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Cyclohexene oxidation with *tert*-butylhydroperoxide and hydrogen peroxide catalyzed by new square-planar manganese(II), cobalt(II), nickel(II) and copper(II) bis(2-mercaptoanil)benzil complexes supported on alumina

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Abstract

New square-planar manganese(II), copper(II), nickel(II) and cobalt(II) complexes of a tetradentate Schiff-base ligand “bis(2-mercaptoanil)benzil, H_2[mabenzil]” 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_2S_2 donors derived from the thiophenole groups and azomethine nitrogen. The formulae was found to be [M(mabenzil)] for the 1:1 non-electrolytic complexes. Alumina-supported metal complexes (ASMC; [M(mabenzil)/Al_2O_3]) catalyze the oxidation of cyclohexene with *tert*-buthylhydroperoxide (TBHP) and H_2O_2.

Keywords: Alumina; Oxidation; Cyclohexene; Schiff-base

1. Introduction

Hydrocarbon oxidation to give oxygen-containing compounds (alcohols, aldehydes, ketones, acids, etc.) is an extremely important and useful reaction in the chemical industry. Normally more than one oxygenate and all products are susceptible to complete combustion to give CO_2 [1]. The search for new selective oxidation catalysts is one of the most important current topics, connected with both industrial and academic research. In this field, the use of homogeneous catalysts has received great attention in the last few years, given that they have shown to be useful in the oxidation of olefins [2]. Despite its interest, this method of oxidation suffers from some drawbacks from a practical point of view. The low conversion, the catalyst deactivation by μ-dimerization through the formation of oxygen bridges, the high cost of the complex and the lack of recycling methods make it difficult for application of this system on a large scale. To avoid these problems, to improve the separation of the catalyst from the reaction medium and to increase its active life, various strategies can be employed. The encapsulation in zeolites [3–10], the grafting on polymers [11–14] or MCM-41 silica [15] and the immobilization in polysiloxane membranes [16] have been used as supporting methods, with moderate to excellent results. Application of alumina-supported catalysis in organic transformation has been receiving attention in recent years [17–27]. Immobilization of homogeneous transition metal catalysts to alumina carriers offers several practical benefits of heterogeneous catalysis, while retaining the advantages of homogeneous catalytic reactions [17–29]. Some of the attractive features of alumina-supported catalysis include: (1) easy separation of the catalysts from the reagents and reaction products; (2) simplification of methods to recycle expensive catalysts; (3) nonvolatile and nontoxic characteristics to high molecular weight alumina backbones; (4) minimization of certain catalyst deactivation pathways by site isolation. These attractive features of these catalysts could possibly help in developing high throughput discovery applications as well as in developing continues catalytic processes for industrial scale synthesis.

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-mercaptoanil)benzil, H_2[mabenzil]; and these complexes

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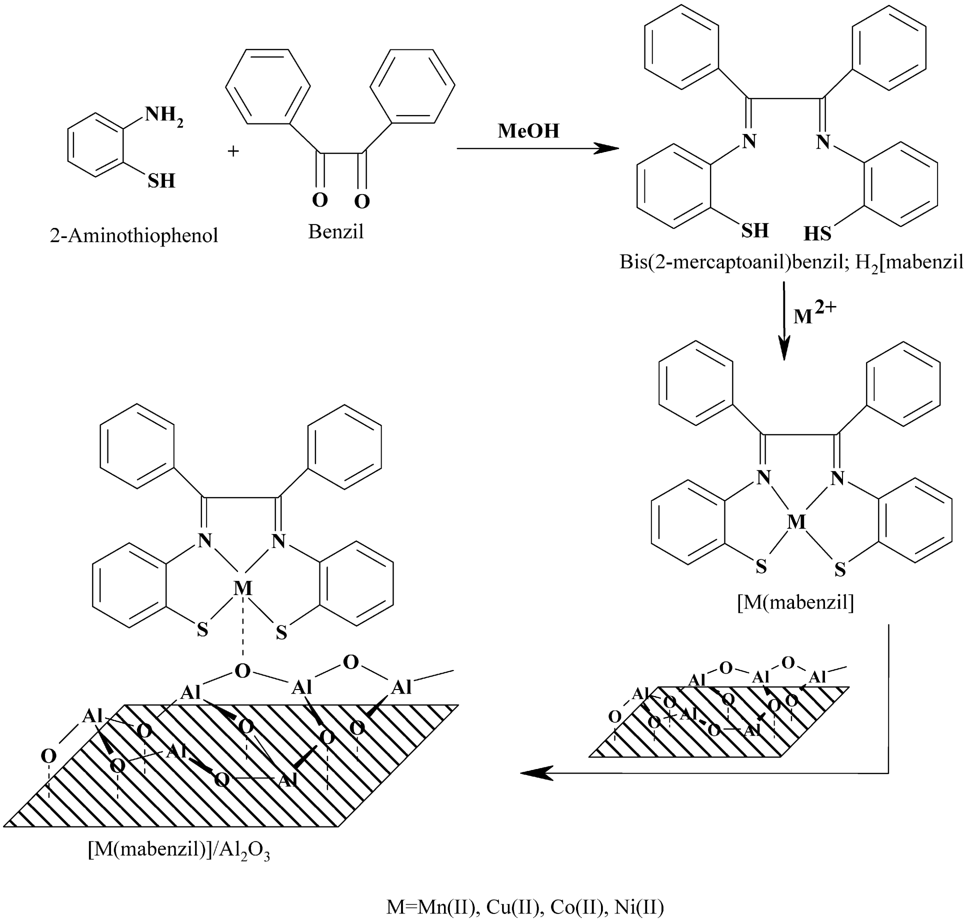

