Oxidation of cyclohexane with *tert*-butylhydroperoxide and hydrogen peroxide catalyzed by nano-sized γ-alumina supported metallophthalocyanines

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Abstract In this study, nano-γ-alumina-supported unsubstituted Fe-, Co- and Mn-phthalocyanines were prepared and characterized. Catalytic activities of the supported phthalocyanines for the oxidation of cyclohexane with *tert*-butylhydroperoxide (TBHP) and H_2O_2 as the oxidant in the liquid phase were considered. For the MPc/nano-γ-alumina catalysts, a dimethylformamide:dichloromethane (3:7) solvent mixture was employed. The products of the catalytic reaction are cyclohexanone and cyclohexanol. The conversion percent of cyclohexane depended on the oxidant and the catalyst. TBHP was found to be a better oxidant than H_2O_2 since minimal destruction of the catalyst and higher conversion of cyclohexane were observed when this oxidant was employed. Under these reaction conditions, the order of catalytic activities is as follows: CoPc/γ-alumina > FePc/γ-alumina > MnPc/γ-alumina. Over γ-alumina, the conversion was much lower than on supported catalysts. The highest conversion of cyclohexane (13.21%) was observed on 10% CoPc supported.

Keywords Oxidation · γ-Alumina · Supported · Metallophthalocyanines · Cyclohexane

Introduction

The selective aerobic oxidation of hydrocarbons is a major goal of today's research in catalysis as selectively oxidized hydrocarbons can be used as feedstock for the preparation of fine chemicals [1, 2]. Among the oxidation of various alkanes, partial oxidation of cyclohexane to cyclohexanol and cyclohexanone, the intermediates in manufacturing nylon 6 or nylon 6,6, have attracted commercial interest [3]. The present industrial process for cyclohexane oxidation is carried out around 150 °C

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and 1–2 MPa pressure under homogeneous reaction conditions which result in the conversion of less than 6% and selectivity of cyclohexanol and cyclohexanone of around 80% using metal cobalt salt or metal-boric acid. Because of the relatively harsh conditions and limited conversion, scientists have been trying to improve aerobic conversion of cyclohexane to desired products since the 1960s [4–9].

Metalloporphyrin complexes as models of cytochrome P-450, have been studied extensively as catalysts for hydrocarbon oxidations in the last decades [10]. Metallophthalocyanines (MPc) which have structures similar to metalloporphyrins have also been used as catalysts for hydrocarbon oxidation but to a lesser extent. Metallophthalocyanines, however, can have remarkable potential for industrial applications, because they are cheaper and thermally more stable than the metalloporphyrins. Therefore MPc catalysts for oxidation of cyclohexane have attracted interest in recent years [11].

Due to the inherent advantages of heterogeneous catalysts over homogeneous catalysts, much effort [12, 13] has been devoted to immobilize these homogeneous catalysts onto solid supports, such as polymers [14], clays [15] and zeolites [13]. Application of alumina-supported catalysts in organic transformations has been receiving attention in recent years [16, 17]. Immobilization of homogeneous transition metal catalysts to alumina carriers offers several practical benefits of heterogeneous catalysis, while retaining the advantages of homogeneous catalytic reactions [16–19].

Fe, Cu and Co phthalocyanine complexes have shown good efficiencies for oxidation of cyclohexane in the presence of TBHP. Encapsulations of metallophthalocyanines in supports have been chosen to synthesize selective and stable catalysts with high activity [20]. Encapsulated Fe(II) and Ru(II) phthalocyanines have also shown promise as catalysts for the oxidation of cyclohexane, using alkyl peroxides or iodosyl benzene as the oxidants [21–24]. The use of halogenated metallophthalocyanines as heterogeneous catalysts for the oxidation of cyclohexane has been reported in a patent application [25]. Armengol et al. have used perfluorinated CoPc supported on aluminosilicate for cyclohexane oxidation and have shown that this supported catalyst is more active and selective than the unsupported complex [26]. Higher activity of MPcs (M = Cu, Co, Fe) for cyclohexane oxidation has been reported when it was encapsulated in zeolite X and Y [20, 25, 26]. In another report, Neys and coworkers have employed FePc supported on carbon active for selective oxidation of cyclohexane [27]. However, to the best of our knowledge, there is no report for the application of MPc supported on γ-alumina for partial oxidation of cyclohexane with H_2O_2 and TBHP. In this work, Fe, Mn and CoPc supported on γ-alumina were reported as catalysts for aerobic oxidation of cyclohexane to cyclohexanol and cyclohexanone in the liquid phase.

