-41

FTIR, UV-Vis Spectroscopy Studies

FTIR spectrum of Cu(His)₂ complex, Al-MCM-41 and Cu(His)₂/Al-MCM-41 are shown in Figure 1a-c, respectively. The broad band (Figure 1a) appearing from 3500 to 3400 cm^{-1} may be attributed to the surface silanol and -OH groups of the adsorbed water. The bands at 1217, 1081 cm^{-1} are due to the asymmetric stretching vibrations of Si-O-Si bridges, and those that appear at 967 to 950 cm^{-1} arise from Si-O-Al, stretching vibrations. The bands at 806 and 459 cm^{-1} are related to symmetric stretching vibrations and bending vibrations of Si-O-Si bridges respectively [20]. FTIR of Cu(His)₂ complex after immobilization in Al-MCM-41 (Figure 1c) shows that asymmetric stretching vibration of Si-OH in Al-MCM-41 is accompanied with symmetric stretching vibration of C-H group of imidazole ring and aliphatic stretching vibrations of C-H and CH₂ groups present in copper complex. The bending vibration of Si-OH group in Al-MCM-41 is also accompanied with asymmetric stretching vibration of COO⁻ in copper complex.

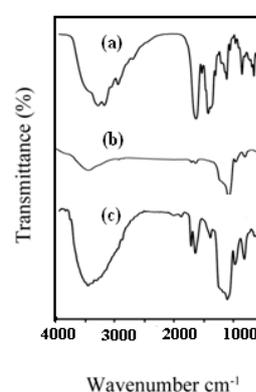


Figure 1. FTIR of (a) Cu(His)₂ complex, (b) Al-MCM-41 and (c) Cu(His)₂/Al-MCM-41.

UV-Vis spectrum of $\text{Cu}(\text{His})_2$, $\text{Cu}(\text{His})_2/\text{Al-MCM-41}$ and Al-MCM-41 are shown in Figures 2a-c respectively. Based on these results, copper complex immobilization within the Al-MCM-41 is rationalized.

Powder X-ray Diffraction

The powder X-ray diffraction pattern of calcined Al-MCM-41 presented in Figure 3a includes one strong and two weak peaks, consistent with those previously reported [21] and can be indexed on a hexagonal lattice. The XRD patterns of $\text{Cu}^{2+}/\text{Al-MCM-41}$ and $\text{Cu}(\text{His})_2/\text{Al-MCM-41}$, are shown in Figures 3b and 3c respectively. Compared to the calcined Al-MCM-41 peaks, a decrease in peak intensities indicates that the Al-MCM-41 pore and surface silanol groups have reacted with the Cu compounds (Table 1).

N_2 adsorption-Desorption Studies

The N_2 adsorption-desorption isotherms of Al-MCM-41 , $\text{Cu}(\text{His})_2/\text{Al-MCM-41}$ and $\text{Cu}^{2+}/\text{Al-MCM-41}$ are shown in Figure 4 and Table 1. The type IV isotherms [22] indicate that adsorption takes place as a thin layer on the walls at low relative pressures, P/P_0 (monolayer coverage). In addition, the inflection heights of $\text{Cu}(\text{His})_2/\text{Al-MCM-41}$ in the nitrogen adsorption isotherm plots are smaller than those of Al-MCM-41 . This phenomenon is attributed to the reduced pore volume that decreases from 0.9601 to $0.7064 \text{ cm}^3\text{g}^{-1}$, which reflects the decrease in surface area (Table 1). This effect is due to the inclusion of $\text{Cu}(\text{His})_2$ into the Al-MCM-41 pores. The same results are obtained for immobilized $\text{Cu}^{2+}/\text{Al-MCM-41}$.

Epoxidation of Alkenes Catalyzed by $\text{Cu}(\text{His})_2/\text{Al-MCM-41}$

To choose the best reaction time, the epoxidation reactions were carried out in the presence of 0.1 g of the $\text{Cu}(\text{His})_2/\text{Al-MCM-41}$ as catalyst at different reaction times using norbornene as the representing substrate. The results are presented in Table 2. Notably, norbornene is mostly oxidized during 6 h , beyond which no further oxidation occurs. The conversion of norbornene increases significantly by increasing the amount of catalyst in the range of 0.025 to 0.10 g (Table 3).