Scheme 1.

were immobilized on acidic alumina (Scheme 1); [M(mabenzil)]/Al_2O_3; and used in the oxidation of cyclohexene with *tert*-butylhydroperoxide and hydrogen peroxide as oxygen donors. The α,β-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 and physical measurements

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_2/Al_2O_3; M = Mn(II), Co(II), Ni(II), Cu(II)) was prepared according to the procedure described previously [13]. All the solvents were purchased from Merck (pro analysi) and were distilled and dried using molecular sieves (Linde 4 Å) [30]. Manganese(II) acetate, copper(II) acetate, nickel(II) acetate, cobalt(II) acetate, benzil, 2-aminothiophenol, hydrogen peroxide and *tert*-butlhydroperoxide (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.

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 $CDCl_3$ solutions and referenced to the solvent signals. XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu Kα 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.

Tetradentate Schiff-base ligand (bis(2-mercaptoanil)benzil, H_2[mabenzil]) was prepared by following the procedures reported in Ref. [31]. 2-Aminothiophenol (2.50 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 reducting 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 60%.

2.2. Preparation of [Mn(mabenzil)]

Bis(2-mercaptoanil)benzil (4.67 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(mabenzil)] which purified by recrystallization from chloroform (yield: 51%).

2.3. Preparation of [Co(mabenzil)]

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 °C under a nitrogen atmosphere. Bis(2-mercaptoanil)benzil (6.79, 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(mabenzil)] which was purified by recrystallization from chloroform (yield: 54%).

2.4. Preparation of [Ni(mabenzil)], [Cu(mabenzil)] and [Zn(mabenzil)]

[Ni(mabenzil)] (yield: 57%), [Cu(mabenzil)] (yield: 59%) and [Zn(mabenzil)] (yield: 42%) were prepared similarly. H_2[mabenzil] (5.94 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 and 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.

2.5. Preparation of alumina-supported metal complexes (ASMC)

A solution of the [M(mabenzil)] (2.0 g) in $CHCl_3$ was added to a suspension of alumina (10.0 g) in $CHCl_3$ and stirred at 50 °C under Ar atmosphere. The solid was filtered, washed with $CHCl_3$. The [M(mabenzil)]/Al_2O_3 catalyst was dried at 40 °C under vacuum overnight prior to use.

2.6. Heterogeneous oxidation of cyclohexene

A mixture of 1.02×10^{-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 *tert*-buthylhydroperoxide (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_2 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.

2.7. Homogeneous oxidation of cyclohexene

Neat metal complex (1.02×10^{-5} mol) in dichloromethane (10 ml), TBHP (2 ml) was added to a solution of cyclohexene (1 ml). The resulting mixture was then refluxed for 8 h under N_2 atmosphere, the solvent was 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

3.1. Synthesis and characterization

Synthesis of the metal complexes was essentially the same and involved heating and stirring of stoichiometric amounts of H_2[mabenzil] 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 [mabenzil]. 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 Λ_M values of 12–25 Ω^{-1} cm^2 mol^{-1} and confirm that they are non-electrolytes.

