The oxyfunctionalization of cyclohexane catalyzed by Mn(II) complexes included in zeolite Y

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Abstract

The oxygen transfer from *tert*-butylhydroperoxide (TBHP) to cyclohexane and the formation of cyclohexanol and cyclohexanone is catalyzed by Cr(III), Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) exchanged with zeolite Y. This oxidation was successfully achieved on complex Mn(II) with ligands of 2,2′-bipyridine, ethylenediamine, tetramethylethylenediamine, and tetramethyl 1,8-naphtalenediamine included in zeolite Y. The enhancement of the conversion percentage from 2.4% to 60% shows that the transition metal complex immobilized on zeolite Y represent a good cytochrome *P*-450 type oxidation system. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Oxyfunctionalization; Zeolite Y; Mn complexes; Cyclohexane

1. Introduction

Catalytic oxidation of C–H bonds in saturated hydrocarbons under mild conditions is a key step in the functionalization of many organic compounds and continues to be an important challenge for chemists [1–4]. The ability of cytochrome *P*-450 to activate dioxygen with resultant oxygen transfer to otherwise relatively unreactive organic substrates has prompted chemists to mimic such remarkable catalyst [5]. It is well known that transition metal porphyrins and phthalocyanines are potential catalysts which control the fate of formed radicals or prevent their formation during the oxidation of C–H bonds and many authors have tried to make a surrogate of the active entity of cytochrome *P*-450 [6,7]. There have been several reports concerning the immobilization of these complexes on microporous solids such as zeolite Y to prevent rapid deactivation and poor selectivity [8–10].

Following our research on zeolites and their applications in organic chemistry [11–13], it was interesting for us to use simple catalyst systems in the oxidation of olefins [14]. In this paper, we report the role of some transition metals and complexes of Mn(II) included in

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Table 1
Oxidation of cyclohexane with TBHP in the presence of MY[a]

Catalyst	Conversion (%)	Alcohol (%)	Ketone (%)
NaY	–	–	–
CrY	9.2	34.5	65.5
MnY	2.4	45.5	54.5
FeY	1.5	33.3	66.7
CoY	4.0	50.0	50.0
NiY	0.6	–	100
CuY	3.0	66.5	33.5

[a] Conditions: cyclohexane = 30 mmol, TBHP = 12 mmol, catalyst = 1 g.

zeolite Y as catalysts in the oxidation of cyclohexane.

2. Experimental

2.1. Materials

All the materials were of commercial reagent grade. The solvents were distilled before using. *tert*-Butylhydroperoxide (TBHP; 70% in water) was purchased from Merck and extraction to the organic phase (methylene chloride) was carried out according to the standard procedure [15].

2.2. Preparation of zeolite catalysts

2.2.1. Preparation of MY catalysts
These catalysts were prepared and activated according to the procedure described previously [12]. The concentration determination of filtrate solution showed that about 1 mmol of the ion per each gram of zeolite has been exchanged.

Table 2
Effect of the amount of CrY and substrate to oxidant ratio on the oxidation of cyclohexane

Catalyst (g)	Substrate/ oxidant	Conversion (%)	Alcohol (%)	Ketone (%)
0.5	2.5[a]	5.2	45.6	54.4
1.0	2.5	9.2	34.5	65.5
1.5	2.5	3.1	45.7	54.3
1.0	1.25[b]	7.4	32.5	67.5
1.0	5.0[c]	14.8	36.0	64.0

[a] Conditions: cyclohexane = 30 mmol, TBHP = 12 mmol.
[b] Conditions: cyclohexane = 15 mmol, TBHP = 12 mmol.
[c] Conditions: cyclohexane = 60 mmol, TBHP = 12 mmol.

Table 3
Effect of solvent on the oxidation of cyclohexane in the presence of CrY[a]

Solvent	Conversion (%)	Alcohol (%)	Ketone (%)
Chloroform	2.6	66.7	33.3
Dichloromethane	9.2	34.5	65.5
Acetone	3.4	36.6	55.4
N,N-dimethylformamide	–	–	–
Acetonitrile	9.4	32.9	67.1

[a] Conditions: cyclohexane = 30 mmol, TBHP = 12 mmol, catalyst = 1 g.

