Schiff base ligand derived from (±)*trans*-1,2-cyclohexanediamine and its Cu(II), Co(II), Zn(II) and Mn(II) complexes: Synthesis, characterization, styrene oxidation and a hydrolysis study of the imine bond in the Cu(II) Schiff base complex

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Abstract: A Schiff base ligand (H_2L) derived from 2′-hydroxypropiophenone and (±)*trans*-1,2-cyclohexanediamine was synthesized. The reactions of $MCl_2·xH_2O$ (M = Cu(II), Co(II), Zn(II) and Mn(II)) with the di-Schiff base ligand (H_2L) were studied. When stirred with 1 equivalent of $CuCl_2.2H_2O$ in a solution of ethanol and chloroform, this ligand undergoes partial hydrolysis of the imino bond and the resultant tridentate ligand (HL′) immediately forms the complex$[CuL′Cl]·3/2CHCl_3$ (**1**) with an N_2O coordination sphere. Under the same condition, the reaction of H_2L with $MCl_2·xH_2O$ (M = Co(II) (**3**), Zn(II) (**4**) and Mn(II) (**5**)) gave the complexes $[ML]·1/2CHCl_3·3/2H_2O$ (**3**–**5**) with an N_2O_2 coordination sphere and no hydrolytic cleavage occurred. In addition, the reaction of H_2L with $CuCl_2·2H_2O$ in THF gave the complex CuL (**2**) with an N_2O_2 coordination sphere. The ligand and the complexes were characterized by FTIR, UV–Vis, ^{1}H-NMR spectroscopy and elemental analysis. The homogeneous catalytic activities of complexes **1**, **3** and **5** were evaluated for the oxidation of styrene using *tert*-butyl hydroperoxide (TBHP) as oxidant. Finally, the copper(II) complex **1** was encapsulated in the nanopores of zeolite Y by the flexible ligand method (CuL′–Y) and its encapsulation was demonstrated in different studies. The catalytic performance of heterogeneous catalyst in the styrene oxidation with TBHP was investigated. The catalytic tests showed that the homogeneous and heterogeneous catalysts were active in the oxidation of styrene.

Keywords: hydrolytic cleavage, solvent effect; catalyst; homogeneous; heterogeneous.

INTRODUCTION

During the last decades, great attention has been paid by many researchers to the Schiff base ligands and their metal complexes due to their crucial role in

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many fields, such as catalysis,[1] optoelectronic materials,[2] inhibition of corrosion,[3] magnetochemistry[4,5] and biological models.[6] They also exhibit antibacterial[7,8] and anticancer[9,10] activity. Various reactions have been catalyzed by transition metal Schiff base complexes, such as ring opening reactions of epoxides,[11] aldol condensations[12,13] and oxidation.[14] In the catalytic oxidation reactions, these complexes represent a very useful class of compounds because as their structures are similar to the porphyrine ring, they are good at loading oxygen and mimicking enzymes.[15] Especially, olefin oxidation has received considerable attention as several types of chemicals that find widespread applications in the chemical and pharmaceutical industries are produced by this method, including aldehydes, ketones, alcohols, acids and epoxides,.[16] Therefore, the homogeneous or heterogeneous catalytic role of several Schiff base transition metal complexes, such as Cu(II),[17–19] Co(II),[20,21] Mo(VI),[22–24] V(V),[25,26] Ni(II)[27,28] and Mn(II)[29–31] complexes in the oxidation of olefins have been extensively studied. However, homogeneous catalysts have some drawbacks, such as difficulty in separation from the product for reuse and instability at high temperatures, which preclude their industrial utilization. Hence, many efforts involving encapsulation in zeolites,[32,33] grafting on polymers[34,35] and silica[36,37] have been made to heterogenize homogeneous catalysts. Entrapment of metal complexes into the supercages of zeolites is an interesting technique because of reusability, chemical and thermal stability, and improved selectivity.[38]

Although the synthesis of Schiff base metal complexes is well documented,[39–41] there are some reports concerning the hydrolysis of the Schiff base during complex formation. The hydrolytic cleavage of a Schiff base depends on different parameters, such as solvent,[42,43] nature of the metal ion,[44–47] the counter anion,[48,49] pH of the reaction medium[50] and the nature of the carbonyl compound.[51]

In this study, the synthesis and characterization of the di-Schiff base ligand (H$_2$L) derived from 2′-hydroxypropiophenone and (±)-*trans*-1,2-cyclohexanediamine and its complexes (**1**–**5**) were investigated. In addition, the influence of solvent and metal ion on the hydrolytic behavior of the azomethine linkage (C=N) of H$_2$L were examined. The homogeneous catalytic potential of the complexes **1**, **3** and **5** in the oxidation of styrene with *tert*-butyl hydroperoxide (TBHP) were studied. Moreover, the copper(II) Schiff base complex encapsulated in the nanopores of zeolite-Y by the flexible ligand method and its catalytic performance in the oxidation of styrene was tested.

