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Copper(II) complex of (±)*trans*-1,2-cyclohexanediamine azo-linked Schiff base ligand encapsulated in the nanocavity of zeolite-Y for the catalytic oxidation of olefins

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Abstract: A Schiff base ligand derived from 2-hydroxy-5-(phenylazo)-benzaldehyde and (±)*trans*-1,2-cyclohexanediamine (H_2L) and its corresponding Cu(II) complex (CuL) were synthesized and characterized by FT-IR, UV–Vis and ^{1}H-NMR spectroscopy. The copper Schiff base complex was encapsulated in the nanopores of zeolite-Y (CuL-Y) by the flexible ligand method and its encapsulation was confirmed by different studies. The homogeneous and the corresponding heterogeneous catalysts were used for the oxidation of different alkenes with *tert*-butyl hydroperoxide. Under the optimized reaction conditions, the oxidation of cyclooctene, cyclohexene, styrene and norbornene catalyzed by CuL gave 89, 63, 46 and 13 % conversion, respectively. These olefins were oxidized efficiently with 50, 96, 95 and 92 % conversion, respectively, in the presence of CuL-Y. Comparison of the catalytic behavior of CuL and CuL-Y showed the higher catalytic activity and selectivity of the heterogeneous catalyst with respect to the homogenous one.

Keywords: catalyst; 2-hydroxy-5-(phenylazo)-benzaldehyde; styrene; zeolite; encapsulated.

INTRODUCTION

Various transition metal complexes have been used in the catalytic oxidation of organic substrates.[1] In particular, the catalysis of alkene oxidation by transition metal complexes is an area of current interest.[2,3] Schiff base ligands are easily synthesized by the condensation of amines and aldehydes.[4] The development of the salen transition metal complexes has provided a useful catalyst for epoxidation reactions. In 1990, the Jacobsen[5] and Katsuki[6] groups first reported that Mn(III) salen complexes were applied in the epoxidation of non-functionalized alkenes. They extensively studied the steric[7] and electronic effects[8] of sub-

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stituent groups on the salen ligand that could affect the enantioselectivity and rate of this reaction.[9] Schiff bases having both azo and azomethine groups are called azo Schiff bases. These compounds are used in the textile, leather and plastic industries[10–12] and have the potential for use in electronic and drug delivery applications.[13,14] Azo compounds are useful in analytical applications, *e.g.*, as complexometric and pH indicators.[15] Moreover, these derivatives show biological activities.[16,17] A few azo Schiff base complexes were reported to be catalytically active towards oxidation.[18] Therefore, it is of interest to study azo-linked compounds as catalysts.

Immobilization of homogeneous catalysts onto or into an insoluble solid, which can be either an inorganic solid or an organic polymer, provides higher activity, selectivity and reusability of catalysts.[19–22] Several examples of heterogenization of homogeneous catalysts onto some inorganic supports, such as MCM-41,[23,24] SBA-15[25,26] and zeolites[27–29] have been reported.

Among the different metal complexes, Cu(II) Schiff base complexes are known for their oxygenation reactions. Various copper complexes catalyzed olefin oxidation reactions in homogeneous[30,31] and heterogeneous[32,33] media and the mechanisms of these reactions are well established.

In this study, the copper(II) complex of an azo-linked Schiff base ligand was encapsulated in the nanocavity of zeolite-Y and the catalytic activity of the homogeneous and heterogeneous catalysts in the oxidation of various olefins with *tert*-butyl hydroperoxide (TBHP) was investigated.

EXPERIMENTAL

Materials

All starting materials and solvents were purchased from Merck and were used without further purification.

Physical measurements

IR spectra (KBr discs, 500–4000 cm^{-1}) were recorded using a Bruker FTIR model Tensor 27 spectrometer. UV–Vis absorption spectra were recorded on a Perkin–Elmer Lambda 35 spectrophotometer. ^{1}H-NMR spectra were collected on a Bruker FT-NMR 250 MHz spectrometer in $CDCl_3$ with TMS as the internal reference. X-Ray diffractograms were recorded using a Seifect 3003 PTS diffractometer with a Cu-K$_\alpha$ target. The reaction products of oxidation were determined and analyzed by GC–MS Quadrupole Agilent 5973 MSD spectrometer.

