

Alumina-supported Mn(II), Co(II), Ni(II) and Cu(II) bis(2-hydroxyanil)acetylacetonate complexes as catalysts for the oxidation of cyclohexene with *tert*-butylhydroperoxide

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Abstract

New Mn(II), Co(II), Ni(II) and Cu(II) complexes of a tetradentate Schiff base ligand [bis(2-hydroxyanil)acetylacetonate], “2-[[1-methyl-3-[(2-hydroxyphenyl)imino]butylidene]amino]phenol”, H₂haacac, have been prepared and characterized by elemental analyses, IR and conductometry. The results suggest that the Schiff base is a bivalent anion with tetradentate ONNO donors derived from the phenolic oxygen and azomethine nitrogen. The formulae was found to be [M(haacac)] for the 1:1 non-electrolytic complexes. Alumina-supported [M(haacac)] complexes catalyze the oxidation of cyclohexene with *tert*-butylhydroperoxide (TBHP). The major products of the reaction were 2-cyclohexene-1-ol (–OH), 2-cyclohexene-1-one (C=O) and 2-cyclohexene-1-(*tert*-butylperoxy) (–OO^tBu). The influence of temperature, solvent and time for the oxidation reaction has been studied. The selectivity of 2-cyclohexene-1-(*tert*-butylperoxy) varied with reaction temperature. Mn(haacac)-alumina shows significantly higher catalytic activity than other alumina-supported complexes.

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1. Introduction

Selective and catalytic oxyfunctionalization of alkanes under homogenous condition is an important research objective [1]. Many homogenous catalysts for selective activation of C–H bonds show a tendency to autooxidation and deactivation by μ -dimerization through the formation of oxygen bridges [2]. To avoid these problems, to improve the separation of the cat-

alyst from the reaction medium and to increase its active life, various strategies can be employed. For immobilizing active sites (redox-active elements or transition metal complexes) in an inorganic solid matrix the following procedures could be applied:

1. Isomorphous substitution in framework position of molecular sieves, e.g. zeolites, silicalites aluminophosphates (APOs), silico-aluminophosphates (SAPOs), via hydrothermal synthesis or post modification [3–5].
2. Grafting or impregnation onto the surface of silica or alumina [6–8].

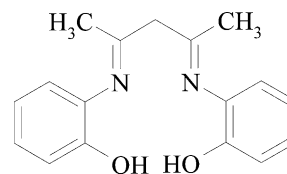
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- Tethering to the surface of a solid, e.g. silica, via a spacer ligand. Examples of the former include the synthesis of surface grafted Ti(VI) [9] and oxomanganese [10] by the reaction of MCM-41 with titanocene dichloride and $\text{Mn}_2(\text{CO})_{10}$, respectively, followed by calcination.
- Encapsulation of metal complexes in a solid matrix. For example, the so-called ship-in-a-bottle concept, which involves the entrapment of a bulky complex in a zeolite cage, has been widely used to immobilize metal complexes of phthalocyanines, bipyridine and Schiff base type ligand [11].
- Immobilization by cation exchange into zeolites or acidic clays, e.g. oxoanions such as molybdate and tungstate can be exchanged into hydrotalcite-like anionic clays (so-called layered double hydroxides, LDHs) [12,13].

Indeed the whole area of supported transition metal complex catalysts is expanding rapidly again as the advantages are arising from ease of handling, recovery, separation and recycling, coupled with the potential for automation which has become recognized by more and more rank-and-file industrial and academic synthetic chemistry [14,15]. In terms of immobilizing transition metal complex catalysts, key targets are highly active and selective asymmetric catalysts, which are available nowadays. Heterogeneous analogues [16,17] of these homogeneous catalysts would not only simplify their use and facilitate product separation and isolation, but would also offer considerable economic benefits if recycling and re-use would be possible.



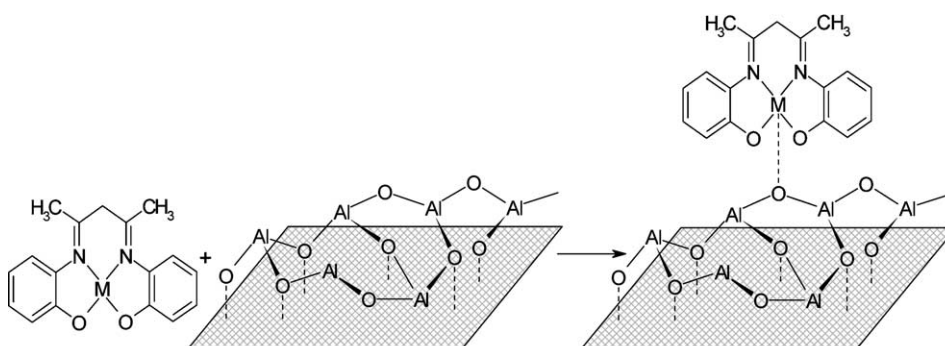
Scheme 1. Tetradentate Schiff base ligand (H_2haacac).