EXPERIMENTAL

Materials

All the starting materials and solvents, except (±)*trans*-1,2-cyclohexanediamine (Alfa Aesar) and 2′-hydroxypropiophenone (Across), were purchased from Merck and used without further purification. The synthetic reactions and work-up were performed in open air.

Physical measurements

The IR spectra (KBr discs, 500–4000 cm^{-1}) were recorded using a Bruker FTIR model Tensor 27 spectrometer. The far IR spectrum (CsI disc, 150–700 cm^{-1}) was recorded using a Perkin–Elmer, model spectrum 400 imaging system. The elemental analyses were realized in a 2400 Series II CHN analyzer, Perkin-Elmer, USA. The UV–Vis absorption spectra were recorded on a Perkin–Elmer Lambda 35 spectrophotometer. Diffuse reflectance spectra (DRS) were registered on an Ava Spec 2048 TECH spectrometer, using $BaSO_4$ as the reference. The ^{1}H-NMR spectra were recorded on a Bruker 500 MHz model DRX spectrometer in $CDCl_3$ or DMSO-d_6 with tetramethylsilane (TMS) as the internal reference. The X-ray diffraction patterns were obtained using a Philips X'Pert diffractometer with CoK$_\alpha$ radiation (λ = 1.78897 Å). The oxidation products were analyzed by GC and GC–mass spectrometry using an Agilent 6890 Series with a FID detector, an HP-5 phenyl methyl siloxane capillary and an Agilent 5973 network, and a mass selective detector, HP-5ms 6989 network GC system, respectively.

Physical and spectral data of the synthesized compounds are given in Supp

Preparation of the ligand (H$_2$L)

An ethanolic solution (10 mL) of 2′-hydroxypropiophenone (0.150 g, 2 mmol) was added to an ethanolic solution (10 mL) of (±)*trans*-1,2-cyclohexanediamine (0.114 g, 1 mmol). The bright yellow solution was stirred and heated to reflux for 1 h. The mixture was kept in air to allow the solvent to evaporate, whereby yellowish crystals of the ligand were obtained. Yield: 97 %.

Preparation of complexes 1–5

[CuL'Cl]·3/2CHCl$_3$ (1). This copper complex was prepared by adding an ethanolic solution (10 mL) of $CuCl_2·2H_2O$ (0.170 g, 1 mmol) to a chloroform solution (10 mL) of H$_2$L (0.378 g, 1 mmol). The resulting mixture was stirred for about 1 h. Finally, the precipitate of the complex was recovered by filtration, washed several times with absolute ethanol and dichloromethane and dried at 65 °C for 2 h. Yield: 30 %.

CuL (2). This complex was prepared by adding a THF solution (20 mL) of H$_2$L (0.378 g, 1 mmol) to a THF solution (10 mL) of $CuCl_2·2H_2O$ (0.170 g, 1 mmol). After stirring the resulting mixture for about 1 h, the precipitated complex was recovered by filtration, washed with THF and Et_2O and finally dried at 65 °C for 1 h. Yield: 40 %.

[CoL]·1/2CHCl$_3$·3/2H$_2$O (3). The cobalt complex was prepared in a similar manner to **1** but using $CoCl_2·6H_2O$ (0.237 g, 1 mmol). Yield: 70 %.

[ZnL]·1/2CHCl$_3$·3/2H$_2$O (4). The zinc complex was prepared in a similar manner to **1** but using $ZnCl_2$ (0.136 g, 1 mmol). Yield: 77 %.

[MnL]·1/2CHCl$_3$·3/2H$_2$O (5). The manganese complex was prepared in a similar manner to **1** but using $MnCl_2·4H_2O$ (0.197 g, 1 mmol). Yield: 56 %.

