

# Synthesis, characterization and catalytic oxyfunctionalization of cyclohexene with *tert*-butylhydroperoxide and hydrogen peroxide in the presence of alumina-supported Mn(II), Co(II), Ni(II) and Cu(II) bis(2-hydroxyanil)benzil complexes

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## Abstract

New square-planar Mn(II), Cu(II), Ni(II) and Co(II) complexes of a tetradentate Schiff-base ligand “bis(2-hydroxyanil)benzil, H<sub>2</sub>[habenzil]”; have been prepared and characterized by elemental analyses, IR, UV–vis, conductometric and magnetic measurements. The results suggest that the symmetrical Schiff-base is a bivalent anion with tetradentate N<sub>2</sub>O<sub>2</sub> donors derived from the phenolic oxygen and azomethine nitrogen. The formulae was found to be [M(habenzil)] for the 1:1 non-electrolytic complexes. Alumina-supported metal complexes (ASMC; [M(habenzil)/Al<sub>2</sub>O<sub>3</sub>]) catalyze the oxidation of cyclohexene with *tert*-butylhydroperoxide (TBHP) and H<sub>2</sub>O<sub>2</sub>. Oxidation of cyclohexene with TBHP gave 2-cyclohexene-1-one, 2-cyclohexene-1-ol and 1-(*tert*-butylperoxy)-2-cyclohexene whereas, oxidation with H<sub>2</sub>O<sub>2</sub> resulted in the formation of cyclohexene oxide and cyclohexene-1,2-diol. Manganese(II) complex supported on alumina “[Mn(habenzil)]/Al<sub>2</sub>O<sub>3</sub>” shows significantly higher catalytic activity than other catalysts. The activity of the immobilized catalyst remains nearly the same after three cycles, suggesting the true heterogeneous nature of the catalyst.

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**Keywords:** Alumina; TBHP; H<sub>2</sub>O<sub>2</sub>; Oxidation; Cyclohexene; Schiff-base

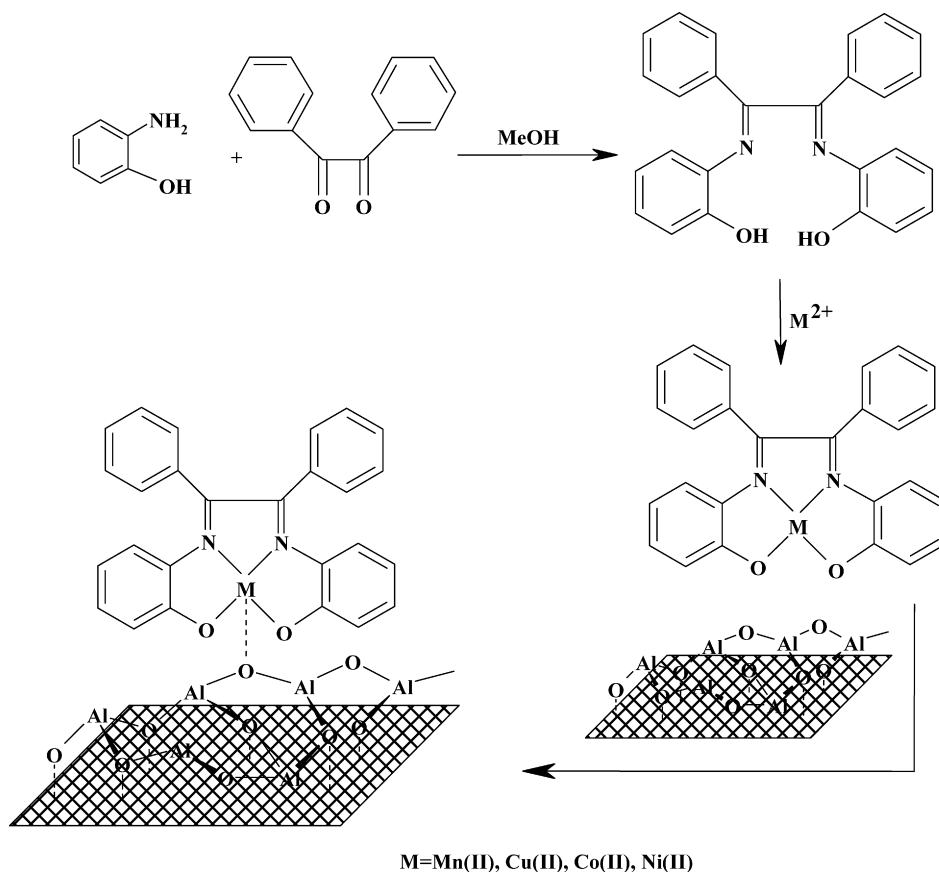
## 1. Introduction

The catalytic oxyfunctionalization of hydrocarbons, the main crude oil and natural gas constituents, into value-added oxygenated derivatives such as alcohols, aldehydes, ketones or carboxylic acids, using peroxides as oxidants have been extensively studied over the last few decades, primarily because such products are important intermediates in many industrial processes [1–9]. More environment-friendly processes for the oxidative transformation of organics have gained considerable momentum [10]. The main area of concern is the large volume of effluents produced by a variety of chemical processes. Improvement can be made in several ways, such as using alternative reagents and catalysts, increasing the efficiency of the

process, easier separation of products from reactants and recycling reagents or catalysts and thus eliminating the requirement for laborious and inefficient extraction processes. One of the major contributors to waste in a chemical process is the separation of product or catalyst from the reaction mixture. At the same time during the extraction, the catalyst often gets destroyed. Thus, elimination of these steps is highly desirable and this is one of the major goals of green chemistry [11].

We have recently reported the activation of C–H bond with TBHP and H<sub>2</sub>O<sub>2</sub> in the presence of exchanged zeolite NaY with transition metal elements [12c], alumina-supported and zeolite-encapsulation of metal complexes [12,13]. We showed that some complexes of Mn(II) included in zeolite Y, catalyzed the oxygen transfer from TBHP to cyclohexene and concluded that such simple systems mimic the behavior of cytochrome P-450 type oxidation systems [12c]. We also showed the [Mn(haacac)]/Al<sub>2</sub>O<sub>3</sub>; (haacac = bis(2-hydroxyanil)acetylacetone), catalyzed cyclohexene oxidation

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Scheme 1.