Experimental

Instrument and reagents

FT-IR spectra were recorded on a Bomem MB102 model in KBr plates. UV–VIS spectra were recorded on a Shimadzu UV-2100 spectrometer. Powder X-ray

diffraction measurements were performed by a Siemens D 5000 instrument. Specific surface area was measured by BET techniques in liquid N_2 temperature by a Strohlien instrument. The surface morphology of the samples was obtained using a Jeol-JSM-5610 LV scanning electron microscope (SEM). The reaction products of oxidation were identified by GC-MS (Finnigan TSQ-7000) and were analyzed by GC (Shimadzu 8A). All the reagents were commercial grade obtained from Merck. MPc were synthesized according to the reported procedures [28].

Preparation of the catalysts

Aluminum nitrate {$Al(NO_3)_3 \cdot 9H_2O$}, aqueous ammonia {$NH_3 \cdot H_2O$} and deionized water were used as starting chemicals. An aluminum nitrate (1.5 M) solution was prepared by dissolving 225 g in 400 mL of deionized water. Two hundred milliliters of deionized water was taken in a 2-liter round-bottom flask and stirred well using a magnetic stirrer. Then, the aluminum nitrate solution and some solution of aqueous ammonia (12 M) were added to the deionized water drop by drop to precipitate Al cations in the form of hydroxides. The temperature was maintained at about 50 °C during the precipitation/digestion experiment. The pH after precipitation was found to be in the range of 6–6.5. The precipitates were further digested at 50 °C for 1 h. After the alumina gel was formed, it was filtered and washed by distilled water. Metal salt (9.6×10^{-5} mol), phthalonitrile (3.84×10^{-4} mol), urea (1.92×10^{-3} mol) and ammonium heptamolybdate (8×10^{-4} mol) were mixed and finely grounded and were added to the alumina gel. This gel was stirred and homogenized and was placed in an oven under temperature of 100 °C for 24 h. The mixture was heated in air to 250 °C at a heating rate of 2 °C/min and then the mixture was calcined at 500 °C under vacuum for 4 h. γ-Alumina was made with the same procedure with the exclusion of urea/phthalonitrile/metal salt/ammonium heptamolybdate from the gel [29, 30]. Formation of γ-alumina was confirmed with XRD and for MPc with UV–VIS and IR spectra.

CoPc/γ-alumina: IR (KBr): v, cm^{-1} 1522, 1427, 1334, 1291, 1164, 1122, 1090/3444, 1637, 1384, 1072, 731, 611.

FePc/γ-alumina: IR (KBr): v, cm^{-1} 1516, 1411, 1333, 1290, 1165, 1120/3433, 1639, 1384, 1074, 733, 613.

MnPc/γ-alumina: IR (KBr): v, cm^{-1} 1420, 1333, 1289, 1164, 1119/3434, 1640, 1384, 1073, 735, 614.

Experimental procedure

In a typical procedure, a mixture of 1.0 g catalyst, 25 mL solvent mixture of DMF/CH_2Cl_2 (3:7) and 10 mmol cyclohexane was stirred under nitrogen 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 or H_2O_2 was added as oxidizing reagents. The resulting mixture was then refluxed for 8 h under N_2 atmosphere. After filtration, the solid was washed with solvent and then the reaction mixture was analyzed by GC. Product identification was done with GC-MS and confirmed by

comparison of their retention times with authentic commercial samples of these compounds.

Results and discussion

Characterization of the catalysts

Formation of MPc was confirmed with UV-VIS and IR spectra. It was found that the spectra of the supported and unsupported metallophthalocyanines were identical.

Fig. 1 shows the UV–VIS spectrum of supported CoPc, FePc and MnPc. These spectra confirm formation of different polymorphs of MPcs in the alumina matrix [11]. They also indicate that the yields of MPc formation are CoPc > FePc > MnPc which has been confirmed in the literature [31].