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

The Cu–Y was prepared using the standard procedure.[52] 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. Cu content: 6.7 %

Immobilization of H$_2$L in Cu–Y

Cu–Y (0.29 g, 0.3 mmol of Cu) and ligand H$_2$L (0.67 g, 1.8 mmol) were mixed in a 1.5:1 volume ratio of acetonitrile and chloroform solution (25 mL) and the reaction mixture was refluxed for 8 h in an oil bath under constant stirring. The resulting material was taken out and

Soxhlet extracted with acetonitrile to remove the unreacted ligand from the cavities of the zeolite as well as those located on the surface of the zeolite along with neat complexes, if any. The non-complexed metal ions present in the zeolite were removed by exchanging with aqueous 0.01 M NaCl solution. The resulting solid was finally washed with hot distilled water until no precipitation of AgCl was observed on reaction of the filtrate with AgNO$_3$ solution. The product was then dried at 150 °C for several hours until constant weight was achieved.

General procedure for the homogeneous oxidation of styrene catalyzed by complexes 1, 3 and 5

All oxidation reactions were performed in 50 mL round bottom flasks equipped with a water condenser. Typically, to a solution of styrene (10 mmol) and catalyst (complex **1**: 0.04 mmol, complexes **3** and **5**: 0.045 mmol) in CH$_3$CN (10 mL), TBHP (for complex **1**: 35 mmol, for complexes **3** and **5**: 30 mmol) was added. The resulting mixture was refluxed for 6 h for complex **1** and 10 h for complexes **3** and **5**. The products were identified and quantified by GC and verified by GC–MS.

General procedure for the heterogeneous oxidation of styrene catalyzed by CuL'–Y

Catalyst (0.04 g), styrene (10 mmol) and TBHP (35 mmol) were mixed in 10 mL of CH$_3$CN and the reaction mixture was refluxed with continuous stirring in an oil bath for 4 h. The products were collected at different times and identified and quantified by GC, and verified by GC–MS.

<div align="center">RESULTS AND DISCUSSION</div>

Synthesis and formulation

The ligand H$_2$L was synthesized by condensation of a 1:2 mole ratio of (±)*trans*-1,2-cyclohexanediamine with 2′-hydroxypropiophenone (Scheme 1). When H$_2$L reacted with CuCl$_2$·2H$_2$O in a solution of ethanol and chloroform, it underwent partial hydrolytic cleavage to form the N$_2$O coordination sphere of complex **1**. Notably, a subtle change in the reaction conditions, such as changing the solvent, caused a change in the type of complex produced. Thus, when H$_2$L
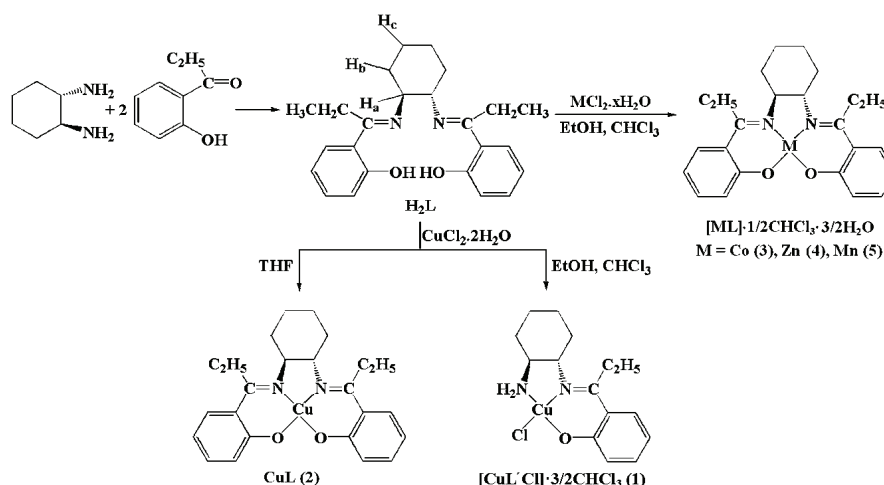
Scheme 1. Synthetic routes to the ligand (H$_2$L) and the complexes **1**–**5**.

reacted with $CuCl_2·2H_2O$ in THF, complex **2** with a N_2O_2 coordination sphere was formed (Scheme 1). It is likely that under the conditions of the reaction, an activated nucleophile was generated at the metal, which was responsible for the ensuing cleavage reaction.[43,53] Additionally, no hydrolytic cleavage was observed when H_2L reacted with Co(II), Zn(II) and Mn(II) chloride salts and complexes **3**–**5** were obtained.