In this paper, we report the synthesis and characterization of transition metal (Mn(II), Co(II), Ni(II) and Cu(II)) complexes of the Schiff base ligand; bis(2-hydroxyanil)acetylacetonate; shown in Scheme 1, and the same complex immobilized in acidic alumina (Scheme 2); $\text{M}(\text{haacac})$ -alumina; and used in the oxidation of cyclohexene with *tert*-butylhydroperoxide as oxygen donor.

2. Experimental

2.1. Materials

All the solvents were purchased from Merck (pro-analysis) and were dried using molecular sieves (Linda 4 Å). Manganese(II) acetate, copper(II) acetate, nickel(II) acetate, cobalt(II) acetate, acetylacetonate, 2-aminophenol and *tert*-butylhydroperoxide (solution 80% in di-*tert*-butylperoxide) were obtained from Merck. Acidic alumina was also purchased from Merck and was activated at 500 °C for 8 h before use. Cyclohexene was distilled under nitrogen and stored over molecular sieves (4 Å). Cyclohexanone was used as an internal standard for the quantitative



Scheme 2. Immobilization of $[\text{M}(\text{haacac})]$ on alumina.

analysis of the product using gas chromatography. 2-Cyclohexene-1-ol and 2-cyclohexene-1-one were identified by comparisons of their retention times with those of pure compounds (obtained from Merck).

2.2. Physical measurements

The elemental analysis (carbon, hydrogen and nitrogen) of the ligand and neat complexes were obtained from Carlo ERBA Model EA 1108 analyzer. The manganese, iron, cobalt, nickel and copper contents of the samples were measured by atomic absorption spectrophotometer (AAS, Perkin-Elmer 4100-1319) using a flame approach, after acid (HF) dissolution of known amount of the alumina material in Parr digest pump. The products were analyzed by GC-MS, using a Philips Pu 4400 Chromatograph (1.5 m, 3% OV-17 column), Varian 3400 Chromatograph (25 m, DB-5 column) coupled with a QP Finnigan MAT INCOF 50, 70 eV. FTIR spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. The electronic spectra of the neat complexes were taken on a Shimadzu UV-Vis scanning spectrometer (Model 2101 PC). ^1H NMR spectra were determined for solution in CDCl_3 with tetramethylsilane as internal standard on a Bruker AC 80.

2.3. Preparation of bis(2-hydroxyanil)acetylacetonone (H_2haacac)

2-Aminophenol (2.18 g, 0.02 mol) was dissolved in 75 ml ethanol, and a solution of acetylacetonone (1.0 g, 0.01 mol) in 25 ml ethanol was added to it. The mixture was refluxed on a water bath for 8 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 (2×20 ml) and dried. Finally, the ligand was recrystallized from ethanol to give pure crystals, yield 84%. Anal. Calcd. for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_2$ (%): C, 72.32; H, 6.43; N, 9.92. Found (%): C, 72.12; H, 6.56; N, 10.06. The ^1H NMR spectrum of the tetradentate Schiff base in chloroform shows the following signals: C_6H_5 multiplet at 6–9 δ range, $-\text{CH}_3$ at 1.90 δ , $-\text{CH}_2$ at 2.27 δ and OH at 5.27 δ .

2.4. Preparation of neat complexes

2.4.1. Preparation of [Co(haacac)]

The flask containing a stirred suspension of cobalt(II) acetate tetrahydrate (4.0 g, 0.016 mol) in propanol (100 cm^3) was purged with nitrogen, and then warmed to 50 °C under a nitrogen atmosphere. bis(2-Hydroxyanil)acetylacetonone (4.53 g, 0.016 mol) was added in one portion, and the resulting black suspension was then stirred and heated under reflux under a 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(haacac)] which was purified by recrystallization from chloroform. Anal. Found (%): C, 59.96; H, 4.81; N, 8.26; Co, 17.37. Calc. for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2\text{Co}$ (%): C, 60.19; H, 4.75; N, 8.26; Co, 17.37. IR (KBr, cm^{-1}): 1612 (s), 2869 (m), 2730 (m), 1528 (m), 1171 (s), 1008 (s), 1400 (s), 769 (s).

2.4.2. Preparation of [Mn(haacac)]

The Schiff base ligand (3.0 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 red crystalline Mn(haacac) which purified by recrystallization from chloroform. Anal. Found (%): C, 60.90; H, 4.81; N, 8.35; Mn, 16.39. Calc. for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2\text{Mn}$ (%): C, 60.78; H, 4.74; N, 8.46; Mn, 16.18. IR (KBr, cm^{-1}): 1607 (s), 2866 (m), 2725 (m), 1548 (m), 1183 (s), 1028 (s), 1410 (s), 1110 (w), 771 (s).