Further characterization of γ-alumina and 5% CoPc/γ-alumina was performed with the XRD technique. The XRD pattern presented in Fig. 2 indicates that γ-alumina is formed. There is no significant change in the XRD pattern with 5% CoPc supported γ-alumina which confirms that metallophthalocyanine dispersed through pores does not change the γ-alumina structure. The reduction of intensity in 5% CoPc/γ-alumina is possibly due to encapsulation of CoPc in the γ-alumina holes. Similar XRD patterns were obtained for the catalysts FePc and MnPc supported on γ-alumina.

A scanning electron micrograph (SEM) of a typical sample of 5% CoPc/γ-alumina is shown in Fig. 3. It is clarified from Fig. 3 that the sizes of the particles are in the ranges of 35–50 nm. This result was coincident with the particle sizes calculated from the Scherrer equation. The spherical morphology of the particles is also evident from the figure. Similar images were obtained for the other catalysts. The specific surface area measured with the BET method was 191 m^2/g for γ-alumina and 159 m^2/g for 5% CoPc/γ-alumina. This decrease of the specific surface
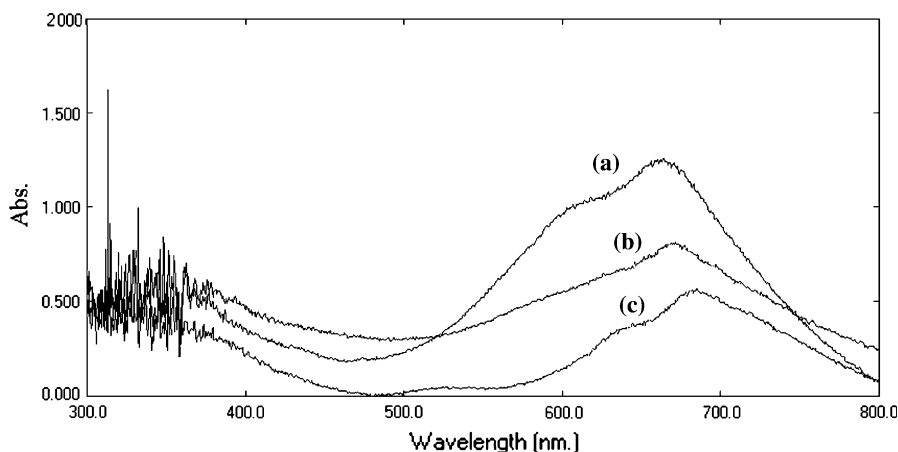

Fig. 1 Diffuse reflectance spectrum of (**a**) CoPc/γ-alumina; (**b**) FePc/γ-alumina; and (**c**) MnPc/γ-alumina
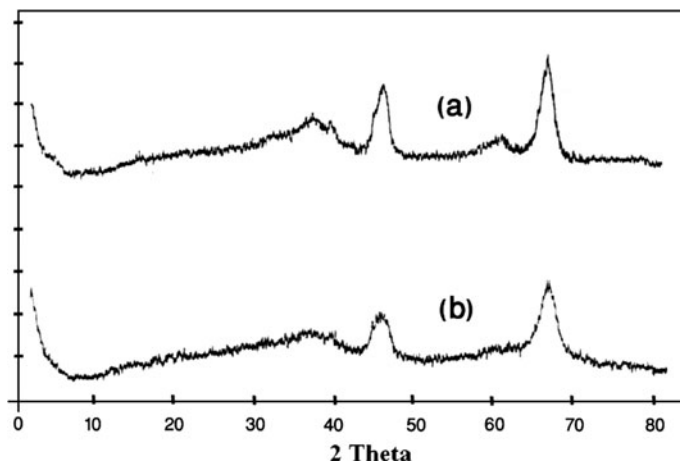
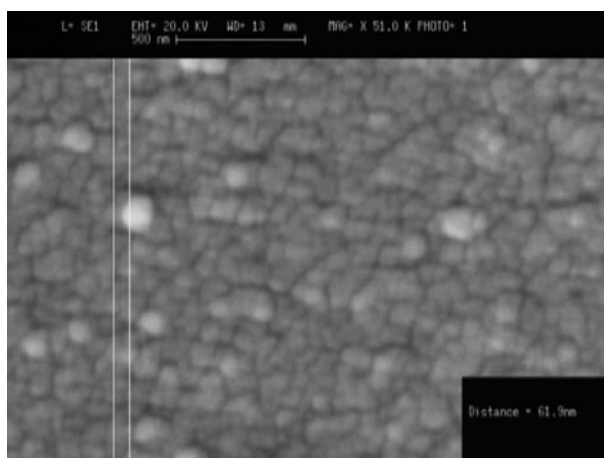**Fig. 2** XRD patterns of (**a**) γ-alumina; and (**b**) 5% CoPc/γ-alumina