FTIR and UV–Vis studies

In the infrared spectrum of the ligand (H_2L), a strong and sharp band corresponding to the azomethine group $\nu(C=N)$ appeared at 1609 cm^{-1}. The bands at 2857 and 2931 cm^{-1} are indicative of the presence of the 1,2-cyclohexanediyl groups.

In the IR spectrum of **1**, the two primary NH_2 stretching modes were seen at around 3288 and 3223 cm^{-1} as sharp bands (doublet) for the asymmetric and symmetric vibrations, respectively. Strong bands at 2857 and 2931 cm^{-1} corroborated the presence of 1,2-cyclohexanediyl groups in the complex. In addition, the bands due to azomethine $\nu(C=N)$ and $\nu(Cu–Cl)$ were observed at 1603 and 304 cm^{-1},[54] respectively. In the IR spectrum of complex **2**, strong bands appeared at 2863 and 2936 cm^{-1}, corresponding to the presence of 1,2-cyclohexanediyl group in the complex. The sharp band due to azomethine $\nu(C=N)$ was centered at 1603 cm^{-1}. A comparison of the IR spectra of **1** with that of **2** provided clear evidence of the hydrolytic cleavage that had occurred in one imine bond of H_2L (Fig. 1). The IR spectra of complexes **3**–**5** showed a strong band due to the azomethine group at 1604 cm^{-1}. Moreover, the spectra of these complexes showed bands in the range 2858–2936 cm^{-1}, corresponding to the 1,2-cyclohexanediyl group (Fig. 1). The C=N stretching vibration of the complexes **1**–**5** showed a slightly lower frequency shift in comparison to the corresponding vibration in the spectrum of the free ligand. This indicates the involvement of azomethine nitrogen in the coordination to the metal centers.[55] The band corresponding to C–O of H_2L appeared at 1273 cm^{-1}. For the synthesized complexes, the C–O band was shifted to a lower frequency and was observed in the 1257–1265 cm^{-1} region, indicating coordination through the phenolic oxygen.[56]

In the IR spectra of CuL′–Y, an intense band appeared at 1021 cm^{-1}, attributable to the asymmetric stretching of the Al–O–Si chain of the zeolite. The symmetric stretching and bending frequency bands of the Al–O–Si framework of the zeolite appeared at 789 and 458 cm^{-1}, respectively.[57] The band corresponding to $\nu(C=N)$ appeared at 1580 cm^{-1}. In addition, the bands due to the two primary NH_2 stretching modes were observed at 3224 and 3288 cm^{-1}. Other bands at 2856 and 2931 cm^{-1} were indicative of the presence of 1,2-cyclohexanediyl groups (Fig. 2). These observations confirmed the partial hydrolysis of the azomethine group in the encapsulated complex. The intensities of the peaks
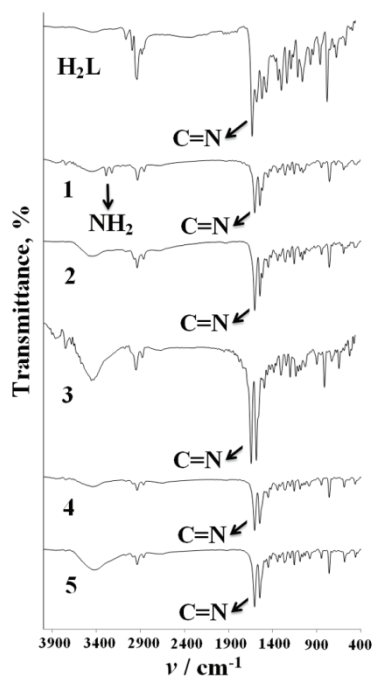
Fig. 1. IR spectra of the ligand (H_2L) and complexes **1**–**5**.

in the spectrum of the encapsulated complex were weak due to their low concentration in the zeolite matrix.

The electronic absorption spectra of complexes **1**–**3** consist of higher energy bands at 258–400 nm which are due to π–π* or n–π* transition. The diffuse reflectance spectra of complexes **1** and **2** showed a broad d–d band with a maximum at 508 and 502 nm, respectively. This is consistent with square-planar geometry around the copper ion.[58] However, the electronic spectra of **1** and **2** in DMSO are entirely different and show d–d bands at 675 and 887 nm, respectively. This suggests that in solution, the solvent molecules are coordinated to metal ions.[59] The cobalt(II) complex **3** exhibited d–d transition bands at 611 and 673 nm, suggesting a tetrahedral geometry.[60] In the electronic spectra of **4** and **5**, absorption bands appeared in the range 260–387 nm, which may be assigned to intra-ligand or charge-transfer transitions.