with the highest reactivity and selectivity and 2-cyclohexene-1-one was formed as the main product [13g], and we showed a simple catalyst system of alumina-supported Mn(II) complexes with a number of bidentate ligands of N,N; N,O and O,O donor atoms in the oxidation of cyclohexene [13]. Since, alumina-supported metal systems exhibit catalytic activity in a wide ranging of the industrially important processes and have been extensively studied, we decided to investigate the effect of transition metal complexes with a tetradentate Schiff-base ligand; bis(2-hydroxyanil)benzil, H<sub>2</sub>[habenzil]; supported on acidic alumina in the oxidation of cyclohexene with TBHP. In this paper, we report the synthesis and characterization of transition metal (cobalt(II), manganese(II), nickel(II) and copper(II)) complexes of the Schiff-base ligand; bis(2-hydroxyanil)benzil, H<sub>2</sub>[habenzil]; and these complexes were immobilized on acidic alumina (Scheme 1); [M(habenzil)]/Al<sub>2</sub>O<sub>3</sub>; and used in the oxidation of cyclohexene with *tert*-butylhydroperoxide and hydrogen peroxide as oxygen donors. The  $\alpha,\beta$ -unsaturated ketone, which is obtained by allylic oxidation, is an important intermediate in natural product synthesis; due to the presence of a highly reactive carbonyl group, it is also used in cycloaddition reactions. We have studied different catalytic reaction mediums, especially water, to make the process more cost effective and environment-friendly. Modified alumina has been selected as surface for immobilization due to its chemical and thermal stability and its strong ability to bind to the metal complex.

## 2. Experimental

### 2.1. Materials

All the solvents were purchased from Merck (pro analysi) and were distilled and dried using molecular sieves (Linde 4 Å) [14a]. Manganese(II) acetate, copper(II) acetate, nickel(II) acetate, cobalt(II) acetate, benzil, 2-aminophenol, hydrogen peroxide and *tert*-butylhydroperoxide (solution 80% in di-*tert*-butylperoxide) were obtained from Merck Co. Cyclohexene was distilled under nitrogen and stored over molecular sieves (4 Å). Cyclohexanone was used as an internal standard for the quantitative analysis of the product using gas chromatography. Reference samples of cyclohexene oxide, 2-cyclohexene-1-ol and 2-cyclohexene-1-one (Aldrich) were distilled and stored in the refrigerator. Acidic alumina was purchased from Merck (art. no. 1078, aluminum oxide 90 active acidic, 0.063–0.200 mm). It was activated at 500 °C for 8 h before use. The alumina-supported metal(II) chloride (MCl<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>; M = Mn(II), Co(II), Ni(II), Cu(II)) was prepared according to the procedure described previously [13d].

### 2.2. Physical measurements

XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu K $\alpha$  radiation. Elemental analyses were obtained from Carlo ERBA Model EA

1108 analyzer. The transition metal contents of the samples were measured by atomic absorption spectrophotometer (AAS-Perkin-Elmer 4100–1319) using a flame approach. The products were analyzed by GC–MS, using a Philips Pu 4400 Chromatograph (capillary column: DB5MS, 30 m), Varian 3400 Chromatograph (15 m capillary column of HP-5; FID) coupled with a QP Finnegan MAT INCOF 50, 70 eV. Diffuse reflectance spectra (DRS) was registered on a Shimadzu UV/3101 PC spectrophotometer the range 1500–200 nm, using MgO as reference. The stability of the supported catalyst was checked after the reaction by UV–vis and possible leaching of the complex was investigated by UV–vis in the reaction solution after filtration of the alumina. Magnetic moments were calculated from magnetic susceptibility data obtained using a Johnson Matthey MK-1 magnetic susceptibility balance and conductance measurements with a Metrohm Herisau conductometer E 518. Chlorine was determined gravimetrically. H NMR (400 MHz) spectra were measured in  $CD_3NO_2$  solutions and referenced to the solvent signals.

### 2.3. Preparation of bis(2-hydroxyanil)benzil; $H_2$ [habenzil]

2-Aminophenol (2.18 g, 0.02 mol) was dissolved in 75 ml ethanol, and a solution of benzil (2.10 g, 0.01 mol) in 25 ml ethanol was added to it. The mixture was refluxed on a water bath for 10 h. After reducing the volume of the solution to ca. 50 ml, the flask was kept at ambient temperature for 4 h. On cooling the white–yellow crystalline Schiff-base ligand was collected by filtration, washed with ethanol twice ( $2 \times 20$  ml) and dried. Finally, the ligand was recrystallized from ethanol to give pure crystals, yield 60%. Anal. calcd. for  $C_{26}H_{20}N_2O_2$ : C, 79.57; H, 5.14; N, 7.14; C/N, 11.14. Found: C, 79.30; H, 5.01; N, 7.29; C/N, 10.88%;  $\nu_{C=N}$ ,  $1630\text{ cm}^{-1}$ .

### 2.4. Preparation of [Mn(habenzil)]

The Schiff-base ligand (4.32 g, 0.011 mol) was dissolved in 100 ml of refluxing ethanol and a stream of nitrogen was purged for 4 h to eliminate the oxygen. A solution containing 2.69 g (0.011 mol) of manganese(II) acetate tetrahydrate in water was added dropwise to the deoxygenated ligand solution. The resulting mixture was agitated and refluxed under nitrogen with 5 ml of ethanol followed by 5 ml of water. The mixture was then cooled and filtered under reduced pressure. The collected solid was washed with diethyl ether and dried in air to give yellow crystalline [Mn(habenzil)] which purified by recrystallization from chloroform (yield: 51%). Anal. calcd. for  $C_{26}H_{18}N_2O_2Mn$ : C, 70.14; H, 4.04; N, 6.29; Mn, 12.34; C/N, 11.15; C/Mn, 5.68. Found: C, 69.93; H, 3.91; N, 6.41; Mn, 12.22; C/N, 10.91; C/Mn, 5.72%;  $\nu_{C=N}$ ,  $1624\text{ cm}^{-1}$ ;  $\mu_B$ , 5.92 B.M;  $\Lambda_M$ ,  $21\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ .

### 2.5. Preparation of [Co(habenzil)]

The flask containing a stirred suspension of cobalt(II) acetate tetrahydrate (4.0 g, 0.016 mol) in propanol (100 ml) was purged with nitrogen, and then warmed to  $50^\circ\text{C}$  under a nitrogen atmo-

sphere. Bis(2-hydroxyanil)benzil (6.28, 0.016 mol) was added in one portion, and the resulting black suspension was then stirred and reflux under nitrogen atmosphere for 8 h. Then the mixture was cooled and filtered under reduced pressure. The collected solid was washed with diethyl ether and dried in air to give black crystalline [Co(habenzil)] which was purified by recrystallization from chloroform (yield: 54%). Anal. calcd. for  $C_{26}H_{18}N_2O_2Co$ : C, 69.52; H, 4.01; N, 6.23; Co, 13.12; C/N, 11.16; C/Co, 5.30. Found: C, 69.30; H, 3.88; N, 6.34; Co, 13.02; C/N, 10.93; C/Co, 5.32%;  $\nu_{C=N}$ ,  $1620\text{ cm}^{-1}$ ;  $d \leftrightarrow d$ , 420 nm;  $\mu_B$ , 1.74 B.M;  $\Lambda_M$ ,  $17\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ .

### 2.6. Preparation of [Ni(habenzil)], [Cu(habenzil)] and [Zn(habenzil)]

[Ni(habenzil)] (yield: 57%), [Cu(habenzil)] (yield: 59%) and [Zn(habenzil)] (yield: 42%) were prepared similarly.  $H_2$ [habenzil] (5.49 g, 0.014 mol) was dissolved in 100 ml of ethanol, and the solution was refluxed. Metal acetate (0.014 mol) dissolved in 100 ml of ethanol was added to this hot solution was added. Refluxing continued for 8 h. Upon cooling the solution, a solid crystalline was obtained which was filtered, washed with ethanol, and dried in vacuum and purified by recrystallization from chloroform. Anal. calcd. for  $C_{26}H_{18}N_2O_2Ni$ : C, 69.55; H, 4.01; N, 6.24; Ni, 13.07; C/N, 11.14; C/Ni, 5.32. Found: C, 69.36; H, 3.87; N, 6.35; Ni, 12.89; C/N, 10.92; C/Ni, 5.38%;  $\nu_{C=N}$ ,  $1618\text{ cm}^{-1}$ ;  $d \leftrightarrow d$ , 471 nm;  $\mu_B$ ,  $-0.017$  B.M;  $\Lambda_M$ ,  $15\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ . Anal. calcd. for  $C_{26}H_{18}N_2O_2Cu$ : C, 68.81; H, 3.97; N, 6.17; Cu, 14.00; C/N, 11.15; C/Cu, 4.92. Found: C, 68.70; H, 3.81; N, 6.30; Cu, 13.85; C/N, 10.90; C/Cu, 4.96%;  $\nu_{C=N}$ ,  $1615\text{ cm}^{-1}$ ;  $d \leftrightarrow d$ , 478, 550 nm;  $\mu_B$ , 1.73 B.M;  $\Lambda_M$ ,  $21\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ . Anal. calcd. for  $C_{26}H_{18}N_2O_2Zn$ : C, 68.53; H, 3.95; N, 6.14; Zn, 14.35; C/N, 11.16; C/Zn, 4.78. Found: C, 68.40; H, 3.86; N, 6.29; Zn, 14.23; C/N, 10.87; C/Zn, 4.81%;  $\nu_{C=N}$ ,  $1613\text{ cm}^{-1}$ ;  $\Lambda_M$ ,  $14\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ .

### 2.7. Preparation of alumina-supported metal complexes (ASMC)

A solution of the [M(habenzil)], (2.0 g) in  $CHCl_3$  was added to a suspension of alumina (10.0 g) in  $CHCl_3$  and stirred at  $50^\circ\text{C}$  under Ar atmosphere. The solid was filtered, washed with  $CHCl_3$ . The [M(habenzil)]/ $Al_2O_3$  catalyst was dried at  $40^\circ\text{C}$  under vacuum overnight prior to use. Anal. calcd. for [Mn(habenzil)]/ $Al_2O_3$ : C, 6.84; H, 1.56; N, 0.63; Mn, 1.25; C/N, 10.84; C/Mn, 5.50%;  $\nu_{C=N}$ ,  $1620\text{ cm}^{-1}$ . Anal. calcd. for [Co(habenzil)]/ $Al_2O_3$ : C, 6.81; H, 1.54; N, 0.63; Co, 1.30; C/N, 10.81; C/Co, 5.24%;  $\nu_{C=N}$ ,  $1615\text{ cm}^{-1}$ ;  $d \leftrightarrow d$ , 418 nm. Anal. calcd. for [Ni(habenzil)]/ $Al_2O_3$ : C, 6.79; H, 1.52; N, 0.62; Ni, 1.29; C/N, 10.87; C/Ni, 5.27%;  $\nu_{C=N}$ ,  $1616\text{ cm}^{-1}$ ;  $d \leftrightarrow d$ , 470 nm. Anal. calcd. for [Cu(habenzil)]/ $Al_2O_3$ : C, 6.78; H, 1.51; N, 0.62; Cu, 1.43; C/N, 10.89; C/Cu, 4.73%;  $\nu_{C=N}$ ,  $1610\text{ cm}^{-1}$ ;  $d \leftrightarrow d$ , 476 nm.

### 2.8. Heterogeneous oxidation of cyclohexene

A mixture of  $1.02 \times 10^{-5}$  mol catalyst, 25 ml solvent and 10 mmol cyclohexene was stirred under nitrogen atmosphere in a

50 ml round-bottom flask equipped with a condenser and a dropping funnel at room temperature for 30 min. Then 16 mmol of TBHP (solution 80% in di-*tert*-butylperoxide) or hydrogen peroxide (30% in water) was added. The resulting mixture was then refluxed for 8 h under N<sub>2</sub> atmosphere. After filtration and washing with solvent, the filtrate was concentrated and then subjected to GC analysis. The concentration of products was determined using cyclohexanone as internal standard.

### 2.9. Homogeneous oxidation of cyclohexene

To a solution of cyclohexene (1 ml), neat metal complex ( $1.02 \times 10^{-5}$  mol) in dichloromethane (10 ml), TBHP (2 ml) was added. The resulting mixture was then refluxed for 8 h under N<sub>2</sub> atmosphere, the solvent evaporated under reduced pressure and the crude analyzed by GC and GC–MS. The concentrations of products were determined using cyclohexanone as internal standard.

## 3. Results and discussion

The metal content of the ASMC catalysts was estimated by dissolving the known amounts of the heterogeneous catalyst in concentrated HCl and from these solutions, transition metal contents were estimated by atomic absorption spectrometer. The metal content of the different catalysts synthesized was almost the same in all the supported system and was  $0.012 \text{ mol g}^{-1}$ . The chemical composition confirmed the purity and stoichiometry of the neat and alumina-supported complexes. The chemical analysis of the samples reveals the presence of organic matter with a C/N ratio roughly similar to neat complexes. In the case of the immobilized catalyst, the ratios of carbon to metal (C/M) and carbon to nitrogen (C/N) have been provided to ensure the immobilization of complex on the alumina.

Synthesis of the metal complexes was essentially the same and involved heating and stirring of stoichiometric amounts of H<sub>2</sub>[habenzil] and metal acetate in ethanol. Elemental analysis indicates that all of the complexes are formed by coordination of 1 mol of the metal ion and 1 mol [habenzil]. All of the metal chelates in this study are insoluble in water but soluble in most organic solvents. Electrical conductivity measurements of the metal complexes give  $\Lambda_M$  values of  $12\text{--}25 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  and confirm that they are non-electrolytes.