2.4.3. Preparation of [Ni(haacac)] and [Cu(haacac)]

[Ni(haacac)] and [Cu(haacac)] were prepared similarly. H_2haacac (4.0 g, 0.014 mol) was dissolved in 100 ml of ethanol, and the solution was refluxed. To this hot solution was added metal acetate (0.014 mol) dissolved in 100 ml of ethanol. The color of the solution changed to red. Refluxing was continued for 8 h. Upon cooling the solution, a red solid crystalline was obtained which was filtered, washed with ethanol,

and dried in vacuum and purified by recrystallization from chloroform. Anal. Found (%): C, 60.22; H, 4.75; N, 8.26; Ni, 17.31. Calc. for $C_{17}H_{16}N_2O_2Ni$ (%): C, 59.91; H, 4.69; N, 8.43; Ni 17.16. IR (KBr, cm^{-1}): 1617 (s), 2870 (m), 2733 (m), 1517 (m), 1167 (s), 1004 (s), 1392 (s), 770 (w).

Anal. Found (%): C, 59.21; H, 4.57; N, 8.25; Cu, 18.35. Calc. for $C_{17}H_{16}N_2O_2Cu$ (%): C, 59.38; H, 4.69; N, 8.14; Cu, 18.48. IR (KBr, cm^{-1}): 1620 (s), 2881 (m), 2742 (m), 1503 (m), 1154 (s), 998 (s), 1387 (s), 1103 (w), 768 (w).

2.5. Preparation of $[M(\text{haacac})]-Al_2O_3$

A solution of the $[M(\text{haacac})]$ (2.0 g) in $CHCl_3$ was added to a suspension of Al_2O_3 (10.0 g) in $CHCl_3$. The resulting suspension was stirred at $50^\circ C$ under Ar atmosphere. The yellow solid was filtered, washed with $CHCl_3$. The $[M(\text{haacac})]-Al_2O_3$ catalyst was dried at $70^\circ C$ under vacuum overnight prior to use. IR (KBr, cm^{-1}) for $Mn(\text{haacac})-Al_2O_3$: 1607 (m), 2866 (m), 2725 (m), 1549 (m), 1183 (m), 1183 (m), 1029 (m), 1410 (m), 1111 (w), 771 (m); $Co(\text{haacac})-Al_2O_3$: 1613 (m), 2869 (m), 2731 (m), 1529 (w), 1171 (w), 1009 (m), 1400 (m), 769 (w); $Ni(\text{haacac})-Al_2O_3$: 1617 (m), 2871 (m), 2734 (w), 1518 (s), 1003 (m), 1392 (m), 770 (w) and $Cu(\text{haacac})-Al_2O_3$: 1621 (m), 2882 (m), 2743 (m), 1503 (m), 1154 (s), 997 (m), 1386 (m), 1103 (w), 768 (w).

2.6. Oxidation of cyclohexene: general procedure

A mixture of 1.0 g 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) was added. The resulting mixture was then refluxed for 8 h under N_2 atmosphere. After filtration and washing with solvent, the filtrate was concentrated and then subjected to GC analysis.

3. Results and discussion

3.1. Synthesis of complexes

Manganese(II), cobalt(II) and copper(II) complexes were prepared with Schiff base ligand

[bis(2-hydroxyanil)acetylacetone], “2-[[1-methyl-3-[(2-hydroxyphenyl)imino]butylidene}amino]phenol”, ($H_2\text{haacac}$). Syntheses of all the metal complexes were essentially the same and involved heating and stirring of stoichiometric amounts of the appropriate tetradentate ligand and metal acetate in a suitable solvent, such as ethanol or water–ethanol mixtures. The desired complexes crystallized upon cooling and recrystallized from chloroform. When Mn(II) and Co(II) were the metal being used, all solvents were deaerated with nitrogen and the entire procedure was carried out under an inert atmosphere. The complexes are easy to prepare and cheap. They are stable in water, even on high pH and temperature.

Elemental analyses indicate that all of the complexes are monomeric species formed by coordination of 1 mol of the metal ion and 1 mol of the Schiff base ligand. All of the metal chelates in this study are insoluble in water but soluble in most organic solvents. Electrical conductivity measurements of the metal chelates give Λ_M values of $0.5 \Omega^{-1} \text{ cm}^{-1} \text{ mol}^{-1}$ and confirm that they are non-electrolytes.

The IR spectra of complexes show a significant change in some important bands from the free Schiff base ligand. For example, the free ligand exhibits a $\nu(\text{C}=\text{N})$ stretch at 1580 cm^{-1} . In the complexes, this band shifts to lower frequency and appears at $1503\text{--}1549 \text{ cm}^{-1}$, indicating the coordination of azomethine nitrogen to the transition metal. The appearance of two or three bands in the low frequency region (between 420 and 540 cm^{-1}) indicates the coordination of phenolic oxygen in addition to azomethine nitrogen. The presence of several bands of medium intensity in $2700\text{--}2890 \text{ cm}^{-1}$ region indicate the existence of C–H group of the tetradentate Schiff base ligand. The OH stretching vibration; $\nu_{\text{O-H}}$ found as a medium band at 3270 cm^{-1} disappears in the spectra of the complexes.