^{1}H-NMR studies of the ligand (H_2L) and complex 4

In the ^{1}H-NMR spectrum of H_2L, the phenolic protons were present at 16.6 ppm. The aromatic protons were found in the range 6.74–7.45 ppm as a multiplet. The spectrum showed signals at 3.91–3.93 ppm, 2.69–2.90 ppm and 1.53––1.76 ppm with integrations corresponding to H_a, H_b and H_c, respectively. Furthermore, the signals of the methyl protons were observed at 1.22–1.25 ppm and those of the methylene protons at 1.93–1.98 ppm.
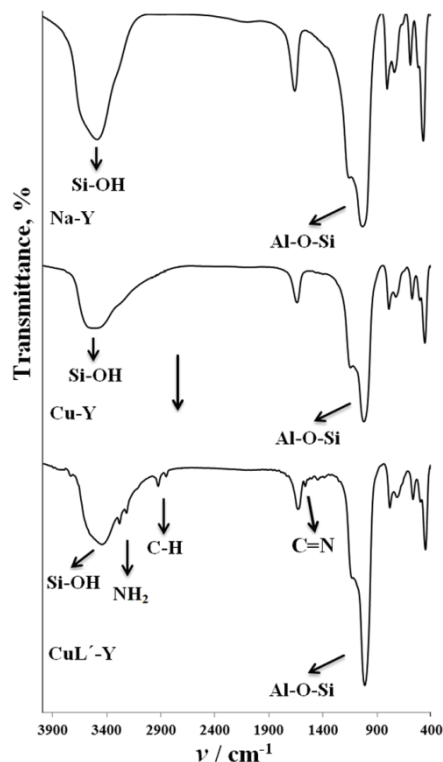
Fig. 2. IR spectra of Na–Y, Cu–Y and CuL′–Y.

A comparison of the ^{1}H-NMR spectrum of H_2L with that of complex **4** showed the disappearance of the phenolic protons present in the free ligand, which is in agreement with a bis-deprotonation of the ligand. In the ^{1}H-NMR spectrum of **4,** the aromatic protons appeared in the range 6.72–7.53 ppm. The signals at 3.66–3.98 ppm, 2.70–2.84 ppm and 1.51–1.86 ppm were related to H_a, H_b and H_c, respectively. The signals of the methyl and methylene protons were observed at 1.08–1.21 ppm and 2.5–2.7 ppm, respectively.

XRD studies

The X-ray powder diffraction patterns of Cu–Y and CuL′–Y were recorded at 2θ values between 5° and 80° (Fig. 3). The XRD of Cu–Y and CuL′–Y were essentially similar except the intensities were slightly changed in the encapsulated complex. This fact indicates that the framework of the zeolite had not structurally changed during encapsulation.
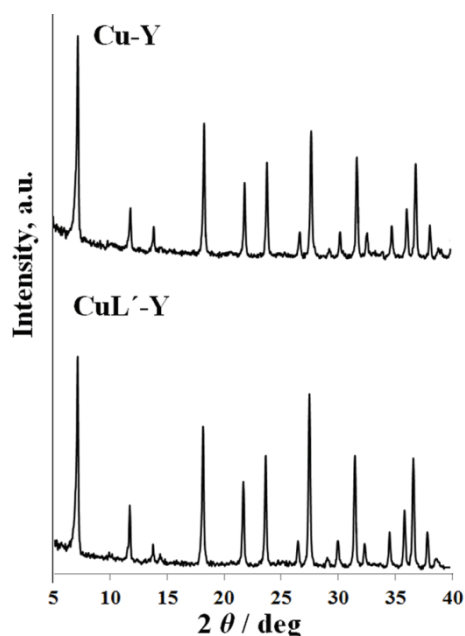
Fig. 3. XRD patterns of Cu–Y and CuL′–Y.

Catalytic activity studies in the oxidation of styrene

The oxidation of styrene catalyzed by complexes **1**, **3**, **5** and CuL′–Y was realized using TBHP as the oxidant. A series of blank experiments (Table I) showed that the presence of both catalyst and oxidant was essential for an effective catalytic reaction. Different reaction parameters, such as reaction time, reaction solvent, amount of catalyst, the nature and the amount of oxidant that may affect the conversion and selectivity of the reaction were optimized.