2.2.2. Preparation of Mn(II) complexes included in zeolite Y; general procedure
The procedure described by Peter-Paul et al. [16] was followed. One gram of active MnY zeolite was ground (or mixed in the case of liquid ligands) with 1.25 mmol of ligand. The mixture was then heated at 90°C in an autoclave saturated with nitrogen gas for 24 h. The catalyst was then cooled and Soxhelt extracted with CH_2Cl_2 to remove the unreacted ligands.

2.3. Oxidation of cyclohexanone; general procedure

A mixture of 1 g zeolite, 10 ml CH_2Cl_2 and 30 mmol cyclohexane was stirred under nitrogen in a 100-ml round bottom flask equipped with a condenser and a dropping funnel at 40°C for 30 min. Then, 12 mmol of TBHP solution in CH_2Cl_2 was added over a period of 5 h and stirred continuously for three additional hours.

Table 4
Oxidation of cyclohexane with TBHP in the presence of Mn complexes included in zeolite Y[a]

Catalyst	Conversion (%)	Alcohol (%)	Ketone (%)	Peroxide (%)
MnY	2.4	45.5	54.5	–
$Mn(bpy)_2^{2+}$–Y	30.8	41.8	43.8	14.4
$Mn(etda)_2^{2+}$–Y	24.5	51.0	32.6	16.4
$Mn(tmetda)_2^{2+}$–Y	28.3	45.2	38.5	16.3
$Mn(tmnda)_2^{2+}$–Y	10.2	56.5	43.5	–

[a] Conditions: cyclohexane = 60 mmol, TBHP = 12 mmol, catalyst = 1 g.

After filtration and washing with solvent, the filtrate was concentrated on a rotary evaporator and then subjected to GC analysis using a Philips Pu-4400 chromatograph (1.5 m, 3% OV-17 column).

3. Results

3.1. MY catalytic oxidation of cyclohexane

Oxidation of cyclohexane with TBHP under the catalytic effect of MY yielded cyclohexanol and cyclohexanone as shown in Table 1.

3.2. The effects of changes in the amount of CrY and substrate to oxidant ratio

The effect of the amount of CrY and substrate to oxidant ratio is shown in Table 2.

3.3. The effect of solvent

The effect of solvent on the oxidation of cyclohexane with TBHP in the presence of CrY is provided in Table 3.

3.4. Zeolite included Mn complex catalytic oxidation of cyclohexane

Oxidation of cyclohexane with TBHP in the presence of zeolite included Mn complex catalysts resulted in the formation of cyclohexanol, cyclohexanone and cyclohexane-*tert*-butyl-peroxide (Table 4).

3.5. The effect of changes in the amount of substrate to oxidant in the presence of $Mn(bip)_2^{2+}$–Y catalyst

The effect of the amount of substrate to oxidant ratio is shown in Table 5.

4. Discussion

On the basis of the results listed in Table 1, it can be seen that MY exhibits catalytic activity in the oxidation of cyclohexane. According to Fig. 1, CrY shows the highest activity on the oxidation path. As shown in Table 1, with the exception of CuY, all catalysts show selectivity toward the formation of cyclohexanone. Since CrY showed the highest conversion percentage of cyclohexane, the amount of catalyst, the substrate to oxidant ratio and the role of solvent on oxidation with this catalyst was investigated. As can be seen from Table 2, the maximum conversion percentage of cyclohexane is obtained by using 1 g of catalyst per 30 mmol of substrate. Increasing or decreasing the catalyst concentration strongly decreases the conversion yield, while increasing the substrate to oxidant ratio increases it.

The results obtained through the investigation of the role of solvent on the reactivity of oxidation is shown in Table 3. These results are interesting and might be helpful in understanding the reaction mechanism.