The structural information of the transition metal complexes and its immobilized analogue over alumina was obtained from the FT-IR spectroscopy. The presence of Schiff-base moiety was indicated by the appearance of absorption band at  $1630 \text{ cm}^{-1}$  due to C=N stretching vibration, which shifted to lower frequency and appears at  $1613\text{--}1625 \text{ cm}^{-1}$  indicating the coordination of azomethine nitrogen to the metal. The phenolic (C–O) stretching frequency was observed in the region of  $1275 \text{ cm}^{-1}$  (of ligand), which shifted to higher frequency region of  $1297 \text{ cm}^{-1}$  in complex, indicating coordination through phenolic oxygen [14b]. In the complex strong to medium intensity bands are observed in  $\sim 400$  and  $\sim 530 \text{ cm}^{-1}$  attributed to  $\nu_{M-N}$  and  $\nu_{M-O}$  stretching frequencies, respectively. The presence of several bands of medium intensity at  $1599$  and  $1468 \text{ cm}^{-1}$  have been assigned to

the aromatic skeletal vibration. In the immobilized catalyst, the presence of Schiff-base moiety was indicated by the appearance of an absorption band at  $\sim 1625 \text{ cm}^{-1}$  due to C=N stretching vibration. The intensity of the alumina-supported metal complexes (ASMC) are though, weak due to low concentration of the complex, the IR spectra of supported complexes are essentially similar to the free metal complexes. The adsorbing tendency of the acidic alumina might arise from the presence of oxygen groups on the surface in order to coordinate to metal ion center (Scheme 1).

The X-ray diffractograms of Al<sub>2</sub>O<sub>3</sub>, NiCl<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and [Ni(habenzil)]/Al<sub>2</sub>O<sub>3</sub> were recorded to study their crystallinity and to ensure supporting. After careful comparison of XRD patterns of Al<sub>2</sub>O<sub>3</sub> and NiCl<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, it was observed that there is one new peak with a *d* value of  $17.30 \text{ \AA}$  in NiCl<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. This peak was also observed in [Ni(habenzil)]/Al<sub>2</sub>O<sub>3</sub> and [Ni(habenzil)] at the same position. In addition, the [Ni(habenzil)]/Al<sub>2</sub>O<sub>3</sub> exhibits one new signal with value of  $82.70 \text{ \AA}$ , which is a part of the ligand as this signal was also observed in [Ni(habenzil)] but not observed in Al<sub>2</sub>O<sub>3</sub> or NiCl<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. This information clearly indicates the supported of [Ni(habenzil)] on alumina. Very low intensity of other peaks made it difficult to distinguish them from the other peaks in the XRD pattern of the ASMC.

Comparison of <sup>1</sup>H NMR spectral data of the H<sub>2</sub>[habenzil] and the neat diamagnetic [Zn(habenzil)] and [Ni(habenzil)] complexes recorded in DMSO-*d*<sub>6</sub> further supplements the conclusion drawn from IR data. The <sup>1</sup>H NMR spectrum of H<sub>2</sub>[habenzil] exhibits the following signals: 13.85 (s, 2H, OH), 6.80–7.12 (m, 10H, C<sub>6</sub>H<sub>5</sub>) and 7.25–7.40 (m, 8H, C<sub>6</sub>H<sub>4</sub>). The disappearance of phenolic signal and down field shift (7.70 ppm) of C<sub>6</sub>H<sub>4</sub> signal indicates of the coordination of phenolic oxygen after deprotonation and azomethine nitrogen atoms. <sup>1</sup>H NMR spectrum of [Cu(habenzil)], [Co(habenzil)] and [Mn(habenzil)] complexes could not be recorded due to its partial paramagnetic nature of complex as noticed earlier [15].

Electronic spectra of [Cu(habenzil)] complexes were recorded in CHCl<sub>3</sub> solution over the range 400–700 nm (see Section 2). The visible spectra of the [Cu(habenzil)] complexes consists of a shoulders at  $\sim 478 \text{ nm}$  and a maximum or a broad shoulder around  $550 \text{ nm}$ , which can be assigned to the  $d_{xz,yz} \leftrightarrow d_{xy}$  and  $d_{x^2-y^2} \leftrightarrow d_{xy}$  transitions in *D*<sub>2</sub>*h* symmetry [15]. The room temperature magnetic moments of [Cu(habenzil)] fall in the range  $1.74 \mu_B$  which are typical for square-planar (*D*<sub>4</sub>*h*) and tetrahedrally distorted (*D*<sub>2</sub>*h*) mononuclear copper(II) complexes with a *S* = 1/2 spin state and did not indicate any antiferromagnetic coupling of spines at this temperature. The tetrahedral geometry of the [Mn(habenzil)] is strongly indicated by similarities in the visible spectra of this chelate with those of known tetrahedral complexes containing oxygen–nitrogen donor atoms [16]. The electronic spectrum of the [Ni(habenzil)] exhibit one band at  $471 \text{ nm}$  which can be assigned to a *d* ↔ *d* transition of the metal ion. The average energy of this absorption is comparable to *d* ↔ *d* transitions of other square-planar Schiff-base of nickel(II) chelates with nitrogen and oxygen donor atoms [17,18], which have reported values in the range of 465–485 nm. The electronic spectrum of [Co(habenzil)] is very similar to that reported for [Co(salen)].

Table 1

Oxidation of cyclohexene with TBHP catalyzed by metal complexes in  $\text{CH}_2\text{Cl}_2$  (solvent = 10 ml; catalyst =  $1.02 \times 10^{-5}$  mol; duration = 8 h, at reflux; cyclohexene = 1 ml, TBHP = 2 ml)

Catalyst	Conversion (%)	Selectivity (%)		
		Ketone <sup>a</sup>	Alcohol <sup>b</sup>	Peroxide <sup>c</sup>
[Mn(habenzil)]	90.6	60.1	21.3	18.6
[Mn(habenzil)] <sup>d</sup>	64.3	56.4	26.3	17.3
[Mn(habenzil)] <sup>e</sup>	85.7	64.8	22.8	12.4
[Mn(habenzil)] <sup>f</sup>	51.4	67.6	21.4	11.0
[Co(habenzil)]	81.4	51.5	28.3	20.2
[Ni(habenzil)]	49.7	33.7	40.8	25.5
[Cu(habenzil)]	61.5	38.5	30.8	30.7

<sup>a</sup> 2-Cyclohexene-1-one.

<sup>b</sup> 2-Cyclohexene-1-ol.

<sup>c</sup> 1-(*tert*-Butylperoxy)-2-cyclohexene.

<sup>d</sup> Catalyst =  $0.5 \times 10^{-5}$  mol.

<sup>e</sup> Catalyst =  $2.04 \times 10^{-5}$  mol.

<sup>f</sup> Catalyst =  $4.08 \times 10^{-5}$  mol.