TABLE I. Blank experiments on the catalytic oxidation of styrene; reaction conditions: styrene (10 mmol), TBHP (30 mmol), acetonitrile (10 mL); the reactions were run for 6 h under reflux

Entry	Catalyst	Oxidant	Conversion, %
1	None	TBHP	0
2	None	H_2O_2	0
3	**1**	None	0
4	**3**	None	0[a]
5	**5**	None	0[a]

[a]The reaction was run for 10 h under reflux

*Catalytic activity of **1** and CuL'–Y in the oxidation of styrene*

The influence of reaction time and nature of the solvent in the oxidation of styrene catalyzed by **1** are illustrated in Fig. 4. To find the best reaction solvent, the oxidation reactions were performed in various solvents, *i.e.*, acetonitrile,

1-butanol, dichloromethane and chloroform, and the highest conversion was obtained in acetonitrile, which may be due to the polarity, hydrophilicity and size of the solvent molecule of acetonitrile.[61] To optimize the reaction time, the oxidation of styrene was performed for different times. It was found that 6 h was the best time for maximum conversion. Increasing the time to 8 h partially increased the conversion, but decreased the selectivity of the product.
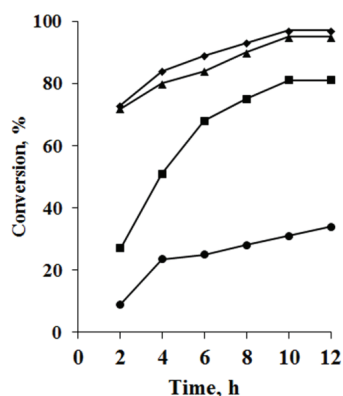

Fig. 4. Effect of time and solvent on the oxidation of styrene by TBHP in the presence of complex **1**. Reaction condition: styrene (10 mmol), catalyst (0.03 mmol), TBHP (30mmol), solvent (10 mL; acetonitrile ◆, chloroform ■, 1-butanol ▲ or dichloromethane ●) and reflux.

In order to investigate the effect of the oxidizing agent in the oxidation reaction, H_2O_2 and TBHP were used (Table II). In the presence of H_2O_2, the reactions did not proceed under reflux.

TABLE II. The influence of kind of oxidant on the oxidation of styrene; reaction condition: styrene (10 mmol), catalyst (0.03 mmol), CH_3CN (10 mL), oxidant (30 mmol), reaction time, 6 h and reflux; catalyst: **1**

Entry	Oxidant	Conversion, %
1	TBHP	89
2	H_2O_2	0

The influence of amount of catalyst has been studied in the oxidation of styrene. As seen in Fig. 5a, the highest conversion (92 %) was obtained with 0.04 mmol of catalyst. Different amount of oxidant (TBHP) have been used in the oxidation of styrene (Fig. 5b). The results indicate that the highest conversion (100 %) was obtained at 1:3.5 molar ratio of styrene to TBHP.

In order to heterogenize the homogenous catalyst, the copper(II) Schiff base complex was encapsulated in the nanopores of zeolite Y by flexible ligand method. The catalytic activity data of **1** and CuL′–Y in the oxidation of styrene are given in Table III. The results showed that when CuL′–Y is used, the reaction times decreased, but no important change in the selectivity of products is observed.
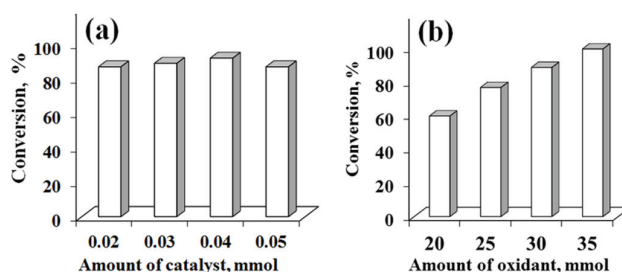
Fig. 5. a) The effect of amount of catalyst **1** on the oxidation of styrene. Reaction condition: styrene (10 mmol), CH$_3$CN (10 mL) and TBHP (30 mmol), reaction time, 6 h and reflux; b) The effect of amount of oxidant on the oxidation of styrene. Reaction condition: styrene, 10 mmol, catalyst, 0.04 mmol and CH$_3$CN, 10 mL, oxidant, TBHP, reaction time, 6 h and reflux.