Preparation of 2-hydroxy-5-(phenylazo)-benzaldehyde

4-(Benzeneazo)salicylaldehyde was prepared using a standard procedure.[34]

Preparation of the ligand (H_2L)

(±)*trans*-1,2-Cyclohexanediamine (0.5 mmol, 0.06 g) in 5 mL ethanol was added to a solution of 2-hydroxy-5-(phenylazo)-benzaldehyde (1 mmol, 0.23 g) in 10 mL ethanol and chloroform at a ratio of 2 to 1. The resulting mixture was refluxed for 4 h. Finally, the precipitate of ligand (H_2L) was recovered by filtration, washed with ethanol and dried. The ligand was recrystallized from ethanol to give the pure product (Fig. 1). Yield: 57 %.

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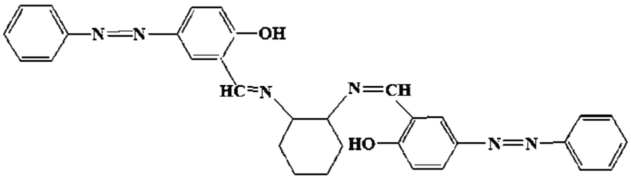

Fig. 1. Structure of the ligand H_2L.

Preparation of CuL

The CuL complex was prepared by adding a chloroform solution of the ligand (H_2L) (1.5 mmol, 0.29 g) to an ethanolic solution of $Cu(CH_3COO)_2 \cdot H_2O$ (1.5 mmol, 0.79 g). The resulting mixture was refluxed for about 2 h and a brown precipitate was obtained. Finally, the precipitate of the complex was recovered by filtration, washed with ethanol and dried at room temperature. Yield: 85 %.

Some physical and spectral data for H_2L and CuL are given in Supplementary material to this paper.

Incorporation of the copper(II) in Na-Y (metal exchanged zeolite-Y)

The Cu-Y was prepared using the standard procedure.[35] Na zeolite-Y (4 g) was suspended in 100 mL distilled water that contained copper(II) nitrate (4 mmol). The mixture was then stirred for 24 h. The solid was filtered and washed with deionized water and dried at room temperature to give a light blue powder of Cu-Y.

Immobilization of H_2L in Cu-Y

Cu-Y (0.6 g) and ligand H_2L (0.1 g) were mixed in 50 mL of acetonitrile and the reaction mixture was refluxed for 7 h in an oil bath under constant stirring. The resulting material was removed and extracted with acetonitrile using a Soxhlet extractor to remove the unreacted ligand from the cavities of the zeolite and the surface of the zeolite along with neat complex, if any. The non-complexed metal ions present in the zeolite were removed by exchanging with an aqueous 0.01 M NaCl solution. The resulting solid was finally washed with hot distilled water until no precipitation of AgCl was observed in filtrate reacted with $AgNO_3$ solution. The final solid was then dried at 150 °C for several hours until a constant weight was achieved (Fig. 2).

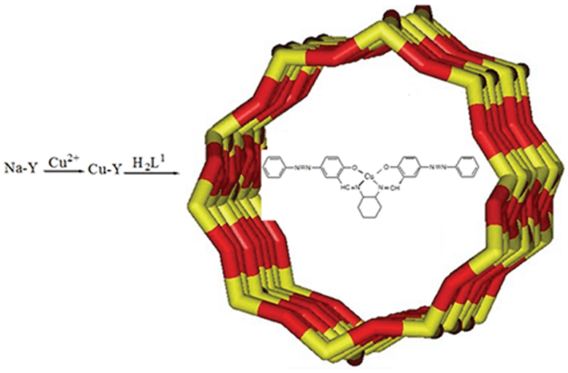

Fig. 2. Preparation of encapsulated complex in the supercages of zeolite-Y.

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Homogeneous oxidation

To a solution of cyclooctene (10 mmol) and CuL (10 mg, 0.02 mmol) in CH_3CN (5 mL), TBHP (25 mmol) was added. The resulting mixture was refluxed and the products were collected at different time intervals, identified and quantified by GC and verified by GC–MS.

Heterogeneous oxidation

Catalyst (20 mg), cyclooctene (10 mmol) and TBHP (25 mmol) were mixed in 5 mL of CH_3CN and the reaction mixture was refluxed under continuous stirring in an oil bath for 8 h. The products were collected at different time intervals, identified, quantified by GC, and verified by GC–MS.

