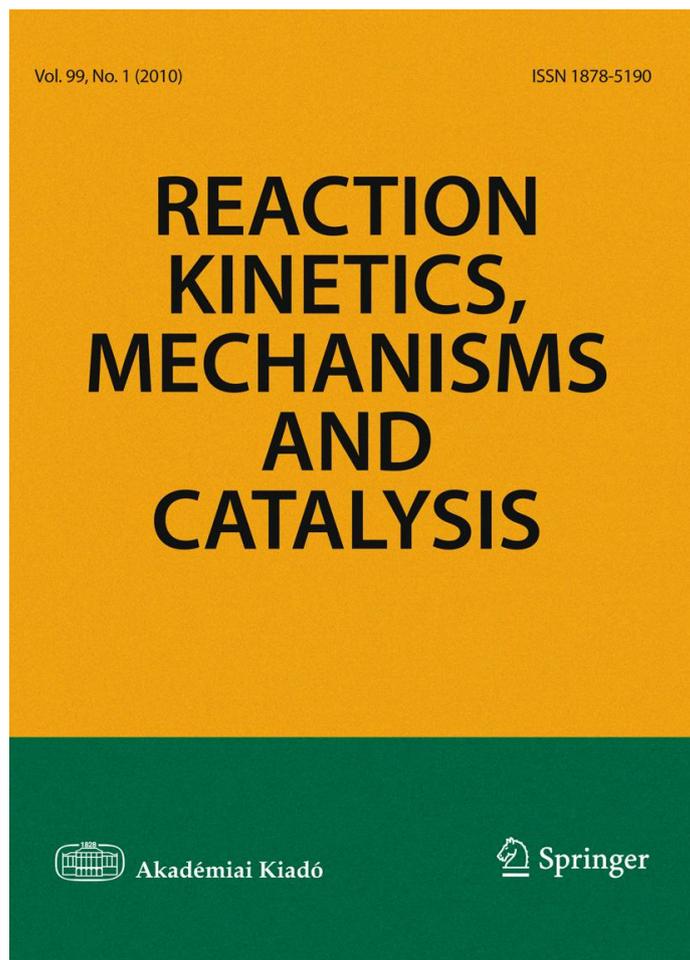


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Oxidation of alcohols with *tert*-butylhydroperoxide catalyzed by nano-sized γ -alumina supported metallophthalocyanines

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Abstract The oxidation of alcohols with *tert*-butylhydroperoxide, in the presence of metallophthalocyanines supported on γ -alumina was investigated. These metallophthalocyanines supported on γ -alumina were effective catalysts for the oxidation of alcohols such as cyclohexanol, benzyl alcohol and hexanol.

Keywords Oxidation · Alcohols · γ -alumina · Metallophthalocyanines

Introduction

Oxidation reactions are among the most important transformations in synthetic chemistry and offer an important methodology for the introduction and modification of functional groups [1]. The selective oxidation of alcohols to aldehydes or ketones is a vital reaction in synthetic organic chemistry. In this way, chemists have used different kinds of metal salts and oxides in the form of homogeneous catalysts [2, 3] or supported metal ions and supported oxometal catalysts as heterogeneous systems [4, 5].

Metallophthalocyanine (MPc) complexes have been used as alternative catalysts, because they have a similar structure to porphyrins and are cheaper and more stable to degradation [6]. The immobilization of MPc on solid supports is highly desirable to synthesize heterogeneous catalysts [7]. There are some reports for the use of cobalt and iron phthalocyanines as homogeneous catalysts for oxidation of alcohols [8, 9]. However, to the best of our knowledge, there is no report for application of MPc supported on γ -alumina for oxidation of alcohols. In this work, the catalytic effect of Fe, Mn and CoPc supported on γ -alumina are investigated for the oxidation of alcohols in heterogeneous systems.

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Experimental

Preparation of catalysts

Aluminum nitrate $\{\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}\}$, aqueous ammonia $\{\text{NH}_3 \cdot \text{H}_2\text{O}\}$ and deionized water were used as starting chemicals. Two hundred milliliters of deionized water was taken in a 2 L round-bottom flask and stirred well using a magnetic stirrer. Then, aluminum nitrate solution (1.5 M) and some solution of aqueous ammonia (12 M) were added to 200 mL of deionized water drop by drop to precipitate Al cations in the form of hydroxides. The temperature was maintained $\sim 50^\circ\text{C}$ 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 salts (9.6×10^{-5} mol) [Cobalt(II) chloride hexahydrate, iron(II) chloride tetrahydrate, manganese(II) acetate tetrahydrate], phthalonitrile (3.84×10^{-4} mol), urea (1.92×10^{-3} mol) and ammonium heptamolybdate (8×10^{-4} mol) were mixed and finely ground 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 300°C at a heating rate of $2^\circ\text{C}/\text{min}$ and then the mixture was calcined at 500°C under vacuum for 4 h [10, 11]. In the presence of 5% MPC/ γ -alumina catalysts, the percentage of the loaded metal is 0.5%. Formation of γ -alumina was confirmed with XRD and for MPC with UV–VIS and IR spectra.

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

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

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

Experimental procedure

In a typical reaction, a mixture of 0.5 g catalyst and 30 mmol of alcohol (cyclohexanol, *n*-hexanol or benzyl alcohol) were 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 14 mmol of TBHP or H_2O_2 was added as an oxidizing reagent. The resulting mixture was then heated at 70°C for 8 h under N_2 atmosphere. After filtration, the solid was washed with solvent and then the reaction mixture was analyzed by GC (Shimadzu 8A). Product identification was done with GC–MS (Finnigan TSQ-7000).