Although the oxidation in acetonitrile and methylene chloride take place with similar reactivity, cyclohexane does not undergo oxidation in dimethylformamide at all. These results clearly indicate that the dielectric constant (ε)

Table 5
Effect of substrate to oxidant ratio in the presence of $Mn(bpy)_2^{2+}$–Y on the oxidation of cyclohexane

Substrate/oxidant	Conversion (%)	Alcohol (%)	Ketone (%)	Peroxide (%)
0.25[a]	5.5	45	45	10
1.25[b]	8.4	39.5	60.5	–
2.5[c]	12.4	39.5	60. 5	–
5[d]	30.8	41.8	43.6	14.6
10[e]	10.6	50	26	24
6.25[f]	60.4	29.5	56.5	14
12.5[g]	40.5	38	52	10

[a] Conditions: cyclohexane = 10 mmol, TBHP = 40 mmol, catalyst = 1 g.
[b] Conditions: cyclohexane = 15 mmol, TBHP = 12 mmol, catalyst = 1 g.
[c] Conditions: cyclohexane = 15 mmol, TBHP = 6 mmol, catalyst = 1 g.
[d] Conditions: cyclohexane = 60 mmol, TBHP = 12 mmol, catalyst = 1 g.
[e] Conditions: cyclohexane = 60 mmol, TBHP = 6 mmol, catalyst = 1 g.
[f] Conditions: cyclohexane = 75 mmol, TBHP = 12 mmol, catalyst = 1 g, no solvent is used.
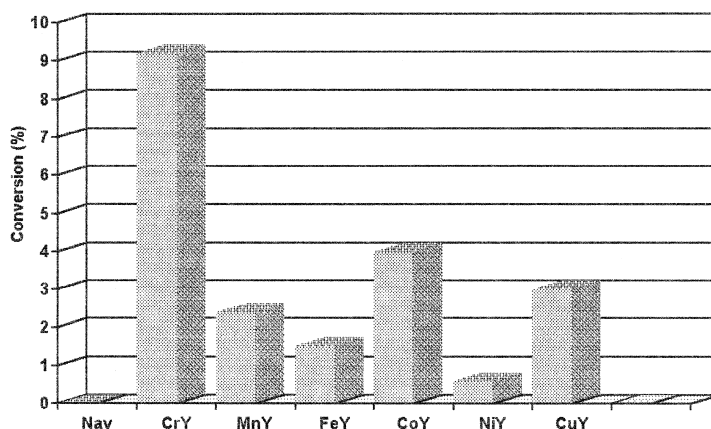[g] Conditions: cyclohexane = 75 mmol, TBHP = 6 mmol, catalyst = 1 g, no solvent is used.

Fig. 1. Oxidation of cyclohexane with TBHP in the presence of zeolite Y exchanged with transition metal ions.

of solvents cannot be considered to be the main factor in oxidation reactivity. We believe that successful attempts to account for the reactivity trend might be made on the basis of the dielectric constant and donor number (DN) of solvent. While the former is a measure of polarity, the latter characterizes the solvent's ability to donate electron density to electron-deficient centers [17]. Therefore, a solvent like dimethylformamide which has the highest dielectric constant of the selected solvents ($\varepsilon = 36.7$) is not a suitable medium for oxidation. Its polarity character is strongly offset by it's high tendency (DN = 26.6) toward the formation of a complex with metal and therefore retards the formation rate of oxometal complexes as the active oxidation species. On the other hand, acetonitrile is a polar solvent ($\varepsilon = 37.5$) and its ability to solvate the polar oxometal intermediates is partly offset by its medium DN (DN = 14.1). Therefore, the oxidation rate is similar in acetonitrile and methylene chloride although the latter is a poor polar solvent ($\varepsilon = 8–9$). This similarity can be attributed to the fact that methylene chloride does not have a tendency to complex with the central metal. Therefore, the oxidant–metal complex can be rapidly formed.