Thus far, the examined data indicate that the complexes are monomeric metal chelates containing a tetradentate oxoiminato Schiff base ligand with some electron delocalization in the oxoimine rings. As the chelates are monomeric, the only possible geometries of this tetradentate chelate is square or tetrahedral, although some weak solid-state interactions between adjacent molecules of metal complex that could result in tetragonal might be anticipated. The coordination

geometry around the metal ion has been deduced from electronic spectra data.

Electronic spectral data for the $[M(\text{haacac})]$ have been measured in chloroform. The spectra are characterized by the presence of a large number of bands in the visible and ultraviolet regions. In addition, some of the complexes exhibit bands in the near infrared region. Bands at energies of approximately $20,000\text{--}35,000\text{ cm}^{-1}$ are assigned as either $M > L$, $L > M$ or ligand transitions. Spectra of the free ligand exhibit more bands in the $26,000\text{ cm}^{-1}$ region due to intraligand transitions of the $\pi > \pi^*$ type. The dissimilarity between the spectra of the free tetradentate Schiff base ligand and the metal chelate may be taken as evidence for the highly covalent character of the metal–donor bonds of the metal chelate [18].

The square planar geometry of the $[\text{Mn}(\text{haacac})]$ is strongly indicated by similarities in the visible spectra of this chelate with those of known square planar complexes containing oxygen–nitrogen donor atoms [19]. The electronic spectrum of the $[\text{Ni}(\text{haacac})]$ exhibit one band at $16,600\text{ cm}^{-1}$ 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 [20,21], which have reported values in the range of $15,000\text{--}17,850\text{ cm}^{-1}$. The spectrum of the $[\text{Cu}(\text{haacac})]$ exhibit two bands at 13,600 and 21,000, which are attributed to d–d transitions. The spectrum of this complex is similar to those reported Cu(II) for complexes [20,22]. The electronic spectrum of $[\text{Co}(\text{haacac})]$ is very similar to that reported for $[\text{Co}(\text{salen})]$. The spectrum of the $[\text{Co}(\text{haacac})]$ exhibit two bands at 10,000 and $15,000\text{--}18,000\text{ cm}^{-1}$ which are assigned to d–d transitions. In addition, a lower energy absorption at 5350 cm^{-1} has been observed such low energy bands which have recently been shown to be characteristic of square planar cobalt(II) chelates [19,23].

3.2. Heterogenisation of complexes

The heterogenization of homogenous catalysts is a field of continuing interest. Although some of homogeneous transition metal complexes exhibit remarkable catalytic properties (activities and selectivity), they are unsuitable to separate intact, from the reaction

medium making their reuse difficult and contaminating the reaction products. Thus, the heterogenization is always a toxicological and environmental challenge; moreover, it has an economical significance unless the activities of the homogeneous catalysts are exceptionally high. We have done the heterogenization by supporting the catalysts on acidic alumina. Acidic alumina was chosen because neither of neutral nor basic alumina did adsorb the complex on its surface. The adsorbing tendency of the acidic alumina might arise from the presence of OH groups on the surface which are able coordinate to the metal ion center (Scheme 2). This hypothesis was further confirmed when we observed that the complex with three bidentate ligands cannot be adsorbed on the acidic alumina surface [24].

Transition metals (Mn(II), Co(II), Ni(II), Cu(II)) contents of the alumina-supported catalysts were estimated by dissolving the known amount of the catalyst in concentrated HCl and from these solution, transition metal contents were estimated by atomic absorption spectrometer (AAS). The concentrations of metal ions were 0.012 mol g^{-1} .

The IR bands of all catalysts are weak due to their low concentration of the complex on alumina. The IR spectra of supported complexes are essentially similar to that of the neat complexes. The adsorbing tendency of the acidic alumina might arise from the presence of OH groups on the surface in order to coordinate to the metal ion center (Scheme 2).

3.3. Catalytic activity

Gemeay et al. [25] have recently reported that the silica-alumina surfaces modified with transition metal ions are easily prepared, and that the surfaces showed a significant catalytic activity toward hydrogen peroxide decomposition. The reaction rate exhibited strong dependence on the type of metal ions.