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 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 and carbon to nitrogen have been provided to ensure the immobilization of complex on the alumina.

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 oxygen groups on the surface in order to coordinate to the metal ion center (Scheme 1). Electronic spectral data for the neat complexes have been measured in chloroform (Table 1). The square-planar geometry of the [M(mabenzil)] is strongly indicated by similarities in the visible spectra of this chelate with known square-planar complexes containing sulfur–nitrogen donor atoms [31–41].

The X-ray diffractograms of Al_2O_3, $NiCl_2/Al_2O_3$ and [Ni(mabenzil)]/Al_2O_3 were recorded to study their crystallinity and to ensure supporting. After careful comparison of XRD patterns of Al_2O_3 and $NiCl_2/Al_2O_3$, it was observed that there is one new peak with a *d* value of 17.29 Å in $NiCl_2/Al_2O_3$. This peak was also observed in [Ni(mabenzil)]/Al_2O_3 and [Ni(mabenzil)] at the same position. In addition, the [Ni(mabenzil)]/Al_2O_3 exhibits one new signal with value of 82.68 Å, which is a part of the ligand as this signal was also observed in [Ni(mabenzil)] but not observed in Al_2O_3 or $NiCl_2/Al_2O_3$. This information clearly indicates the support of [Ni(mabenzil)] 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 ^{1}H NMR spectral data of the H_2[mabenzil] and the neat diamagnetic [Zn(mabenzil)] and [Ni(mabenzil)]) complexes recorded in DMSO-d_6 further supplements the conclusion drawn from IR data. The ^{1}H NMR spectrum of H_2[mabenzil] exhibits the following signals: 12.70 (s, 2H, SH), 6.75–7.10 (m, 10H, C_6H_5) and 7.20–7.35 (m, 8H, C_6H_4). The disappearance of thiophenolic signal and down field shift (7.70 ppm) of C_6H_4 signal indicates of the coordination of thiophenole groups after deportation and azomethine nitrogen atoms. ^{1}H NMR spectrum of other neat complexes could not be recorded due to its partial paramagnetic nature of complex as noticed earlier [33,35].

3.2. *Catalytic activity*

The selectivity and activity results of alumina-supported and homogeneous catalysts on the oxidation of cyclohexene with TBHP have been given in Table 2. 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 the oxidation of cyclohexene with TBHP in dichloromethane and the results have been shown in Table 2. As shown in Table 2, 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 $MnCl_2/Al_2O_3$ was 29.4% [42]. The increase of conversion from 29.4 to 87.6% compared to

Table 1
Chemical composition, DRS absorption, UV–vis and IR stretching frequencies of neat and alumina-supported transition metal complexes

Sample	C (%)	H (%)	N (%)	M (%)	C/N	$\upsilon_{C=N}$[a] (cm^{-1})	d ↔ d (nm)	μ_{eff} (MB)	Λ_M[b] (Ω^{-1} cm^2 mol^{-1})
H_2[mabenzil]	73.55 (73.40)	4.75 (4.61)	6.59 (6.70)	–	11.16 (10.96)	1627	–	–	–
[Mn(mabenzil)]	65.43 (65.32)	3.77 (3.61)	5.87 (5.96)	11.51 (11.38)	11.15 (10.96)	1622	–	5.91	10
[Mn(mabenzil)]/Al_2O_3	6.65	1.48	0.61	1.20	10.90	1617	–	–	–
[Co(mabenzil)]	64.88 (64.73)	3.74 (3.60)	5.82 (5.93)	12.24 (12.10)	11.15 (10.92)	1618	425	1.73	17
[Co(mabenzil)]/Al_2O_3	6.61	1.47	0.60	1.18	10.81	1615	423	–	–
[Ni(mabenzil)]	64.91 (64.70)	3.74 (3.61)	5.82 (5.97)	12.20 (12.03)	11.15 (10.84)	1616	476	−0.016	16
[Ni(mabenzil)]/Al_2O_3	6.53	1.46	0.60	1.17	10.74	1610	474	–	–
[Cu(mabenzil)]	64.26 (64.1)	3.70 (3.63)	5.76 (5.90)	13.20 (13.08)	11.16 (10.87)	1615	485	1.74	20
[Cu(mabenzil)]/Al_2O_3	6.50	1.47	0.60	1.20	10.84	1612	482	–	–
[Zn(mabenzil)]	64.02 (63.88)	3.69 (3.58)	5.74 (5.86)	13.14 (13.01)	11.15 (10.90)	1610	–	–	18

Estimated values are given in parentheses.