RESULTS AND DISCUSSION

Spectral studies

In the IR spectrum of the ligand (H_2L), a sharp band due to the azomethine ν(C=N) appeared at 1630 cm^{-1}. The bands at 2853 and 2919 cm^{-1} are indicative of the presence of 1,2-cyclohexanediamine.[36,37] The band due to ν(C=N) in H_2L was shifted to a lower wave number and appeared at 1608 cm^{-1} in CuL. This indicates the involvement of azomethine nitrogen in the coordination to the copper center. Moreover, ν(C=N) of CuL-Y appeared at 1633 cm^{-1}. This observation suggested that the structure of CuL in the zeolite is not identical to that of the neat complex due to some host–guest interactions. The IR spectrum of the hybrid material showed an intense band at 1022 cm^{-1} attributable to the asymmetric stretching of Al–O–Si chain of the zeolite. The symmetric stretching and bending frequency bands of Al–O–Si framework of zeolite appeared at 789 and 458 cm^{-1}, respectively.[38]

The X-ray powder diffraction patterns of CuL-Y and Na-Y were essentially similar except the intensities were weaker in the immobilized complex (Fig. 3). This observation indicates that the framework of the zeolite had not structurally changed during the immobilization.

The ^1H-NMR spectrum of the ligand (H_2L) was recorded using $CDCl_3$ solvent. Hydrogen atoms of the azomethine groups of H_2L appeared at δ 8.23–8.41 ppm. The hydrogen atoms of the CH_2/CH groups in the cyclohexane ring were observed in the δ 1.49–3.46 ppm range. The phenolic OH protons were found at 10.05 and 11.35 ppm. The aromatic protons appeared in the range δ 7.00–7.94 ppm as a multiplet.[36,37,39]

The electronic spectrum of CuL consisted of one broad d–d transition band at 524 nm, as is usual for square planar geometry Cu(II). The higher energy bands were due to π–π* or n–π* transition.[40]

The catalytic oxidation of alkenes

The catalytic performance of CuL in the oxidation of cyclooctene, as a model substrate, with H_2O_2 and TBHP as oxidizing agents was investigated. The results of a series of blank experiments are shown in Table I, which confirmed the presence of the catalyst is essential for the oxidation of alkenes.

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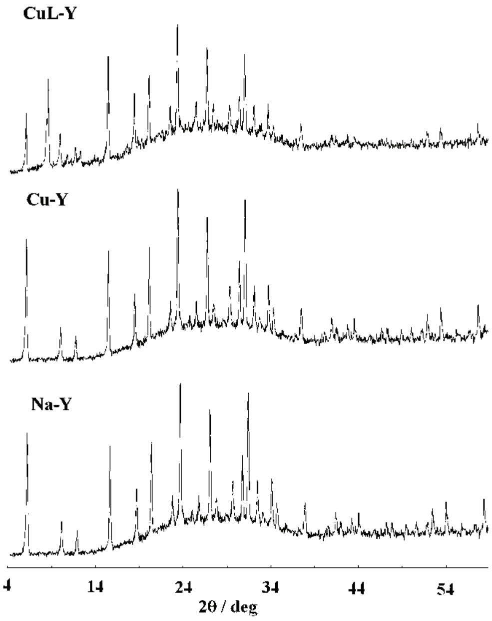

Fig. 3. XRD patterns of Na-Y, Cu-Y and CuL-Y.

TABLE I. Blank experiments; reaction conditions: substrate, 10 mmol, TBHP, 25 mmol, acetonitrile, 5 mL; the reactions were run for 8 h under reflux

Entry	Alkene	Conversion, %	Selectivity, %
1	Cycloctene	5	50[a]
2	Cyclohexene	7	64[b]
3	Styrene	5	72[c]
4	Norbornene	9	58[d]

[a]Cyclooctene oxide; [b]2-cyclohexen-1-ol; [c]benzoic acid; [d]norbornene epoxide

Different reaction parameters, such as reaction time, reaction solvent, catalyst concentration, the nature and the concentration of the oxidant that may affect the conversion and selectivity of the reaction were optimized.