Fig. 3 SEM photograph of 5% CoPc/γ-alumina

area of the supported CoPc was consistent with the average pore diameter of 5.1 nm in γ-alumina and diameter of 1.5 nm of CoPc and may be an indication of encapsulation of CoPc in the γ-alumina pores. Moreover, this decrease of the specific surface area is because the Pc may be on the matrix surface hindering the nitrogen adsorption.

Catalytic oxidation of cyclohexane

The use of TBHP as an oxidant was based on the earlier studies on the oxidation of cyclohexane [32], because this oxidant was found to cause minimal destruction of the phthalocyanine catalyst, and to give better selectivity of the products. For

Table 1 Results of the cyclohexane oxidation using MPc/nano-γ-alumina as catalysts

Catalyst	Oxidant	Conversion C$_6$H$_{12}$ (%)	Product selectivity (%)	
			Cyclohexanol	Cyclohexanone
5% CoPc/γ-alumina	TBHP	12.96	45	55
5% CoPc/γ-alumina	H$_2$O$_2$	8.38	64	36
5% FePc/γ-alumina	TBHP	10.77	46	54
5% FePc/γ-alumina	H$_2$O$_2$	7.41	60	40
5% MnPc/γ-alumina	TBHP	9.12	48	52
5% MnPc/γ-alumina	H$_2$O$_2$	4.84	57	43
γ-alumina	TBHP	1.22	37	63
γ-alumina	H$_2$O$_2$	0.83	54	46

Reaction condition: catalyst 1.0 g, cyclohexane 10 mmol, oxidant 16 mmol, solvent mixture DMF/CH$_2$Cl$_2$ (3:7), reflux temperature, reaction time 8 h, Conversion = (mole of cyclohexane reacted/moles of cyclohexane in the feed) × 100. Selectivity = (moles of cyclohexane converted to i/moles of cyclohexane reacted) × 100

Table 2 Catalytic power of reused γ-alumina-supported CoPc[a]

Runs	Conversion (%)
1	12.96
2	12.33
3	12.15
4	11.85
5	12.21
6	11.56
Average	12.18

[a] Experimental conditions: catalyst 1.0 g, cyclohexane 10 mmol, TBHP 16 mmol, solvent mixture DMF/CH$_2$Cl$_2$ (3:7), reflux temperature, reaction time 8 h

comparative purposes, H$_2$O$_2$ was also employed as an oxidant. The solvent mixture containing DMF and dichloromethane (3:7) was employed for the catalysis, since all the reagents dissolved and this ratio gave the highest yields of the products.

The performance of the set of samples prepared as heterogeneous catalysts for the oxidation of cyclohexane was tested using H$_2$O$_2$ and TBHP as oxidizing reagents (Table 1). In all the cases, the only products observed were cyclohexanol and cyclohexanone. In the presence of 5% CoPc/γ-alumina, conversion percentage of cyclohexane was 12.96% with TBHP as an oxidant. Control experiments show that cyclohexane oxidation with TBHP and H$_2$O$_2$ did not occur in the absence of the catalyst under the same reaction condition. This indicated that the metallophthalocyanine supported on γ-alumina acted as catalysts during the oxidation of cyclohexane. Moreover the supported catalysts have higher catalytic activity than the bulk ones.