[a] Infrared spectra measured as KBr pellets.

[b] In chloroform solutions at 25 °C as never specified for neat complexes.

Table 2
Effect of various solvents, catalyst weight, percent selectivity of 2-cyclohexene-1-one, 2-cyclohexene-1-ol and 1-(*tert*-butylperoxy)-2-cyclohexene formation and percent conversion of cyclohexene oxidation (solvent = 10 ml; duration = 8 h, at reflux; cyclohexene = 1 ml, TBHP = 2 ml)

Entry	Catalyst	Amount of catalyst (mol)	Solvent	Conversion (%)	Selectivity (%)		
					Ketone[a]	Alcohol[b]	Peroxide[c]
1	[Mn(mabenzil)]	1.02×10^{-5}	CH_2Cl_2	92.8	63.2	19.1	17.7
2	[Mn(mabenzil)]	0.50×10^{-5}	CH_2Cl_2	67.5	58.5	24.2	17.3
3	[Mn(mabenzil)]	2.04×10^{-5}	CH_2Cl_2	86.3	66.7	20.6	12.7
4	[Mn(mabenzil)]	4.08×10^{-5}	CH_2Cl_2	40.7	69.1	19.7	11.2
5	[Co(mabenzil)]	1.02×10^{-5}	CH_2Cl_2	83.5	53.6	26.5	19.9
6	[Ni(mabenzil)]	1.02×10^{-5}	CH_2Cl_2	52.7	36.1	37.6	26.3
7	[Cu(mabenzil)]	1.02×10^{-5}	CH_2Cl_2	63.9	40.2	28.9	30.9
8	[Mn(mabenzil)]/Al_2O_3	1.02×10^{-5}	CH_2Cl_2	87.6	85.3	10.5	4.2
9	[Mn(mabenzil)]/Al_2O_3[d]	1.02×10^{-5}	CH_2Cl_2	85.3	84.5	11.6	3.9
10	[Mn(mabenzil)]/Al_2O_3[e]	1.02×10^{-5}	CH_2Cl_2	84.1	81.7	13.0	5.3
11	[Mn(mabenzil)]/Al_2O_3[f]	1.02×10^{-5}	CH_2Cl_2	83.5	80.3	14.6	5.1
12	[Mn(mabenzil)]/Al_2O_3	0.50×10^{-5}	CH_2Cl_2	63.5	71.7	22.9	5.4
13	[Mn(mabenzil)]/Al_2O_3	2.04×10^{-5}	CH_2Cl_2	89.4	87.1	9.6	3.3
14	[Mn(mabenzil)]/Al_2O_3	4.08×10^{-5}	CH_2Cl_2	91.3	87.6	10.6	1.8
15	[Co(mabenzil)]/Al_2O_3	1.02×10^{-5}	CH_2Cl_2	76.4	78.3	18.0	3.7
16	[Ni(mabenzil)]/Al_2O_3	1.02×10^{-5}	CH_2Cl_2	45.7	68.5	23.1	8.4
17	[Cu(mabenzil)]/Al_2O_3	1.02×10^{-5}	CH_2Cl_2	57.3	72.6	18.2	9.2
18	[Mn(mabenzil)]/Al_2O_3	1.02×10^{-5}	CH_3Cl	82.6	81.3	13.4	5.3
19	[Co(mabenzil)]/Al_2O_3	1.02×10^{-5}	CH_3Cl	74.5	76.2	19.2	4.6
20	[Ni(mabenzil)]/Al_2O_3	1.02×10^{-5}	CH_3Cl	45.7	65.6	24.7	9.7
21	[Cu(mabenzil)]/Al_2O_3	1.02×10^{-5}	CH_3Cl	56.4	69.5	20.1	10.4
22	[Mn(mabenzil)]/Al_2O_3	1.02×10^{-5}	CH_3OH	75.6	71.8	17.5	10.7
23	[Co(mabenzil)]/Al_2O_3	1.02×10^{-5}	CH_3OH	70.2	66.4	24.0	9.6
24	[Ni(mabenzil)]/Al_2O_3	1.02×10^{-5}	CH_3OH	40.4	57.5	28.2	14.3
25	[Cu(mabenzil)]/Al_2O_3	1.02×10^{-5}	CH_3OH	49.9	58.3	24.5	17.2
26	[Mn(mabenzil)]/Al_2O_3	1.02×10^{-5}	CH_3CN	53.4	68.5	19.3	12.2
27	[Co(mabenzil)]/Al_2O_3	1.02×10^{-5}	CH_3CN	48.1	62.3	26.0	11.7
28	[Ni(mabenzil)]/Al_2O_3	1.02×10^{-5}	CH_3CN	25.2	54.1	29.2	16.7
29	[Cu(mabenzil)]/Al_2O_3	1.02×10^{-5}	CH_3CN	27.4	53.2	28.3	18.5