The influence of reaction time in the catalytic oxidation of cyclooctene by CuL is illustrated in Fig. 4. It was observed that oxidation of cyclooctene required 8 h for maximum conversion. The effect of the nature of the solvent in the catalytic activity of CuL for the oxidation of cyclooctene was studied. Thus, acetonitrile, ethanol, dichloromethane and chloroform were used and the highest conversion was obtained in acetonitrile (Table II). The higher conversions in acetonitrile (69 %) relative to the others possibly may be due to the polarity, hydrophilicity, size of the solvent molecule and higher boiling point of acetonitrile.[41]

The effect of amount of catalyst was investigated in the oxidation of cyclooctene. As seen in Table III, the highest conversion was obtained with 0.04 mmol (0.02 g) of catalyst. Different amounts of oxidant (TBHP) were studied in

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the oxidation of cyclooctene (Table IV). The results indicate that the highest conversion (89 %) was obtained at 1:2.5 mole ratio of cyclooctene to TBHP.

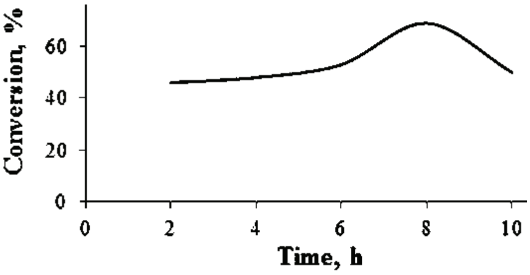

Fig. 4. Effect of the reaction time on the oxidation of cyclooctene. Reaction conditions: cyclooctene, 10 mmol, CuL, 0.02 mmol, TBHP, 25 mmol, solvent, CH_3CN, 5 mL, under reflux.

TABLE II. The influence of various solvents on the oxidation of cyclooctene in the presence of CuL; reaction conditions: cyclooctene, 10 mmol, CuL, 0.02 mmol, TBHP, 25 mmol and solvent, 5 mL; the reactions were run for 8 h under reflux

Entry	Solvent	Conversion %	Selectivity, %		
			Cyclooctene oxide	2-Cycloocten-1-one	Other products
1	Acetonitrile	69	63	34	3
2	Ethanol	28	60	40	0
3	Chloroform	18	57	32	11
4	Dichloromethane	16	49	43	8

TABLE III. The effect of the amount of CuL on the oxidation of cyclooctene; reaction conditions: cyclooctene (10 mmol), CH_3CN (5 mL) and TBHP (25 mmol); the reactions were run for 8 h under reflux

Entry	CuL mmol	Conversion %	Selectivity, %		
			Cyclooctene oxide	2-Cycloocten-1-one	Other products
1	0.02	69	63	34	3
2	0.04	89	53	38	9
3	0.06	80	59	37	4
4	0.08	66	65	31	4

TABLE IV. The effect of amount of oxidant (TBHP) on the oxidation of cyclooctene in the presence of CuL; reaction conditions: cyclooctene (10 mmol), CuL (0.04 mmol) and CH_3CN (5 mL), the reactions were run for 8 h under reflux

Entry	TBHP mmol	Conversion %	Selectivity, %		
			Cyclooctene oxide	2-Cycloocten-1-one	Other products
1	20	59	63	35	9
2	25	89	53	38	9
3	30	81	59	37	5

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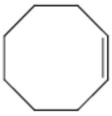
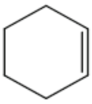
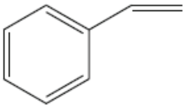
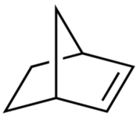
In order to investigate the effect of the oxidizing agent in the oxidation reaction, H_2O_2 and TBHP were used (Table V). In the presence of TBHP, a higher conversion (89 %) was obtained.

TABLE V. The influence of the kind of oxidant on the oxidation of cyclooctene in the presence of CuL; reaction conditions: cyclooctene (10 mmol), CuL (0.04mmol), CH_3CN (5 mL), oxidant (25 mmol); the reactions were run for 8 h under reflux

Entry	Oxidant	Conversion %	Selectivity, %		
			Cyclooctene oxide	2-Cycloocten-1-one	Other products
1	TBHP	89	53	38	9
2	H_2O_2	23	100	0	0

To establish the general applicability of the method, under the optimized conditions, different olefins were subjected to oxidation in the presence of a catalytic amount of CuL and CuL-Y, the results are given in Tables VI and VII respectively.