The oxygen transfer from TBHP to cyclohexane in the presence of a metal catalyst included in zeolite seems likely to follow the Haber–Weiss mechanism in which metal ions undergo one-electron oxidation and reduction [18]. Reactions mechanistic studies have shown that the metal–*t*-butylperoxo complex is the active species in the oxidation of cyclohexane to cyclohexanol and cyclohexanone in the homogenous systems [19]. On the basis of results obtained using the commercially available catalyst Co(II) octoate, a radical pathway with the formation of alkoxyl and peroxyl free radicals finds support [20]. Recent radical initiating and scavenging results on the oxidation of cyclohexane with TBHP in the presence of zeolite-encapsulated perfluorinated ruthenium phthalocyanines suggest a radical mechanism [21]. Although Ganeshpure et al. [22] suggest a nonradical pathway for the oxyfunctionalization of cyclohexane with TBHP catalyzed by manganese(II) N, N'-ethylene bis (salicylideneaminato), they emphasize that the possibility of a free radical pathway operating simultaneously cannot be ruled out.

Synthesis of porphyrin, phthalocyanine and Schiff-base models of enzyme active sites, especially for monooxygenase enzymes of the cytochrome *P*-450 family has been the subject of many research to mimic enzymatic systems [23–25]. On the basis of experimental results obtained on the studies of selectivity and stability in both the synthetic models and natural systems in the case of biomimetic oxidation of hydrocarbons, it can be concluded that selectiv-

ity arises from the steric effects imposed by the environment of the enzyme active site upon substrate approach. Therefore, the replacement of the protein portion of natural enzymes by a size- and shape-selective framework of a mineral matrix such as clays and zeolites has been developed during the last few years. These materials will provide the best arrangement for the catalytically active centers and will direct the substrate towards these centers [5].

Since our model system of MY showed some catalytic activity on the oxidation of cyclohexane with TBHP, we decided to investigate this oxidation reaction in the presence of a zeolite catalyst which is prepared by inclusion of a transition metal complex within its supercages. Such system with efficient activity could provide a rather simple model of biomimetic oxidation of hydrocarbons. In the first step we concentrated our studies on the Mn complexes since this metal has the central role in the photosynthetic oxidation of water to dioxygen.

Synthesis of complexes of manganese(II) with bipyridine(bpy), ethylenediamine (etda), tetramethylethylenediamine (tmetda), and tetramethyl 1,8-naphtalenediamine(tmnda) were carried out according to the procedure described by Peter-Paul et al. [16]. Since the authors have characterized the structure of manganese(II) bipyridine as $Mn(bpy)_2^{2+}$–Y on the basis of thermo-gravimetric and chemical analysis informations, we assigned the structures as $Mn(bpy)_2^{2+}$–Y, $Mn(etda)_2^{2+}$–Y, $Mn(tmetda)_2^{2+}$–Y and $Mn(tmnda)_2^{2+}$–Y, respectively.