Results of the effect of $\text{Cu}(\text{His})_2/\text{Al-MCM-41}$, $\text{Cu}(\text{His})_2$ complex and $\text{Cu}^{2+}/\text{Al-MCM-41}$ are indicated in Table 4. We have included the effect of Al-MCM-41 void of complex in Table 4 in order to make the comparison more convenient. As is observed, norbornene is almost quantitatively oxidized to the corresponding epoxide with 90% conversion and 95% selectivity (entry 1). Epoxidation efficiencies

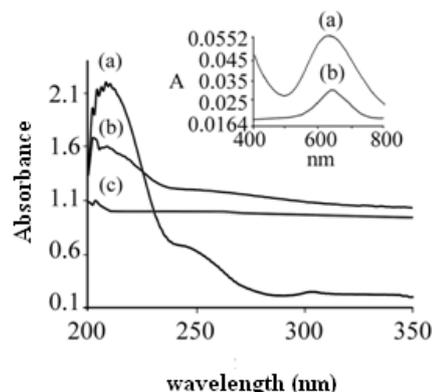


Figure 2. UV-Vis of (a) $\text{Cu}(\text{His})_2$ complex, (b) $\text{Cu}(\text{His})_2/\text{Al-MCM-41}$ and (c) Al-MCM-41 .

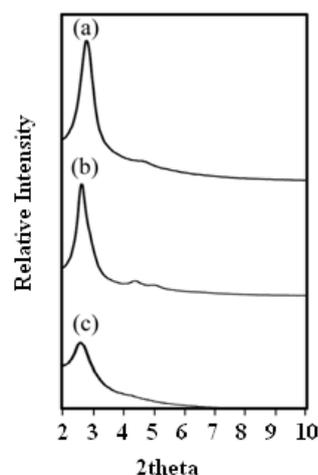


Figure 3. XRD diffraction pattern of (a) Al-MCM-41 , (b) $\text{Cu}^{2+}/\text{Al-MCM-41}$ (c) and $\text{Cu}(\text{His})_2/\text{Al-MCM-41}$.

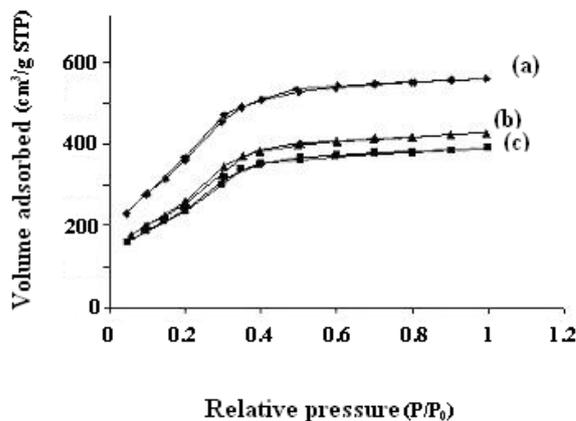


Figure 4. Nitrogen adsorption desorption of (a) Al-MCM-41 , (b) $\text{Cu}(\text{His})_2/\text{Al-MCM-41}$ and (c) Cu^{2+} Al-MCM-41 .

Table 1. Texture parameters of samples taken from XRD and nitrogen sorption studies

Material	XRD d value (Å)	Lattice parameter (Å)	BET ^a (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Average pore diameter (Å)
Al-MCM-41	32.00	36.95	1473	0.9601	2.053
Cu(His) ₂ /Al-MCM-41	35.00	40.41	1062	0.7064	2.158
Cu ²⁺ /Al-MCM-41	36.75	42.43	956	0.6434	2.186

^a Specific surface area.

significantly decreases to 69% (entry 2), 22% (entry 3) and finally 5% (entry 4) under the effect of the other indicated catalysis system. Therefore the key roles of the copper complex as well as the heterogeneous character of the catalyst are evident.

We then examined the epoxidation of other alkenes such as *trans*-stilbene, cyclohexene, cyclooctene and styrene with TBHP in CH₃CN in the presence of Cu(His)₂/Al-MCM-41 (Table 5). Identification of the products was carried out by comparison of their mass spectra with those of the authentic samples. With the exception of cyclohexene, other examined alkenes undergo epoxidation with moderate to good efficiencies.