The catalytic activity of an alumina surface modified with some metal oxides was investigated [26]. The kinetics of heterogeneous decomposition of H_2O_2 by some metal complexes immobilized on alumina have been studied [27,28]. Farzaneh et al. have recently reported the activation of C–H bond with TBHP in the presence of exchanged NaY-zeolite with transition metal elements and showed that the Mn-NaY catalyzed cyclohexene oxidation with the highest

Table 1
Oxidation of cyclohexene with TBHP catalyzed by neat complexes in CH₃Cl

Catalyst	Conversion (%)	Selectivity (%)		
		Peroxide ^a	Alcohol ^b	Ketone ^c
[Mn(haacac)]-alumina	39.9	20.4	28.9	50.7
[Co(haacac)]-alumina	32.8	28.1	31.7	40.2
[Ni(haacac)]-alumina	13.6	34.9	41.6	23.5
[Cu(haacac)]-alumina	27.8	38.6	33.4	28

Conditions: cyclohexene, 10 mmol; TBHP, 16 mmol; temperature, 70 °C; neat catalyst, 0.015 g; reaction time, 8 h.

^a 1-(*tert*-Butylperoxy)-2-cyclohexene.

^b 2-Cyclohexene-1-ol.

^c 2-Cyclohexene-1-one.

reactivity and selectivity and di-(2-cyclohexenyl) ether was formed as the main product [29]. We showed that some complexes of Mn(II) included in Y-zeolite, catalyze the oxygen transfer from TBHP to cyclohexene and conclude such simple systems mimic the behavior of cytochrome P-450 type oxidation systems [30]. We also showed a rather simple catalyst system of alumina-supported manganese(II) complexes with a number of bidentate ligands of N, N; N, O and O, O atoms in the oxidation of cyclohexene [24]. 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 tetradentate Schiff base ligand (H₂haacac) supported on acidic alumina in the oxidation of cyclohexene with TBHP.

Results of Table 1 shows the catalytic activity of homogeneous catalysts. Comparing between neat and alumina-supported complexes as catalyst evidence that alumina-supported catalysts gave higher conversion of cyclohexene than their corresponding neat complexes.

The higher activity of supported complexes is because of site isolation of the complexes.

The selectivity and activity results of these alumina-supported catalysts on the oxidation of cyclohexene with TBHP are given in Tables 2–6. At the end of the reaction, the catalyst was separated by filtration, thoroughly washed with solvent and reused under similar conditions. Although the analysis of the recovered catalysts by AAS showed no reduction in the amount of metal ions, they showed a slightly lower catalytic activity (2%).

The effect of transition metal complexes supported on alumina were studied on the oxidation of cyclohexene with TBHP in dichloromethane and the results are shown in Table 2. As shown in Fig. 1, 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 MnCl₂-Al₂O₃ was 29.1% [24]. The increase of conversion from 29.1 to 77.0% compared to MnCl₂-Al₂O₃ with [Mn(haacac)]-Al₂O₃ indicates that the existence of

Table 2
Oxidation of cyclohexene with TBHP catalyzed by [M(haacac)] complexes on alumina in CH₂Cl₂

Catalyst	Conversion (%)	Selectivity (%)		
		Peroxide ^a	Alcohol ^b	Ketone ^c
[Mn(haacac)]-alumina	76.8	8.9	16.6	74.5
[Co(haacac)]-alumina	68.7	7.3	23.0	69.7
[Ni(haacac)]-alumina	43.2	12.9	28.9	58.2
[Cu(haacac)]-alumina	54.5	14.5	21.7	63.8

^a 1-(*tert*-Butylperoxy)-2-cyclohexene.

^b 2-Cyclohexene-1-ol.

^c 2-Cyclohexene-1-one.

Table 3

Oxidation of cyclohexene with TBHP catalyzed by [M(haacac)] complexes on alumina in chloroform

Catalyst	Conversion (%)	Selectivity (%)		
		Peroxide ^a	Alcohol ^b	Ketone ^c
[Mn(haacac)]-alumina	73.6	9.7	18.9	71.4
[Co(haacac)]-alumina	64.7	7.9	25.4	66.7
[Ni(haacac)]-alumina	40.1	13.1	31.7	55.2
[Cu(haacac)]-alumina	52.6	15.1	24.6	60.3

^a 1-(*tert*-Butylperoxy)-2-cyclohexene.^b 2-Cyclohexene-1-ol.^c 2-Cyclohexene-1-one.

Table 4

Oxidation of cyclohexene with TBHP catalyzed by [M(haacac)] complexes on alumina in CH₃OH

Catalyst	Conversion (%)	Selectivity (%)		
		Peroxide ^a	Alcohol ^b	Ketone ^c
[Mn(haacac)]-alumina	68.9	11.4	22.7	65.9
[Co(haacac)]-alumina	60.6	9.8	28.6	61.6
[Ni(haacac)]-alumina	39.4	17.4	35.6	47.0
[Cu(haacac)]-alumina	49.5	20.8	27.5	51.7

^a 1-(*tert*-Butylperoxy)-2-cyclohexene.^b 2-Cyclohexene-1-ol.^c 2-Cyclohexene-1-one.