The intrazeolite complexes were found to be catalysts for the oxidation of cyclohexane to cyclohexanol and cyclohexanone as the main products using TBHP as the oxidant (Table 4). As seen in Table 4, cyclohexane-*tert*-butylproxide was obtained as the minor product. Since the amount of substrate was found to significantly affect the conversion percentage of cyclohexane, we used 60 mmol of hydrocarbon in the model reaction. As is shown in Fig. 2, the catalytic activity of intrazeolite complexes were found to decrease in the order of $Mn(bpy)_2^{2+}$–Y > $Mn(tmetda)_2^{2+}$–Y > $Mn(etda)_2^{2+}$–Y > $Mn(tmnda)_2^{2+}$–Y. the activity of MnY catalyst has also been included in Table 4 and Fig. 2 in order to compare the effect of the ligand on the activity of catalyst. What is found is that the existence of ligand and especially bipyridine is very reluctant to intensify the oxygen transfer with increasing the conversion percentage from 2.4% to 30.8%. This may be accounted for by the fact that electron transfer from Mn(II) complex included in Y zeolite to TBHP take places faster than MnY catalyst. In other words, ligand would either increase the electron transfer step or stabilize the oxidized metal formed during the formation of metal–peroxide complex as is described in the Haber–Weiss mechanism. That
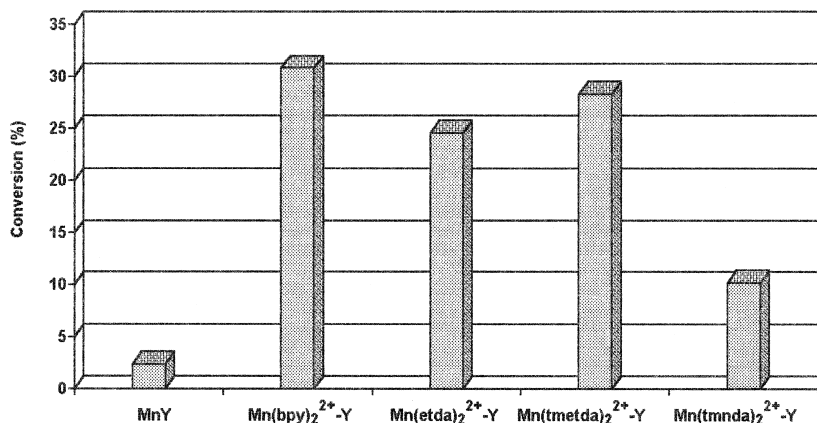

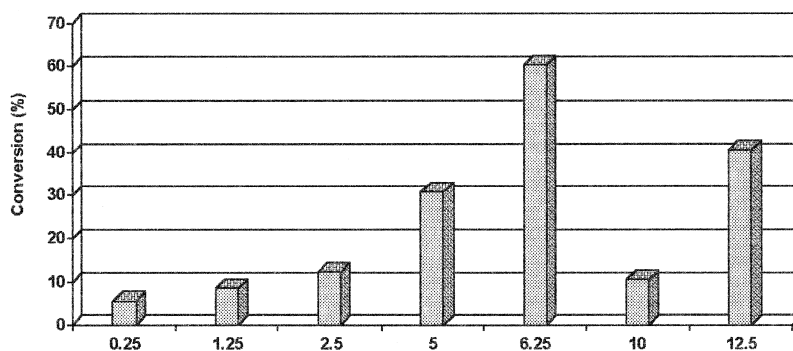Fig. 2. Oxidation of cyclohexane with TBHP in the presence of Mn complexes included in zeolite Y.

Fig. 3. Oxidation of cyclohexane with TBHP in the presence of $Mn(bpy)_2^{2+}$–Y.

aromatic bipyridine ligand is more active with respect to the aliphatic ligand ethylenediamine indicates that the formation of π-cation radical is more favored. To account for the lower activity of $Mn(tmnda)_2^{2+}$–Y catalyst, the substantial steric hindrance of methyl groups which apparently lie in the way of approaching oxidant toward the central metal in the transition state must be taken into consideration.

Reactions of catalyst $Mn(bpy)_2^{2+}$–Y with various cyclohexane to oxidant ratios were examined. The results are shown in Table 5 and Fig. 3. It is important to note that increasing the substrate to oxidant ratio to five dramatically changes the reaction rate and the conversion percentage of cyclohexane reaches 30.8% during the reaction time. The results shown in the last two entries of Table 5 which belong to the reactions in the absence of solvent look promising. The sudden change of conversion percentage of substrate from 30.8% to 60.4% might be accounted for by the fact that higher occupancy level of substrate will bring cyclohexane closer to metal complex and therefore, the oxidation occurs with more efficiency.

5. Conclusion

In this study, it was shown that several transition metals exchanged with zeolite Y can promote the catalytic oxidation of cyclohexane. When several complexes of Mn(II) included in zeolite Y and the oxidation was carried out with these catalyst, the activity was increased by a factor of 25. We believe that our system with a rather simple structure mimics the behavior of cytochrome *P*-450 type oxidation system.

Acknowledgements

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