To make insight into the reaction mechanism [23-24], the oxidation reaction of cyclooctene was carried out in the presence of diphenylamine as a radical scavenger [25]. It was found that both the catalytic epoxidation and allylic oxidation were strongly inhibited in the presence of the diphenylamine. Notably, copper catalysis of olefin oxidations with TBHP have been carried out to high turnover numbers since Cu(His)/Al-MCM-41 was recovered intact. The formation of 1-(*tert*-butylperoxy)-2-cyclohexene in cyclohexene oxidation provides a rather strong evidence for the involvement of *tert*-BuOO radical as a reactive intermediate [26]. Therefore, it seems likely that TBHP decomposes into chain initiating *tert*-BuO and *tert*-BuOO radicals in one-electron transfer processes catalyzed by Cu²⁺. Following alternatives represent the behavior of each alkene:

a) The catalytic oxidation of cyclohexene gives the mixed peroxide 1-(*tert*-butylperoxy)-2-cyclohexene as the principle product in 83% yield but only small amounts of 2-cyclohexene-1-ol and 2-cyclohexene-1-one. It has been shown that in case of lower energy geometry optimized structure of cyclohexene, double bonded carbons as well as the allylic carbons are in one plane [27]. Therefore, cyclohexene with highly active allylic hydrogens is less prone to undergo epoxidation in reaction with *tert*-BuOO free radical. Recall that epoxidation of cyclohexene has been found to occur if it directly reacts with coordinated *t*-BuOO radical [28]. Moreover, the *tert*-BuOO free radical is not selective

enough in addition to double bond [29]. It rather prefers to abstract an allylic hydrogen from cyclohexene to afford cyclohexenyl radical. Subsequent coupling of this radical with *tert*-BuOO radical leads to the formation of the mixed peroxide 1-(*tert*-butylperoxy)-2-cyclohexene (Scheme IIa).

b) In the case of *trans*-stilbene and norbornene, addition of *tert*-BuOO free radical to double bond is inevitable. Whereas the former has no allylic hydrogens, hydrogen atom abstraction by *tert*-BuOO radical from the latter generates an unstable bridgehead radical [30]. Therefore, these two alkenes undergo addition of the *tert*-BuO radical followed by subsequent β-elimination, leading to the *trans*-stilbene and norbornene epoxides, respectively (Scheme IIb). The formation of *trans*-stilbene epoxide from *trans*-stilbene as the sole product

Table 2. The Effect of time in epoxidation of olefins by catalyst Cu(His)₂/Al-MCM-41

Time (h)	Conversion (%)	Product distribution (%)	
		Epoxy	Others
2	43	96	4
4	59	97	3
6	85	95	5
8	86	97	3

Conditions: norbornene, 2mmol; TBHP, 24mmol; solvent, CH₃CN 5ml.

Table 3. Effect of the amount of catalyst in epoxidation of norbornene by Cu(His)₂/Al-MCM-41

Entry	Amount of catalyst (mg)	Conversion (%)	Product distribution (%)	
			Epoxy	Others
1	0.025	59	88	12
2	0.050	60	96	4
3	0.100	90	95	5
4	0.200	91	95	5

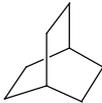
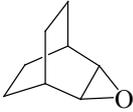
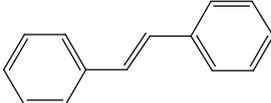
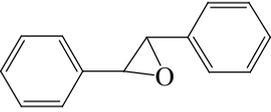
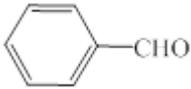
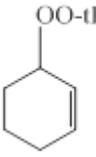
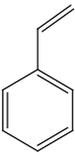
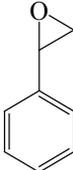
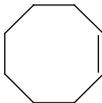
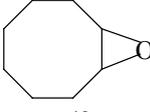
Conditions: norbornene, 2mmol; TBHP, 24mmol; solvent, CH₃CN 5mL, time 6h.

Table 4. Catalytic results with catalysts for epoxidation of norbornene

Entry	Type of catalyst	Conversion (%)	Product distribution (%)		
			Epoxy	Aldehyde	Others
1	Cu(His) ₂ /Al-MCM-41	90	95	5	0
2	Cu ²⁺ /Al-MCM-41	69	95	1	4
3	Cu(His) ₂ complex	22	92	4	4
4	Al-MCM-41	5	90	-	-

Conditions: norbornene, 20mmol; TBHP, 24mmol; solvent, CH₃CN 5ml, time 6h.

Table 5. Results of the oxidation of organic hydrocarbons with TBHP in the presence of Cu(His)₂/Al-MCM-41

Substrate	Conversion (%)	Major product (%)	Minor product(s) (%)	TON
	90	 95	5	1307
	90 ^a	 45	 55	69
	62	 83	17 ^c	954
	78	 53	47 ^d	1200
	36 ^b	 43	57 ^e	554

Reaction conditions: substrate, 20 mmol; TBHP, 24 mmol; acetonitril, 5 mL; time 6 h.