Table 5

Oxidation of cyclohexene with TBHP catalyzed by [M(haacac)] complexes on alumina in CH₃CN

Catalyst	Conversion (%)	Selectivity (%)		
		Peroxide ^a	Alcohol ^b	Ketone ^c
[Mn(haacac)]-alumina	48.3	18.9	25.7	55.4
[Co(haacac)]-alumina	40.7	16.6	31.6	51.8
[Ni(haacac)]-alumina	30.6	23.2	38.4	38.4
[Cu(haacac)]-alumina	35.8	28.3	31.5	40.2

^a 1-(*tert*-Butylperoxy)-2-cyclohexene.^b 2-Cyclohexene-1-ol.^c 2-Cyclohexene-1-one.

Table 6

Oxidation of cyclohexene with TBHP catalyzed by [M(haacac)] complexes on alumina in cyclohexene

Catalyst	Conversion (%)	Selectivity (%)		
		Peroxide ^a	Alcohol ^b	Ketone ^c
[Mn(haacac)]-alumina	84.3	6.7	12.4	80.9
[Co(haacac)]-alumina	77.5	4.5	20.5	75.0
[Ni(haacac)]-alumina	50.6	9.7	26.7	63.6
[Cu(haacac)]-alumina	59.2	11.9	20.2	67.9

^a 1-(*tert*-Butylperoxy)-2-cyclohexene.^b 2-Cyclohexene-1-ol.^c 2-Cyclohexene-1-one.

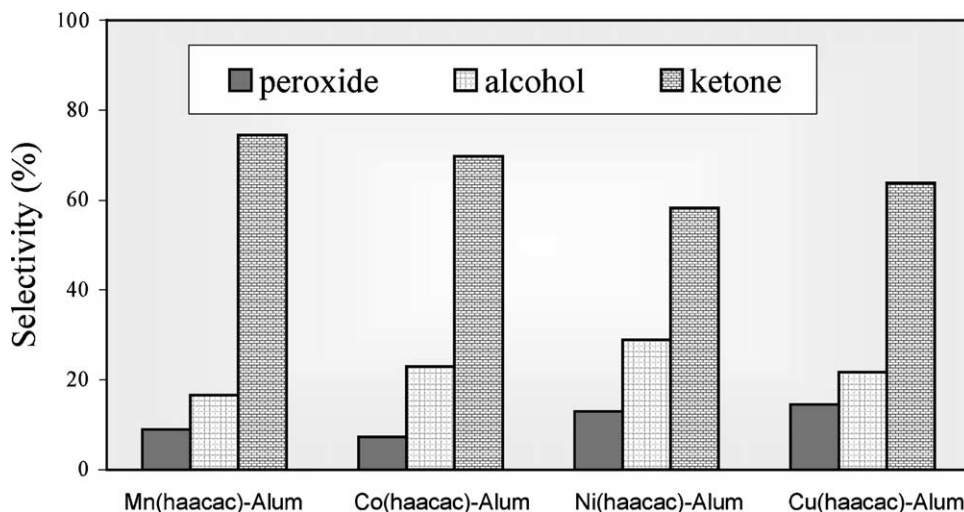


Fig. 1. Oxidation products distribution in CH₂Cl₂ with [M(haacac)]-Al₂O₃/TBHP.

ligand has increased the activity of the catalyst by a factor of 2.6. From the results indicated in Table 2, it is evident that cyclohexene-2-one is selectively formed in the presence of all catalysts.

The trend observed in Figs. 2–6 can be explained by the donor ability of ligand available in the complex catalysts. As Wang et al. have pointed out recently, the key point in the conversion of cyclohexene to the products is the reduction of L-Mn³⁺ to L-Mn²⁺. This reduction to L-Mn²⁺ is facilitated with the ligands

available around the metal cation [32]. 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 [31]. That 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

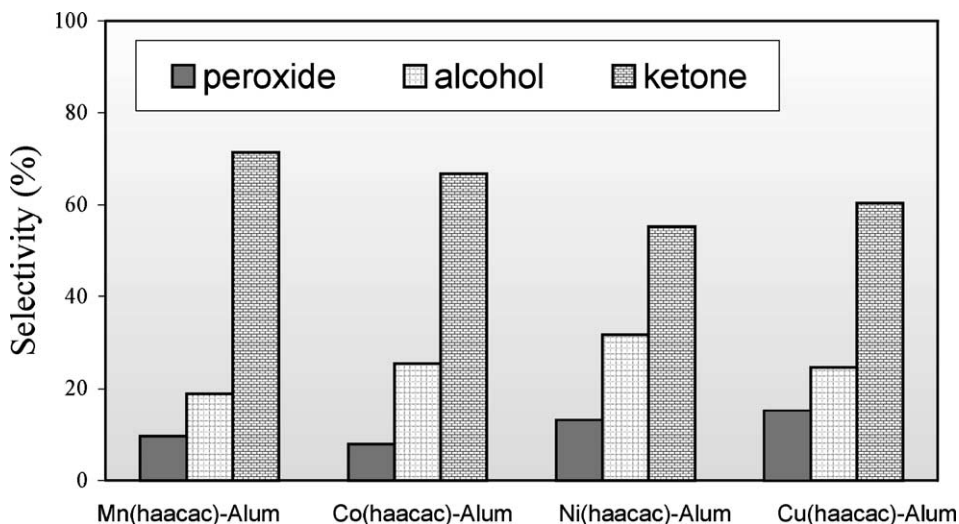


Fig. 2. Oxidation products distribution in chloroform with [M(haacac)]-Al₂O₃/TBHP.