TABLE III. Oxidation of styrene using TBHP catalyzed by **1** and CuL′–Y; reaction conditions: catalyst, 25 mmol, CuL′–Y, 0.04 g, styrene, 10 mmol, TBHP, 35 mmol, acetonitrile, 10 mL; reflux

Entry	Catalyst	Conversion, %	Selectivity, %			Time, h
1	1	100	63[a]	28[b]	9[c]	6
2	CuL′–Y	100	56[a]	44[b]		4

[a]Styrene epoxide; [b]benzoic acid; [c]benzaldehyde

Catalytic activity of complexes 3 and 5 in the oxidation of styrene

The oxidation of styrene, catalyzed by **3** was carried in the presence of H$_2$O$_2$ and TBHP. The effect of the solvent nature in the catalytic activity of **3** for oxidation of styrene has been studied (Fig. 6). Therefore, acetonitrile, ethanol and chloroform were used and the highest conversion was obtained in acetonitrile. As indicated in Fig. 6, increasing the reaction time from 2 to 10 h increases the conversion and it was found that 10 h is the best time for maximum conversion (98 %).
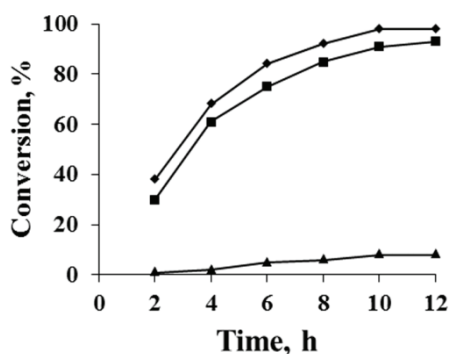

Fig. 6. Effect of time and solvent on the oxidation of styrene with TBHP in the presence of complex **3**. Reaction condition: styrene (10 mmol), catalyst (0.03 mmol), TBHP (35 mmol), solvent (10 mL; acetonitrile ◆, ethanol ■, chloroform ▲) and reflux.

In order to investigate the influence of the oxidizing agent in the oxidation reaction, TBHP and H_2O_2 were used (Table IV). In the presence of TBHP, a higher conversion was achieved. To optimize the amount of catalyst, oxidation of styrene was performed with different amounts of **3**. As indicated in Fig. 7a, 0.045 mmol of catalyst proved to be sufficient for the maximum conversion. Different amounts of oxidant (TBHP) were studied in the oxidation of styrene (Fig. 7b). The results indicated that the best mole ratio of styrene to TBHP for the oxidation of styrene was 1:3.

TABLE IV. The influence of the kind of oxidant on the oxidation of styrene; reaction conditions: styrene, 10 mmol, catalyst, 0.03 mmol, CH_3CN, 10 mL, oxidant, 35 mmol, reaction time, 10 h; reflux; catalyst: **3**

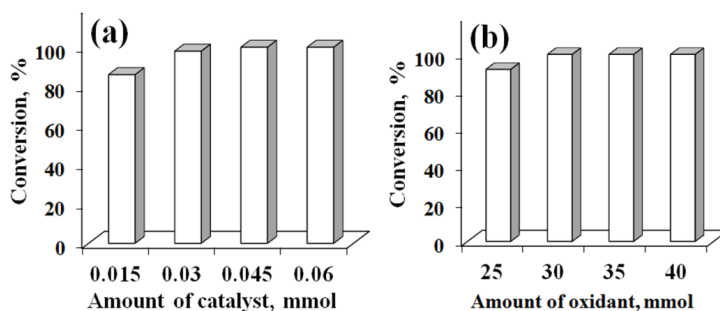| Entry	Oxidant	Conversion, %
1	TBHP	98
2	H_2O_2	0

Fig. 7. a) The influence of the amount of catalyst **3** on the oxidation of styrene. Reaction conditions: styrene, 10 mmol, CH_3CN, 10 mL and TBHP, 35 mmol; reaction time, 10 h; reflux; b) the effect of the amount of oxidant on the oxidation of styrene. Reaction conditions: styrene, 10 mmol, catalyst, 0.045 mmol and CH_3CN, 10 mL; oxidant, TBHP, reaction time, 10 h; reflux.

The catalytic activity of **5** was investigated under the optimized condition for **3**. The results are given in Table V.