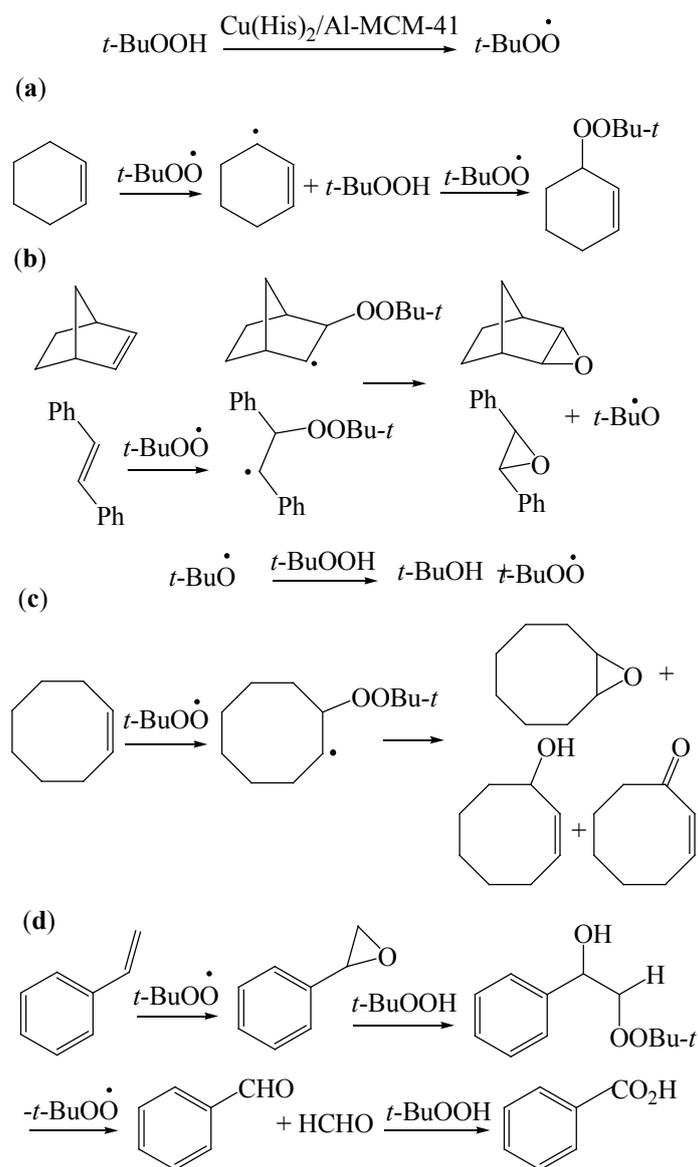
^a1mmol of trans-stilbene was used. ^bReaction time: 12 h. ^c 2-Cyclohexene-1-ol (3.5%), 2-cyclohexene-1-one (10.5%). ^d phenol (7%), benzaldehyde (10%), benzoic acid (13%), unidentified (17%). ^e 2-Cyclooctene-1-ol (12%), 2-cyclooctene-1-one (45%).

via a radical intermediate is expected due to the higher thermodynamic stability of the *trans* in comparison to the *cis* stereoisomer, in which the phenyl groups are located in *anti* position with respect to each other.

c) In the case of *cis*-cyclooctene in which the lower energy optimized structures are in a chair confirmation with the double bond in one plane and all other carbons

in another plane [27]. Reactivity of cyclooctene allylic hydrogens is lower than those of cyclohexene. Therefore, the formation of cyclooctene oxide in 43%, along with 2-cycloocten-1-ol and 2-cyclooctene-1-one in 42% is not surprising (Scheme IIc).

d) The formation of benzaldehyde and benzoic acid from styrene is explained according to the proposed



Scheme II. Proposed mechanism for the oxidation of (a) cyclohexene, (b) *trans*-stilbene and norbornene, (c) cyclooctene, (d) styrene.

mechanism depicted in Scheme II. As has been explained previously, the preliminary generated styrene oxide partly undergoes ring opening by *tert*-BuOOH. Subsequent degradation and further oxidation, finally affords benzaldehyde and benzoic acid [31-32].

In summary, The Cu(II) complex with His ligand, immobilized within nanoreactors of Al-MCM-41 was prepared and characterized. Catalytic activity of Cu(His)₂/Al-MCM-41 was examined for the epoxidation and oxidation of norbornene, *trans*-stilbene, cyclohexene, cyclooctene and styrene with TBHP in

acetonitrile. High to moderate conversions toward the formation of the corresponding epoxides were observed in most cases. It was concluded that the Al-MCM-41 nanoreactors is a suitable medium for immobilization of biomimetic molecules. Particularly significant is that no desorption was observed during the course of reactions.

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