To investigate the catalytic power of reused metallophthalocyanines supported on γ-alumina, the catalyst used in each catalytic oxidation was isolated from the reaction mixture for reuse later. The experimental results listed in Table 2 showed that cobalt phthalocyanine supported on γ-alumina could be reused several times. The average conversion of cyclohexane was 12.18% when 5% CoPc supported on γ-alumina was reused to catalyze cyclohexane oxidation with TBHP.
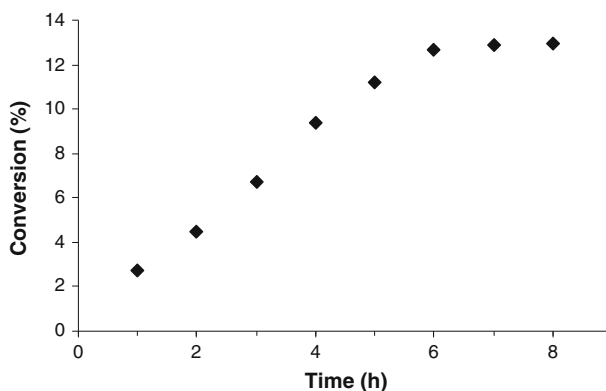
Fig. 4 The effect of reaction time on cyclohexane conversion

Influences of reaction time on cyclohexane oxidation reaction

In this experiment, the change in conversion (%) of cyclohexane in the presence of TBHP oxidant and 5% CoPc/nano-γ-alumina catalyst was monitored and plotted with respect to time (Fig. 4). The reaction was carried out at reflux temperature for 8 h with 1.0 g catalyst and 10 mmol cyclohexane and 16 mmol TBHP in a round bottom flask and some samples was drawn out at regular intervals and analyzed by GC. Fig. 4 shows that the conversion of cyclohexane increases continuously until 12.9% as time increases and then remains constant after 7 h, therefore duration about 7–8 h is proper reaction time.

Influences of various metals on cyclohexane oxidation reaction

We have studied the catalytic properties of iron, cobalt and manganese phthalocyanines and to investigate the effects of different metals on cyclohexane oxidation reaction under the same reaction conditions. Table 1 summarizes the results and confirms the high catalytic activities of these MPcs. The research results indicated that all the three metallophthalocyanines could catalyze cyclohexane oxidation with TBHP and H_2O_2. The activity of the catalysts was as follows: CoPc/γ-alumina > FePc/γ-alumina > MnPc/γ-alumina. Can-Cheng Guo [33, 34] has also reported that, with a Co porphyrin in the liquid phase, a conversion percent of around 16% with 82% selectivity toward cyclohexanol + cyclohexanone was obtained. They also concluded that the Co porphyrin acts better than Mn and Fe porphyrins. In addition 10% MPc were also synthesized and tested as catalyst. The result obtained with 10% CoPc/nano-γ-alumina shows a slight increase in the conversion percent of cyclohexane (13.21%). Similar results for the catalysts 10% FePc and 10% MnPc/nano-γ-alumina were obtained, the cyclohexane conversion in these catalysts were 10.85 and 9.23%. However, the selectivity of the products did not change considerably.
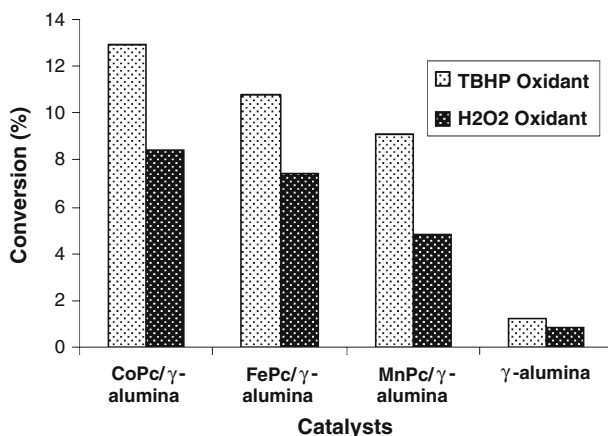
Fig. 5 The effect of oxidant type on cyclohexane conversion in the presence of various catalysts. Reaction condition: 5% MPc/nano-γ-alumina catalyst 1.0 g, cyclohexane 10 mmol, oxidant 16 mmol, reflux temperature

Influence of the type of the oxidant

Fig. 5 shows that the reactivity of the cyclohexane toward oxidation with TBHP and H_2O_2 on metallophthalocyanines supported on nano-γ-alumina catalysts depend on type of oxidant. TBHP is the better oxidant because of the higher conversion. In addition, the catalysts degradation is also smaller in this case. In this regard, it is worth noting that using H_2O_2 as reactant the complexes (both encapsulated and unsupported MPc) lose their characteristic color during the course of the reaction. UV–VIS spectroscopy of the recovered catalysts evidenced the degradation of the MPc complexes. This behavior contrasts with that of TBHP which does not produce decomposition of the MPc complexes as assessed by UV–VIS and IR spectra at the end of the reaction.