The spectrum of the [Co(habenzil)] exhibit two bands at 555–660 nm which are assigned to  $d \leftrightarrow d$  transitions. In addition, a lower energy absorption at 420 nm has been observed such low energy bands which have been shown to be characteristic of square-planar cobalt(II) chelates [17,19,20]. This geometry is confirmed by the values of the effective magnetic moment.

The selectivity and activity results of alumina-supported and homogeneous catalysts on the oxidation of cyclohexene with TBHP have been given in Tables 1–3 and Figs. 1–3. Comparing between neat and ASMC as catalyst evidence that neat catalysts gave higher conversion of cyclohexene than their corresponding alumina-supported complexes. The effect of transition metal complexes supported on alumina was studied on

Table 2

Oxidation of cyclohexene with TBHP catalyzed by metal complexes on alumina in  $\text{CH}_2\text{Cl}_2$

Catalyst	Conversion (%)	Selectivity (%)		
		Ketone <sup>a</sup>	Alcohol <sup>b</sup>	Peroxide <sup>c</sup>
[Mn(habenzil)]- $\text{Al}_2\text{O}_3$	84.5	83.2	13.1	3.7
[Mn(habenzil)]- $\text{Al}_2\text{O}_3$ <sup>d</sup>	83.7	82.5	13.9	3.6
[Mn(habenzil)]- $\text{Al}_2\text{O}_3$ <sup>e</sup>	83.1	80.4	14.5	5.1
[Mn(habenzil)]- $\text{Al}_2\text{O}_3$ <sup>f</sup>	82.4	79.6	15.6	4.8
[Mn(habenzil)]- $\text{Al}_2\text{O}_3$ <sup>g</sup>	62.4	70.3	24.8	4.9
[Mn(habenzil)]- $\text{Al}_2\text{O}_3$ <sup>h</sup>	88.5	85.6	11.6	2.8
[Mn(habenzil)]- $\text{Al}_2\text{O}_3$ <sup>i</sup>	90.3	87.8	10.8	1.4
[Co(habenzil)]- $\text{Al}_2\text{O}_3$	75.2	76.9	20.2	2.9
[Ni(habenzil)]- $\text{Al}_2\text{O}_3$	43.5	67.4	25.1	7.5
[Cu(habenzil)]- $\text{Al}_2\text{O}_3$	55.2	70.6	20.5	8.9

<sup>a</sup> 2-Cyclohexene-1-one.

<sup>b</sup> 2-Cyclohexene-1-ol.

<sup>c</sup> 1-(*tert*-Butylperoxy)-2-cyclohexene.

<sup>d</sup> First reuse.

<sup>e</sup> Second reuse.

<sup>f</sup> Third reuse.

<sup>g</sup> Catalyst =  $0.5 \times 10^{-5}$  mol.

<sup>h</sup> Catalyst =  $2.04 \times 10^{-5}$  mol.

<sup>i</sup> Catalyst =  $4.08 \times 10^{-5}$  mol.

Table 3

Oxidation of cyclohexene with TBHP catalyzed by metal complexes on alumina in  $\text{CH}_3\text{Cl}$

Catalyst	Conversion (%)	Selectivity (%)		
		Ketone <sup>a</sup>	Alcohol <sup>b</sup>	Peroxide <sup>c</sup>
[Mn(habenzil)]- $\text{Al}_2\text{O}_3$	80.7	79.9	15.2	4.9
[Mn(habenzil)]- $\text{Al}_2\text{O}_3$ <sup>d</sup>	78.4	79.0	15.8	5.2
[Mn(habenzil)]- $\text{Al}_2\text{O}_3$ <sup>e</sup>	77.1	78.2	15.9	5.9
[Mn(habenzil)]- $\text{Al}_2\text{O}_3$ <sup>f</sup>	76.2	76.5	17.2	6.3
[Co(habenzil)]- $\text{Al}_2\text{O}_3$	72.4	74.1	22.4	3.5
[Ni(habenzil)]- $\text{Al}_2\text{O}_3$	42.6	64.9	26.5	8.6
[Cu(habenzil)]- $\text{Al}_2\text{O}_3$	53.2	67.1	23.7	9.2

<sup>a</sup> 2-Cyclohexene-1-one.

<sup>b</sup> 2-Cyclohexene-1-ol.

<sup>c</sup> 1-(*tert*-Butylperoxy)-2-cyclohexene.

<sup>d</sup> First reuse.

<sup>e</sup> Second reuse.

<sup>f</sup> Third reuse.

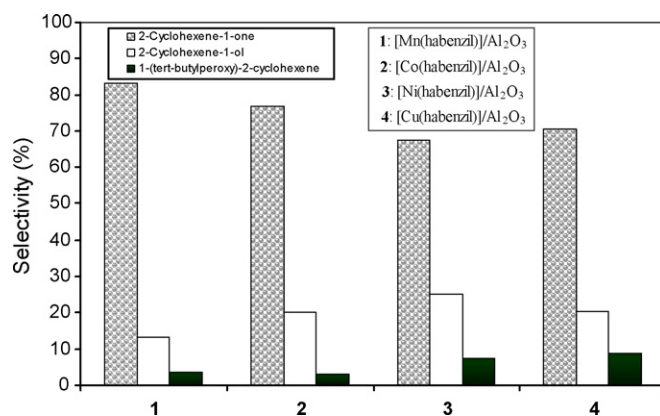


Fig. 1. Oxidation products distribution in dichloromethane with [M(habenzil)]/ $\text{Al}_2\text{O}_3$ /TBHP.

the oxidation of cyclohexene with TBHP in dichloromethane and the results have been shown in Table 2 and Fig. 1. As shown in Tables 1–3, only allylic oxidation has occurred with the formation of 2-cyclohexene-1-one, 2-cyclohexene-1-ol and 1-(*tert*-butylperoxy)-2-cyclohexene. Oxidation with the same oxidant in the presence of  $\text{MnCl}_2/\text{Al}_2\text{O}_3$  was 29.4% [21].