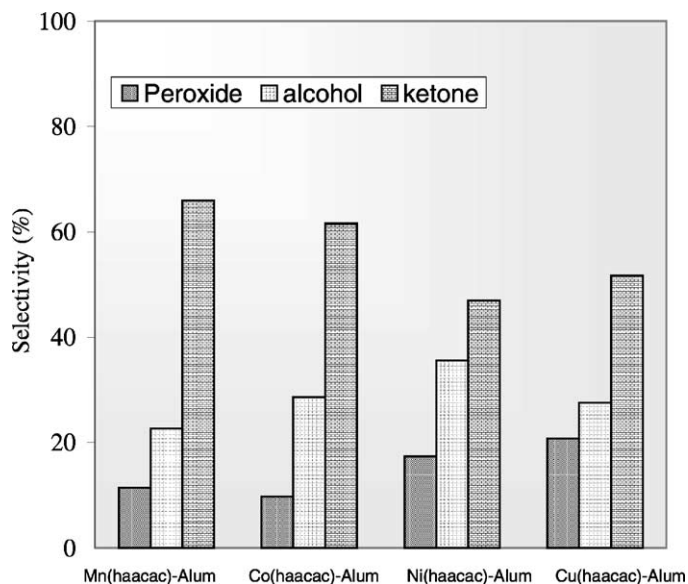


Fig. 3. Oxidation products distribution in CH₃OH with [M(haacac)]-Al₂O₃/TBHP.

been observed by us and others [24,25]. It should be emphasized that the destructive oxidation of alkenes via epoxidation pathway with H₂O₂ under the catalytic effect of alumina-supported Mn(II) complexes seem interesting [24]. Although the two systems are alike, it is the oxidant structure that has changed the fate of the reaction.

3.4. Effect of temperature

The oxidation of cyclohexene was found to be very slow at room temperature (25 °C) while the same could be completed in 8 h in refluxing dichloromethane. Best oxidation results for [M(haacac)]-Al₂O₃ are obtained in the temperature range of 70–85 °C. In some extent,

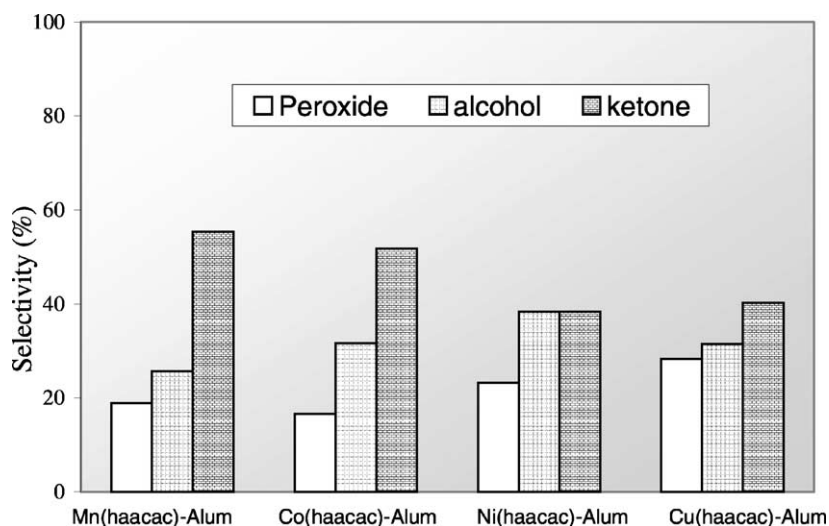


Fig. 4. Oxidation products distribution in CH₃CN with [M(haacac)]-Al₂O₃/TBHP.