[a] 2-cyclohexene-1-one.
[b] 2-cyclohexene-1-ol.
[c] 1-(*tert*-butylperoxy)-2-cyclohexene.
[d] First reuse.
[e] Second reuse.
[f] Third reuse.

$MnCl_2/Al_2O_3$ with [Mn(mabenzil)]/Al_2O_3 indicates that the existence of ligand has increased the activity of the catalyst by a factor of 2.98. From the indicated results in Table 2 it is evident that cyclohexene-2-one is selectively formed in the presence of all catalysts.

The trend observed in Table 2 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-Mn^{3+} to L-Mn^{2+}. This reduction to L-Mn^{2+} is facilitated with the ligands available around the metal cation [43]. 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-(*tret*-butylperoxy)-2-cyclohexene shows the presence of radical reactions [44]. 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 [45,47–52]. It should be emphasized that the destructive oxidation of alkenes via epoxidation pathway with H_2O_2 under the catalytic effect of alumina-supported Mn(II) complexes seem interesting [47–52]. 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. 1), 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_2O_2 and TBHP oxidize cyclohexene in the presence of alumina-supported metal complexes, but only H_2O_2 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

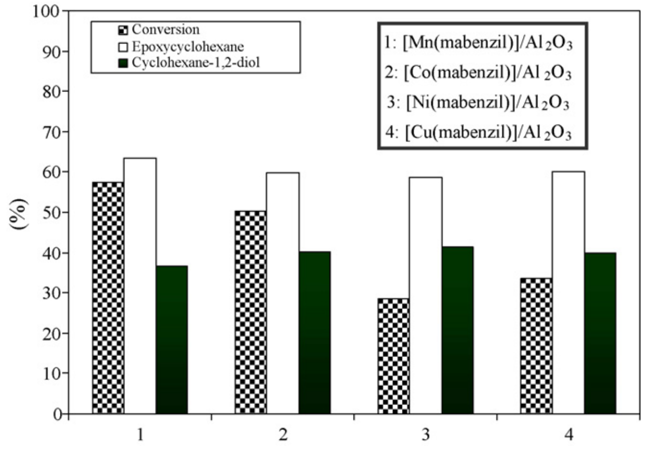

Fig. 1. Oxidation products distribution in acetonitrile with [M(mabenzil)]/Al_2O_3/H_2O_2.

to have a higher activation energy for O–O bond cleavage than a TBOO complex and therefore, to have a longer lifetime [46].

The effect of various solvents for the oxidation of cyclohexene with [Mn(mabenzil)]/Al_2O_3 catalysts was also studied (Fig. 2). The oxidation reactions were carried out in protic and aprotic solvents. The results have been given in Table 2 and Fig. 2. 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_3CN the conversion decreased by a factor of ∼1.56 (Table 2). 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-o1 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.

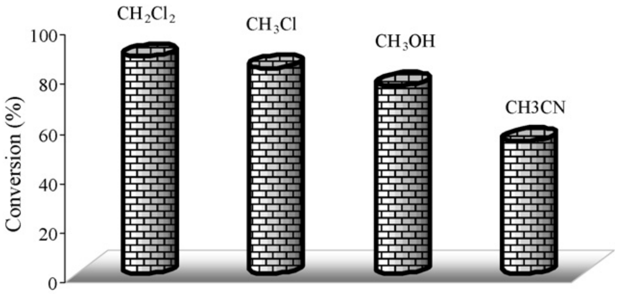

Fig. 2. Oxidation of cyclohexene with TBHP in various solvent with [Mn(mabenzil)]-Al_2O_3.