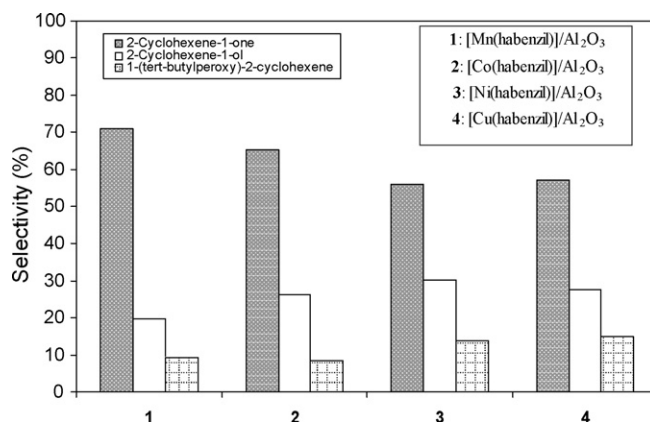
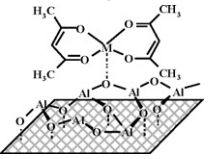
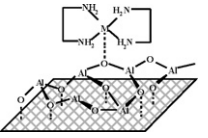
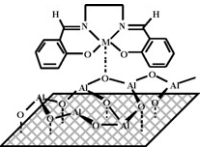
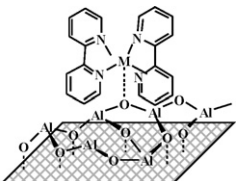
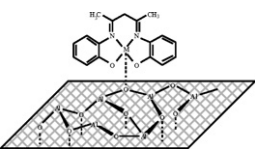
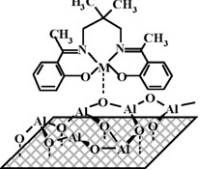
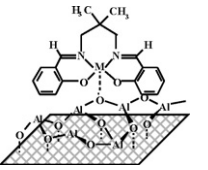
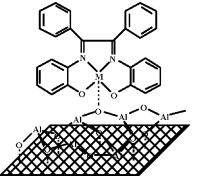


Fig. 2. Oxidation products distribution in methanol with [M(habenzil)]/ $\text{Al}_2\text{O}_3$ /TBHP.

Table 4  
Oxidation of cyclohexene catalyzed by alumina-supported metal complexes in CH<sub>2</sub>Cl<sub>2</sub> with TBHP

Catalyst	Conversion (%)	Selectivity (%)			Ref.
		Ketone <sup>a</sup>	Alcohol <sup>b</sup>	Peroxide <sup>c</sup>	
MnCl <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	29.4	52.3	39.6	8.1	[21]
	44.3	48.6	28.2	23.2	[21]
	52.1	56.1	26.5	17.4	[21]
	65.8	71.6	18.6	9.8	[21]
	73.4	75.4	17.4	7.2	[21]
	76.8	74.5	16.6	8.9	[13g]
	82.8	80.5	14.2	5.3	[13c]
	78.4	77.2	16.5	6.3	[13h]
	84.5	83.2	13.1	3.7	This work

<sup>a</sup> 2-Cyclohexene-1-one.

<sup>b</sup> 2-Cyclohexene-1-ol.

<sup>c</sup> 1-(*tert*-Butylperoxy)-2-cyclohexene.

The increase of conversion from 29.4 to 84.5% compared to MnCl<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> with [Mn(habenzil)]/Al<sub>2</sub>O<sub>3</sub> indicates that the existence of ligand has increased the activity of the catalyst by a factor of 2.90. From the indicated results in Tables 2–4 and

Figs. 1 and 2 it is evident that cyclohexene-2-one is selectively formed in the presence of all catalysts.

The trend observed in Tables 1–3 can be explained by the donor ability of ligand available in the complex catalysts.

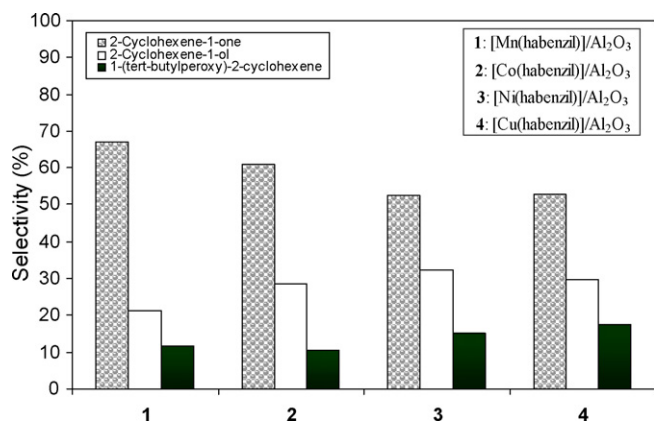


Fig. 3. Oxidation products distribution in acetonitrile with [M(habenzil)]/Al<sub>2</sub>O<sub>3</sub>/TBHP.

As Wang et al. have pointed out, the key point in the conversion of cyclohexene to the products is the reduction of L-Mn<sup>3+</sup> to L-Mn<sup>2+</sup>. This reduction to L-Mn<sup>2+</sup> is facilitated with the ligands available around the metal cation [22]. The formation of the allylic oxidation products 2-cyclohexene-1-one and 2-cyclohexene-1-ol shows the preferential attack of the activated C–H bond over the C=C bond. The formation of 1-(*tert*-butylperoxy)-2-cyclohexene shows the presence of radical reactions [23]. TBHP as oxidant promotes the allylic oxidation pathway and epoxidation is minimized, especially under the highly acidic properties of alumina supported with divalent and trivalent transition metal ions and complexes, has been observed by us and others [12,13,24]. It should be emphasized that the destructive oxidation of alkenes via epoxidation pathway with H<sub>2</sub>O<sub>2</sub> under the catalytic effect of alumina-supported Mn(II) complexes seem interesting [13]. Although the two systems are alike, it is the oxidant structure that has changed the fate of the reaction.

When the oxidant was changed to hydrogen peroxide (Fig. 4), the oxidation occurred on the double bond and cyclohexene epoxide obtained as the sole product. It seems that the diol resulted from the epoxide ring opening under the aqueous acidic conditions. Although both H<sub>2</sub>O<sub>2</sub> and TBHP oxidize cyclohexene

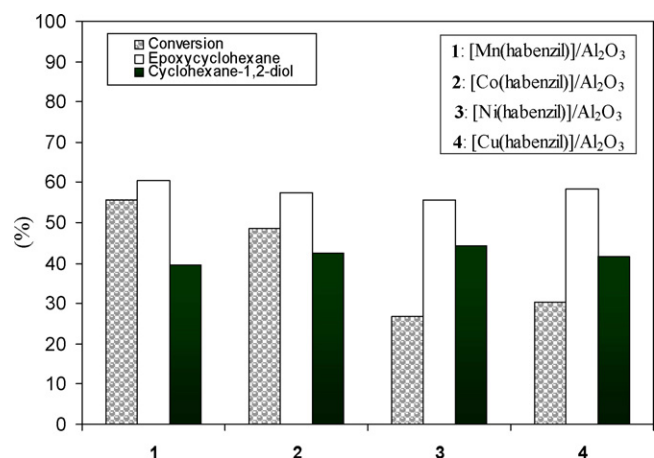


Fig. 4. Oxidation products distribution in acetonitrile with [M(habenzil)]/Al<sub>2</sub>O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>.