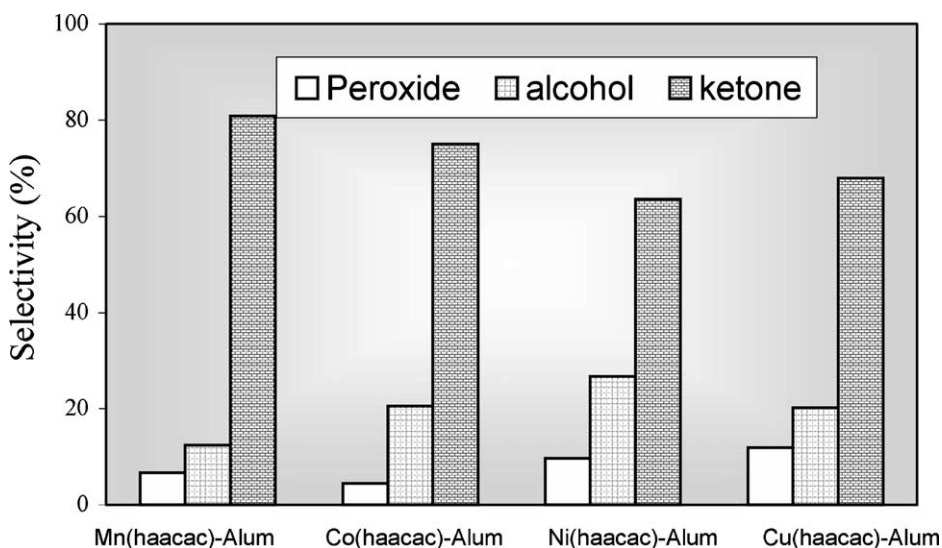


Fig. 5. Oxidation products distribution in cyclohexene with [M(haacac)]-Al₂O₃/TBHP.

the effect of temperature can be related to the solubility of the reagents. The structure of the transition metal complexes supported on alumina affects its endurance at higher temperatures. The conversion percentages for [M(haacac)]-Al₂O₃ at temperature 50, 70 and 90 °C are presented in Table 7 and Fig. 6.

3.5. Effect of solvent

The effect of various solvents for the oxidation of cyclohexene with [M(haacac)]-Al₂O₃ catalysts was

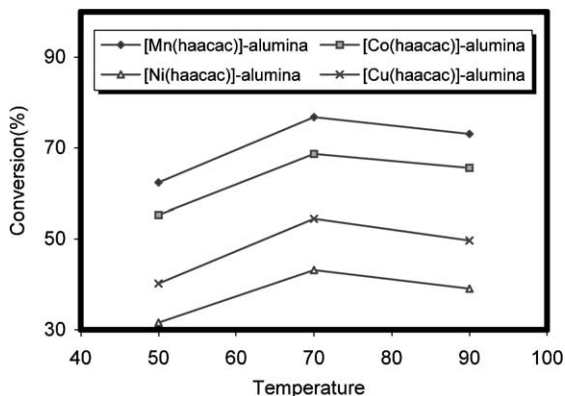


Fig. 6. The temperature needs to be over 70 °C for oxidation of cyclohexene similar behavior is observed for other catalysts as well the amount of cyclohexene in these experiments was 1.5 mmol.

also studied. The oxidation reactions were carried out in protic and aprotic solvents. The results are given in Tables 2–6. In all the oxidation reactions, 2-cyclohexene-1-one was formed as the major product. The selectivity for 2-cyclohexene-1-one formation was almost 60% while the selectivity for 2-cyclohexene-1-ol and 1-(*tert*-butylperoxy)-2-cyclohexene was less than 40%. When the reaction was carried out in a coordinating solvent like CH₃CN the conversion decreased by a factor of 1.4–2.2 (Table 5). This might be attributed to the 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

Table 7

The oxidation of cyclohexene catalyzed by [M(haacac)]-Al₂O₃ at temperatures 50, 70 and 90 °C

Catalyst	Conversion (%)		
	50 °C	70 °C	90 °C
[Mn(haacac)]-alumina	62.4	76.8	73.1
[Co(haacac)]-alumina	55.3	68.7	65.6
[Ni(haacac)]-alumina	31.6	43.2	39.1
[Cu(haacac)]-alumina	40.2	54.5	49.7

The oxidation reactions were performed in dichloromethane as oxidant. The amount of substrate and TBHP in these reactions was 1.5 mmol.

and chloroform, the yields of 2-cyclohexene-1-ol and 2-cyclohexene-1-one were higher and lower yield of the peroxy species was 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.

4. Summary and conclusions

The oxidation of cyclohexene using the haacac complexes of Mn(II), Co(II), Ni(II), Cu(II) supported on alumina has been investigated. When the oxidation is carried out using TBHP as the initiator, significant conversion (in the range of 70%) were achieved. The alumina-supported complexes did not undergo any color change during the reaction and could be easily separated and reused many times. In contrast, the neat complexes, which were active in the first cycle, were completely destroyed during the later runs and changed the color of reaction mixture. The neat complexes however, gave low conversions compared to the supported catalysts. The following points may be noted:

1. The major product of oxidation of cyclohexene in this study is 2-cyclohexene-1-one.
2. The catalysts did not undergo any color change during the reaction and could be easily separated and reused many times. In contrast, the neat complexes active in the first cycle were completely destroyed during the first run and changed color.
3. The Schiff base ligand alone in the absence of transition metals was not catalytically active.
4. The activity of cyclohexene oxidation decreases in the series: [Mn(haacac)] > [Co(haacac)] > [Cu(haacac)] > [Ni(haacac)].
5. The reactions show appreciable solvent effects and activity of oxidation decreases: CH₂Cl₂ > CHCl₃ > CH₃OH > CH₃CN.

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