Similar UV–VIS and IR spectra were obtained for the catalyst before and after the reaction test with TBHP and the result confirms that the catalyst is stable, decomposition of MPc was negligible and its reactivity was preserved.

Comparison of the catalytic power of γ-alumina-supported MPc with that unsupported MPc

The experimental data of cyclohexane oxidation catalyzed by the γ-alumina-supported MPc or unsupported MPc with TBHP as the oxidant shows that the aerobic oxidation of cyclohexane catalyzed by MPc supported on γ-alumina had better conversion than that of unsupported MPc. When CoPc supported on γ-alumina was used as catalyst, the cyclohexane conversion was 12.96%. However, when the unsupported CoPc was used as the catalyst, the cyclohexane conversion was 7.54%. The results about the other unsupported MPc catalysts are listed in Table 3. Table 3 shows that the supported MPc catalysts are more active than the

Table 3 Results of the cyclohexane oxidation with TBHP in the presence of unsupported MPc catalysts

Catalyst	Conversion C_6H_{12} (%)	Product selectivity (%)	
		Cyclohexanol	Cyclohexanone
CoPc	7.54	43	57
FePc	4.87	41	59
MnPc	3.51	46	54

Reaction condition: catalyst 0.01 g, cyclohexane 1 mmol, TBHP 1.6 mmol, solvent mixture DMF/CH_2Cl_2 (3:7), reflux temperature, reaction time 8 h
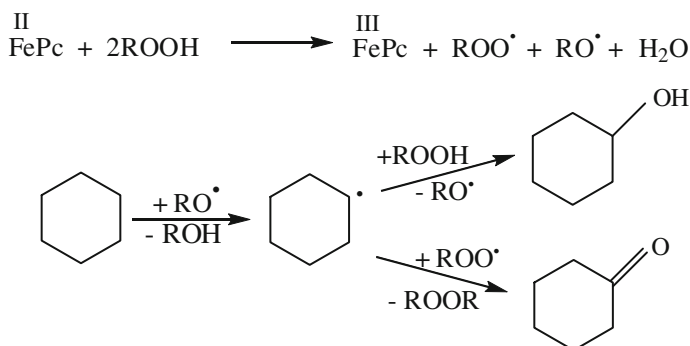
Scheme 1 Proposed mechanism for the formation of cyclohexanol and cyclohexanone in cyclohexane oxidation by metallophthalocyanine

unsupported MPc catalysts. In addition, these results confirm the high stability of the catalyst on the alumina surface or in the alumina cavities.

Discussion

According to the literature [35], the oxidation of cyclohexane by metallophthalocyanine initially forms RO· and ROO· radicals as shown in Scheme 1. The RO· and ROO· radicals formed then react with cyclohexane according to Scheme 1. Cyclohexanol and cyclohexanone may be formed by the direct reaction of cyclohexyl radical.

Conclusions

Metallophthalocyanines encapsulated in nano-γ-alumina were directly synthesized with the addition of metal salt, phthalonitrile, urea and ammonium heptamolybdate to the alumina gel and heated to 500 °C. Cobalt, iron and manganese phthalocyanines inside nano-γ-alumina pores prove to be active, efficient and reusable

catalysts for cyclohexane oxidation with TBHP as the oxidant, in the presence of DMF:dichloromethane (3:7) solvent mixture. They have shown high turnover and conversion percent compared to the unsupported catalyst, which confirms the high stability of the catalyst in the alumina cavities. The catalysts are easy to prepare, possesses particular nanostructure and excellent function and can be easily separated after the reaction, which endow γ-alumina supported metallophthalocyanines with a bright future in industrial applications. Therefore, this catalysis system is very active and suitable for the oxidation of cyclohexane.

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