TABLE V. Oxidation of styrene using TBHP catalyzed by **3** and **5**; reaction conditions: catalyst, 0.045 mmol, styrene, 10 mmol, TBHP, 35 mmol, acetonitrile, 10 mL, reaction time, 10 h; reflux

Entry	Catalyst	Conversion, %	Selectivity, %	
1	**3**	100	47[a]	53[b]
2	**5**	40	46[a]	54[b]

[a]Styrene epoxide; [b]benzoic acid

CONCLUSIONS

A Schiff base ligand (H$_2$L) derived from (±)*trans*-1,2-cyclohexanediamine and 2′-hydroxypropiophenone was prepared. It was found that the reaction between H$_2$L and CuCl$_2$·2H$_2$O in ethanol and chloroform led to partial hydrolysis of H$_2$L and complex **1** was obtained, while under the same conditions, the reaction of H$_2$L with MCl$_2$·xH$_2$O (M = Co(II), Zn(II) or Mn(II)) yielded complexes **3**–**5** without hydrolytic cleavage of the azomethine linkage. Moreover, the reaction between H$_2$L and CuCl$_2$·2H$_2$O in THF gave complex **2**. Therefore, it is reasonable to conclude that the solvent and metal ion can affect the hydrolysis of the Schiff base during complex formation. Complexes **1**, **3** and **5** were used for the oxidation of styrene with TBHP under homogenous conditions. Furthermore, the copper(II) Schiff base complex **1** encapsulated in the nanopores of zeolite Y by the flexible ligand method (CuL′–Y) and its catalytic potential in the oxidation of styrene was examined. The oxidation of styrene catalyzed by **1**, **3**, **5** and CuL′–Y gave 100 % conversion with 63, 47, 46 and 56% selectivity for styrene epoxide, respectively. The results revealed that the homogeneous and heterogeneous catalysts were efficient in the oxidation of styrene.

SUPPLEMENTARY MATERIAL

Physical and spectral data of the synthesized compounds are available electronically from http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

ИЗВОД
ЛИГАНД ТИПА ШИФОВЕ БАЗЕ ДОБИЈЕН ИЗ (±)*trans*-1,2-ЦИКЛОХЕКСАНДИАМИНА И ЊЕГОВИ БАКАР(II), КОБАЛТ(II), ЦИНК(II) И МАНГАН(II) КОМПЛЕКСИ: СИНТЕЗА, КАРАКТЕРИЗАЦИЈА, ОКСИДАЦИЈА СТИРЕНА И ХИДРОЛИЗА ИМИНО ВЕЗЕ У БАКАР(II) КОМПЛЕКСИМА СА ШИФОВОМ БАЗОМ КАО ЛИГАНДОМ

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Полазећи из 2′-хидроксипропиофенона и (±)*trans*-1,2-циклохександиамина синтетизован је лиганд типа Шифове базе (H$_2$L). Изучаване су реакције овог лиганда са солима опште формуле MCl$_2$·xH$_2$O (M =Cu(II), Co(II), Zn(II) или Mn(II)). Када се овај лиганд помеша са еквивалентном количином CuCl$_2$·2H$_2$O у смеши етанола и хлороформа као растварача долази до парцијалне хидролизе имино везе и грађење тридентатног лиганда (HL′). Овај лиганд се тренутно координује са Cu(II) јоном при чему настаје [CuL′Cl]·3/2CHCl$_3$ (**1**) комплекс N$_2$O хромофоре. Под истим експерименталним условима лиганд H$_2$L у реакцији са солима MCl$_2$·xH$_2$O (M = Co(II) (**3**), Zn(II) (**4**) или Mn(II) (**5**)) гради комплексе N$_2$O$_2$ хромафоре чија је општа формула [ML]·1/2CHCl$_3$·3/2H$_2$O (**3**–**5**). Нађено је да у овим реакцијама не долази до хидролитичких реакција. Такође, у реакцији H$_2$L са CuCl$_2$·2H$_2$O у растварачу THF долази до формирања CuL комплекса **2** са N$_2$O$_2$ координованим атомима. Лиганд и одговарајући комплекси су окарактерисани помоћу FTIR, UV–Vis и ^{1}H-NMR спектроскопских метода,

као и на основу резултата елементалне микроанализе. Испитивана је хомогена каталитичка активност комплекса **1**, **3** и **5** у реакцији оксидације стирена у присуству *tert*-бутил-хидропероксида (ТВНР) као оксидационог средства. На крају, применом различитих метода изучавано је капсулирање Cu(II) комплекса у нанопоре зеолита Y помоћу методе флексибилног лиганда (CuL′–Y). Испитивана су каталитичка својства хетерогеног катализатора на оксидацију стирена у присуству ТВНР као оксидационог средства. На основу добијених резултата може се закључити да су сви испитивани хомогени и хетерогени катализатори показали активност у реакцији оксидације стирена.

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