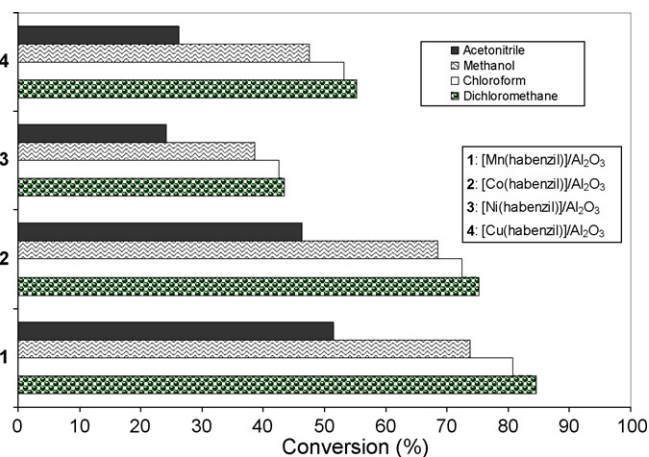


Fig. 5. Effect of solvent on the conversion by heterogeneous catalyst.

in the presence of alumina-supported metal complexes, but only H<sub>2</sub>O<sub>2</sub> and not TBHP gave epoxidation of cyclohexene under the similar conditions leads us to conclude that the two types of reactions do not occur via a common intermediate. As Valentine and co-workers have pointed out one possible explanation is that the species responsible for the cyclohexene oxidation are the products formed from cleavage of the O–O bond, whereas, the epoxidation reaction occurs by a direct reaction of olefin with coordinated HOO radical. Since the O–O bond of HOOH is 5 kcal/mol stronger than TBHP, an HOO complex is expected to have a higher activation energy for O–O bond cleavage than a TBOO complex and therefore, to have a longer lifetime [25].

The effect of various solvents for the oxidation of cyclohexene with [M(habenzil)]/Al<sub>2</sub>O<sub>3</sub> catalysts was also studied (Fig. 5). The oxidation reactions were carried out in protic and aprotic solvents. The results have been given in Tables 1–3 and Figs. 1–5. In all the oxidation reaction, 2-cyclohexene-1-one was formed as the major product. When the reaction was carried out in a coordinating solvent like CH<sub>3</sub>CN the conversion decreased by a factor of ~1.56 (Fig. 3). This might be attributed to donor number of acetonitrile (14.1) and therefore, its higher ability to occupy the vacant spaces around the metal center and prevent the approaching of oxidant molecules. In dichloromethane and chloroform the yields of 2-cyclohexene-1-ol and 2-cyclohexene-1-one were higher and lower yield of the peroxy species were obtained as compared to the other solvents. The efficiency of the catalysts for oxidation of cyclohexene in different solvents decreases in the order: dichloromethane > chloroform > methanol > acetonitrile.

At the end of the heterogeneous reaction, the catalyst was separated by filtration, thoroughly washed with solvent and reused under similar conditions. Although the analysis of the recovered catalysts by Atomic Absorption Spectroscopy showed no reduction in the amount of transition metal ions, they showed a slightly lower catalytic activity (~2%) (Tables 1–3). The results indicate that [M(habenzil)]/Al<sub>2</sub>O<sub>3</sub> are almost stable to be recycled for the oxidation of cyclohexene without much loss in activity (Table 3). Thus, the alumina-supported metal complexes is found to increase the life of the catalyst by reducing dimerization due to the site isolation and restriction of internal framework

structure. IR spectrum of the recycled sample is quite similar to that of fresh sample indicating little changes in the coordination of habenzil after the oxidation reactions.

The results clearly suggest that [Mn(habenzil)]/Al<sub>2</sub>O<sub>3</sub> efficiently catalyses conversion of cyclohexene to 2-cyclohexene-1-one with 83.2% selectivity and conversion 84.5%. The more activity of habenzil system has clearly arisen from the existence of electron donating ligand which facilitates the electron transfer rate, a process that has previously observed by us in other oxidation reactions (Table 4). All conversion efficiency with high selectivity obtained in this study is significantly higher than that obtained using manganese(II) complexes supported on alumina (Table 4).

#### 4. Conclusions

In this study, we have used a rather simple catalysis system of alumina-supported manganese(II), cobalt(II), nickel(II) and copper(II) complexes with a Schiff-base ligand “H<sub>2</sub>[habenzil]” in the oxidation of cyclohexene. Oxidation of allylic site and double bond were resulted with the oxidants of TBHP and H<sub>2</sub>O<sub>2</sub>, respectively. The results clearly suggest that [Mn(habenzil)]/Al<sub>2</sub>O<sub>3</sub> efficiently catalyses conversion of cyclohexene to 2-cyclohexene-1-one with 83.2% selectivity and conversion 84.5%. The efficiency of the catalysts for oxidation of cyclohexene in different solvents decreases in the order: dichloromethane > chloroform > methanol > acetonitrile. The extension of the method to different olefins is currently under investigation in our laboratory.