TABLE VI. Oxidation of olefins using TBHP catalyzed by CuL; reaction conditions: CuL (0.04 mmol), substrate (10 mmol), TBHP (25 mmol), acetonitrile (5 mL); the reactions were run for 8 h under reflux

Alkene	Conversion, %	Selectivity, %		
		Main product		Others
	89	53[a]	38[b]	9
	63	60[c]	40[d]	0
	46	60[e]	25[f]	9
	13	100[g]	0	0

[a]Cyclooctene oxide; [b]2-cycloocten-1-one; [c]cyclohexene oxide; [d]2-cyclohexen-1-ol; [e]benzaldehyde; [f]benzoic acid; [g]norbornene epoxide

Comparison of the catalytic behavior of the copper Schiff base complex encapsulated in the super cages of zeolite-Y and free CuL showed the higher catalytic activity and selectivity of the heterogeneous catalyst with respect to the homogenous one. When the reaction occurred in the cavity of zeolite, the imp-

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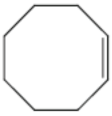
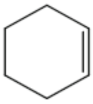
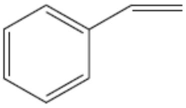
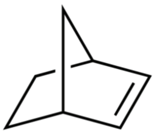
rovement of catalysis event was probably due to diffusional selectivity of the reaction and potentially increased stability *via* site isolation.

TABLE VII. Oxidation of olefins using TBHP catalyzed by CuL-Y; reaction conditions: CuL-Y (20 mg), substrate (10 mmol), TBHP (25 mmol), acetonitrile (5 mL); the reactions were run for 8 h under reflux

Alkene	Conversion, %	Selectivity, %	
		Main product	Other
	50	68[a]	32[b]
	96	80[c]	20[d]
	95	80[e]	20[f]
	92	100[g]	0

[a]Cyclooctene oxide; [b]2-cycloocten-1-one; [c]cyclohexene oxide; [d]2-cyclohexen-1-ol; [e]benzaldehyde; [f]benzoic acid; [g]norbornene epoxide

CONCLUSIONS

In summary, the azo Schiff base ligand (H_2L) derivative of (±)*trans*-1,2-cyclohexanediamine and 2-hydroxy-5-(phenylazo)-benzaldehyde was prepared. The copper Schiff base complex (CuL) was encapsulated in the nanopores of zeolite-Y (CuL-Y). Furthermore, these heterogeneous and homogeneous catalysts were used for the oxidation of different alkenes with *tert*-butyl hydroperoxide. Various reaction parameters were investigated and optimized in the oxidation reaction. The oxidation of cyclooctene, cyclohexene, styrene and norbornene catalyzed by CuL gave 89, 63, 46 and 13 % conversion, respectively. Under the heterogeneous conditions, the oxidation of these olefins with 50, 96, 95 and 92 % conversion, respectively, was obtained. It was observed that CuL-Y has higher catalytic activity and selectivity than CuL. This change was specially seen for norbornene.

SUPPLEMENTARY MATERIAL

Some physical and spectral data for H_2L and CuL are available electronically from http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

*Acknowledgement***.** Financial assistance from Alzahra University is acknowledged.

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ИЗВОД

КОМПЛЕКСИ БАКРА(II) СА (±)*trans*-1,2-ЦИКЛОХЕКСАНДИАМИН ШИФОВОМ БАЗОМ СА АЗО ГРУПОМ, КАО ЛИГАНДОМ, КАПСУЛИРАНИ У НАНОПОРАМА ЗЕОЛИТА-Y КАО КАТАЛИЗАТОРИ ОКСИДАЦИЈЕ ОЛЕФИНА

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Полазећи од 5-(фенилазо)-2-хидроксибензалдехида и (±)*trans*-1,2-циклохександиамина синтетисани су Шифова база као лиганд (H_2L) и одговарајући Cu(II) комплекс (CuL). За карактеризацију ових једињења коришћене су FT-IR, UV–Vis и ^{1}H-NMR спектроскопске методе. Бакар(II) комплекс је методом флексибилног лиганда капсулиран у нанопоре зеолита-Y (CuL-Y) и ово капсулирање је испитивано различитим методама. Хомогено и хетерогено каталитичко својство овог капсулираног бакар(II) комплекса је коришћено за оксидацију различитих алкена у присуству *tert*-бутил-хидропероксида. Под одговарајућим експерименталним условима, оксидација циклооктена, циклохексена, стирена и норборнена уз каталитичко дејство CuL комплекса се одиграва са 89, 63, 46, односно 13 % конверзијом. Ови олефини су у присуству CuL-Y комплекса веома ефикасно оксидовани са 50, 96, 95, односно 92 % конверзијом. Поређена су каталитичка својства CuL и CuL-Y, при чему је нађено да хетерогена катализа показује веће каталитичко дејство и селективност у односу на хомогену катализу.

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