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 AAS showed no reduction in the amount of transition metal ions, they showed a slightly lower catalytic activity (∼2%) (Table 2). The results indicate that [Mn(mabenzil)]/Al_2O_3 are almost stable to be recycled for the oxidation of cyclohexene without much loss in activity (Table 2). 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 mabenzil after the oxidation reactions.

The results clearly suggest that [Mn(mabenzil)]/Al_2O_3 efficiently catalyzes conversion of cyclohexene to 2-cyclohexene-1-one with 85.3% selectivity and conversion 87.6%. The more activity of mabenzil 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. All conversion efficiency with high selectivity obtained in this study is significantly higher than that obtained using manganese(II) complexes supported on alumina (Table 3).

Table 3
Oxidation of cyclohexene catalyzed by alumina-supported metal complexes in CH_2Cl_2 with TBHP

Catalyst	Conversion (%)	Selectivity (%)			Ref.
		Ketone[a]	Alcohol[b]	Peroxide[c]	
$MnCl_2/Al_2O_3$	29.4	52.3	39.6	8.1	[42]
$[Mn(acac)_2]/Al_2O_3$	44.3	48.6	28.2	23.2	[42]
$[Mn(en)_2]/Al_2O_3$	52.1	56.1	26.5	17.4	[42]
$[Mn(salen)]/Al_2O_3$	65.8	71.6	18.6	9.8	[42]
$[Mn(bpy)_2]/Al_2O_3$	73.4	75.4	17.4	7.2	[42]
$[Mn(haacac)]/Al_2O_3$	76.8	74.5	16.6	8.9	[51]
$[Mn(Me_2salpnMe_2)]/Al_2O_3$	82.8	80.5	14.2	5.3	[49]
$[Mn(salpnMe_2)]/Al_2O_3$	78.4	77.2	16.5	6.3	[53]
$[Mn(habenzil)]/Al_2O_3$	84.5	83.2	13.1	3.7	[52]
$[M(mabenzil)/Al_2O_3$	87.6	85.3	10.5	4.2	This work

acac = acetylacetonato. en = ethylenediamine. salen = *N*,*N*-bis(salicylidene)ethylene-1,2-diamine. bpy = 2,2-bipyridine. haacac = bis(2-hydroxyanil)acetylacetone. $Me_2salpnMe_2$ = *N*,*N*′-bis-(α-methylsalicylidene)-2,2-dimethylpropane-1,3-diamine. $salpnMe_2$ = *N*,*N*′-bis(salicylidene)-2,2-dimethylpropane-1,3-diamine. habenzil = bis(2-hydroxyanil)benzil.

[a] 2-cyclohexene-1-one.

[b] 2-cyclohexene-1-ol.

[c] 1-(*tert*-butylperoxy)-2-cyclohexene.

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 "bis(2-mercaptoanil)benzil, H_2[mabenzil]" in the oxidation of cyclohexene. Oxidation of allylic site and double bond were resulted with the oxidants of TBHP and H_2O_2, respectively. Oxidation of cyclohexene with TBHP gave 2-cyclohexene-1-one, 2-cyclohexene-2-ol and 1-(*tert*-butylperoxy)-2-cyclohexene whereas, oxidation with H_2O_2 resulted in the formation of cyclohexene oxide and cyclohexene-1,2-diol. The high percentage yield of reactions especially in the presence of alumina-supported manganese(II) complex seems promising. The prepared catalysts are also highly stable and reusable, as varied by the unchanged activity within three successive reaction runs and no further increase in the cyclohexene conversion with increasing reaction time after removing the catalyst. The activity of cyclohexene oxidation decreases in the series [Mn (mabenzil)]/Al_2O_3 > [Co(mabenzil)]/Al_2O_3 > [Cu(mabenzil)]/ Al_2O_3 > [Ni(mabenzil)]/Al_2O_3. The efficiency of the catalysts for cyclohexene oxidation in different solvents decreases in the order: $CH_2Cl_2 > CH_3Cl > MeOH > MeCN$. Studies on other olefins are currently under investigation in our laboratory and we believe that the observation of similar results on other olefins is not unexpected.

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