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#### References

- [1] (a) R.S. Drago, *Coord. Chem. Rev.* 117 (1992) 185; (b) R.A. Sheldon, J.K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981.
- [2] (a) G.B. Sul'pin, *Organic Reactions Catalyzed by Metal Complexes*, Nauka, Moscow, 1988; (b) S.T. Oyama, J.W. Hightower (Eds.), *Catalytic Selective Oxidation*, American Chemical Society, Washington, DC, 1993.
- [3] C.L. Hill (Ed.), *Activation and Fictionalization of Alkanes*, Wiley-Interscience, New York, 1989.
- [4] (a) M. Salavati-Niasari, *Microporous Mesoporous Mater.* 92 (2006) 173; (b) M. Salavati-Niasari, *Microporous Mesoporous Mater.* 95 (2006) 248.
- [5] H. Arakawa, M. Aresta, J.N. Armor, M.A. Barteau, E.J. Beckman, A.T. Bell, J.E. Bercaw, C. Creutz, E. Dinjus, D.A. Dixon, K. Domen, D.L. Dubois, J. Eckert, E. Fujita, D.H. Gibson, W.A. Goddard, D.W. Goodman, J. Keller, G.J. Kubas, H.H. Kung, J.E. Lyons, L.E. Manzer, T.J. Marks, K. Morokuma, K.M. Nicholas, R. Periana, L. Que, J.R. Nielson, W.M.H. Sachtler, L.D. Schmidt, A. Sen, G.A. Somorjai, P.C. Stair, B. Ray Stults, *Chem. Rev.* 101 (2001) 953.
- [6] T. Katsuki, *Coord. Chem. Rev.* 140 (1995) 189.
- [7] (a) C. Bowers, P.K. Dutta, *J. Catal.* 122 (1990) 271; (b) D.E. de Vos, P.P. Knops-Gerrits, D.L. Vanoppen, P.A. Jacobs, *Supramol. Chem.* 6 (1995) 49.
- [8] (a) M.R. Maurya, S.J.J. Titinchi, S. Chand, *J. Mol. Catal. A: Chem.* 214 (2004) 257; (b) M.R. Maurya, S. Sikarwar, T. Joseph, S.B. Halligudi, *J. Mol. Catal. A: Chem.* 236 (2005) 132; (c) M.R. Maurya, A. Kumar, P. Manikandan, S. Chand, *Appl. Catal. A: Gen.* 277 (2004) 45; (d) M.R. Maurya, U. Kumar, P. Manikandan, *Dalton Trans.* (2006) 3561.
- [9] (a) M. Salavati-Niasari, *Chem. Lett.* 34 (2005) 244; (b) M. Salavati-Niasari, *Chem. Lett.* 34 (2005) 1444.
- [10] J.H. Clark (Ed.), *Chemistry of Waste Minimization*, Chapman & Hall, Glasgow, 1995.
- [11] J.H. Clark, *Supported Reagents in Organic Reactions*, VCH, Weinheim, 1994.
- [12] (a) M. Salavati-Niasari, *J. Mol. Catal. A: Chem.* 229 (2005) 159; (b) M. Salavati-Niasari, *Inorg. Chem. Commun.* 8 (2005) 174; (c) M. Salavati-Niasari, F. Farzaneh, M. Ghandi, *J. Mol. Catal. A: Chem.* 175 (2001) 105; (d) M. Salavati-Niasari, F. Davar, *Inorg. Chem. Commun.* 9 (2006) 304; (e) M. Salavati-Niasari, *J. Mol. Catal. A: Chem.* 217 (2004) 87; (f) M. Salavati-Niasari, *Inorg. Chem. Commun.* 7 (2004) 963; (g) M. Salavati-Niasari, M. Bazarganipour, *Inorg. Chem. Commun.* 9 (2006) 332; (h) M. Salavati-Niasari, *J. Mol. Catal. A: Chem.* 245 (2006) 192; (i) M. Salavati-Niasari, *Inorg. Chem. Commun.* 9 (2006) 628.
- [13] (a) M. Salavati-Niasari, A. Amiri, *Appl. Catal. A: Gen.* 290 (2005) 46; (b) M. Salavati-Niasari, M.R. Elzami, M.R. Mansournia, S. Hydarzadeh, *J. Mol. Catal. A: Chem.* 221 (2004) 169; (c) M. Salavati-Niasari, P. Salemi, F. Davar, *J. Mol. Catal. A: Gen.* 238 (2005) 215; (d) M. Salavati-Niasari, T. Khosousi, S. Hydarzadeh, *J. Mol. Catal. A: Chem.* 235 (2005) 150; (e) M. Salavati-Niasari, S. Hydarzadeh, *J. Mol. Catal. A: Chem.* 237 (2005) 254; (f) M. Salavati-Niasari, J. Hasanalian, H. Najafian, *J. Mol. Catal. A: Chem.* 209 (2004) 209; (g) M. Salavati-Niasari, H. Banitaba, *J. Mol. Catal. A: Chem.* 201 (2003) 43; (h) M. Salavati-Niasari, M. Hassani-Kabutarkhani, F. Davar, *Catal. Commun.* 7 (2006) 955.
- [14] (a) D.D. Perrin, W.L.F. Armarego, D.R. Perrin, *Purification of Laboratory Chemicals*, second ed., Pergamon/Headington Hill Hall, Oxford/London/England, 1980; (b) C.S. Marvel, S.A. Aspey, E.A. Dudley, *J. Am. Chem. Soc.* 78 (1956) 4905.
- [15] (a) W.M. Coleman, L.T. Taylor, *Inorg. Chem.* 10 (1971) 2195; (b) M. Salavati-Niasari, H. Najafian, *Polyhedron* 22 (2003) 2633; (c) M. Salavati-Niasari, M. Rezai-Adaryani, *Polyhedron* 23 (2004) 1325; (d) M. Salavati-Niasari, *Polyhedron* 24 (2005) 1405; (e) M. Salavati-Niasari, F. Davar, *Polyhedron* 25 (2006) 2127; (f) M. Salavati-Niasari, A. Amiri, *Trans. Met. Chem.* 30 (2005) 720; (g) M. Salavati-Niasari, M. Rezai-Adaryani, S. Hydarzadeh, *Trans. Met. Chem.* 30 (2005) 445; (h) M. Salavati-Niasari, *Inorg. Chem. Commun.* 7 (2004) 698.
- [16] N. Raman, Y.P. Raja, A. Kulandaisamy, *Proc. Indian Acad. Sci. (Chem. Sci.)* 113 (2001) 183.
- [17] A.B. Lever, *Inorganic Electronic Spectroscopy*, second ed., Elsevier, New York, 1968.
- [18] (a) R.H. Holm, G.W. Evverett, A. Chakrvorty, *Prog. Inorg. Chem.* 7 (1966) 183; (b) M.R. Ganjali, M. Yousefi, T. Poursaberi, L. Naji, M. Salavati-Niasari, M. Shamsipur, *Electroanalysis* 15 (2003) 1476; (c) M.R. Ganjali, M. Rezapour, M.R. Pourjavid, M. Salavati-Niasari, *Anal. Sci.* 19 (2003) 1127; (d) M.R. Ganjali, M. Golmohammadi, M. Yousefi, P. Norouzi, M. Salavati-Niasari, M. Javanbakht, *Anal. Sci.* 19 (2003) 223; (e) M.R. Ganjali, M. Yousefi, M. Javanbakht, T. Poursaberi, M. Salavati-Niasari, L. Hajiagha-Babaei, E. Latifi, M. Shamsipur, *Anal. Sci.* 18 (2002) 887.



- [19] C.A. Root, B.A. Rising, M.C. Vanderveer, C.F. Hellmuth, *Inorg. Chem.* 11 (1972) 1489.
- [20] (a) F.L. Urbach, R.D. Bereman, J.A. Topido, M. Hariharan, B.J. Kalbacher, *J. Am. Chem. Soc.* 92 (1970) 792;  
(b) M.A. Hitchman, *Inorg. Chem.* 16 (1977) 1985.
- [21] M. Salavati-Niasari, F. Farzaneh, M. Ghandi, *J. Mol. Catal. A: Chem.* 186 (2002) 101.
- [22] M. Wang, C.J. Hao, Y.P. Wang, S.B. Li, *J. Mol. Catal. A: Chem.* 147 (1999) 173.
- [23] D. Koola, J.K. Kochi, *J. Org. Chem.* (1987) 4545.
- [24] A.H. Gemeay, M.A. Salem, I.A. Salem, *Colloid Surf.* 117 (1996) 245.
- [25] W. Nam, R. Ho, J.S. Valentine, *J. Am. Chem. Soc.* 113 (1991) 7052.