Results and discussion

Characterization of the catalysts

Formation of MPC was confirmed with UV–VIS spectra (Fig. 1), which is the same as spectra of unsupported MPC. Phthalocyanines have a high energy absorption band of approximately 670 nm (Q-band), which is shown in Fig. 1. Another high energy band of phthalocyanines is near 340 nm (Soret-band) and has less intensity than Q-band, which is covered by a γ -alumina absorption band shown in Fig. 1. Q and S bands appeared as the

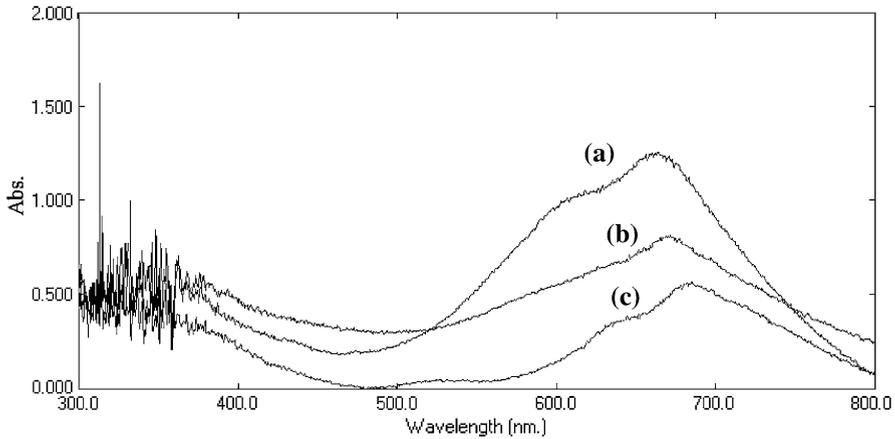


Fig. 1 Diffuse reflectance spectrum of *a* CoPc/ γ -alumina, *b* FePc/ γ -alumina, and *c* MnPc/ γ -alumina

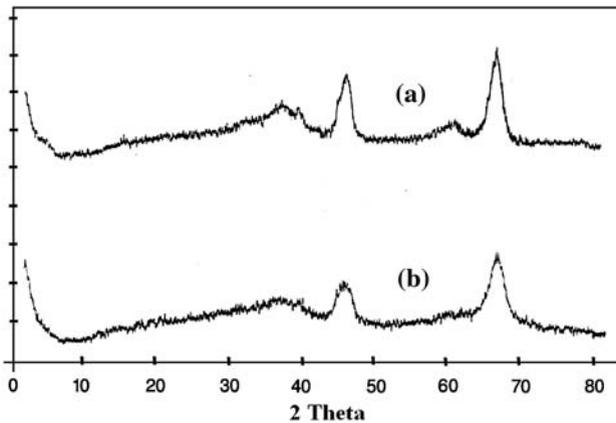


Fig. 2 XRD patterns of *a* γ -alumina, and *b* 5% CoPc/ γ -alumina

result of electronic transitions of π to π^* ($\pi \rightarrow \pi^*$). Thus, these spectra confirm the formation of different polymorphs of MPCs in the alumina matrix [12]. They also indicate that the yields of MPC formation are CoPc > FePc > MnPc, which has been confirmed in the literature [13].

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 on 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.

A scanning electron micrograph (SEM) of a typical sample of 5% CoPc/ γ -alumina is shown in Fig. 3. It is clear 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 specific surface area measured with the BET method was 191 m²/g for γ -alumina and 159 m²/g for 5% CoPc/ γ -alumina. This reduction in specific surface area for the supported

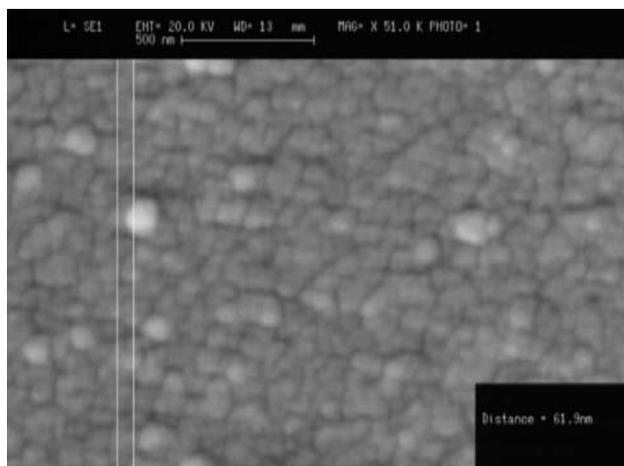


Fig. 3 SEM photograph of 5% CoPc/ γ -alumina

CoPc has consistency with the pore size 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.

Catalytic oxidation of cyclohexanol with TBHP

The use of TBHP as an oxidant was based on the earlier studies on the oxidation of hydrocarbons [14], this oxidant caused minimal destruction of the phthalocyanine catalyst, and gave better selectivity of the products. The performance of the set of samples prepared as catalysts for the oxidation of alcohols was tested with TBHP. At first, the reactivity of a model compound, cyclohexanol, was examined under a variety of experimental conditions (Table 1). In all reactions, only one product (cyclohexanone) was produced, therefore, the selectivity (%) is 100 with respect to it. The research results showed that three kinds of metallophthalocyanines could catalyze cyclohexanol oxidation with TBHP. The activity of the catalysts was as follows: CoPc/ γ -alumina > FePc/ γ -alumina > MnPc/ γ -alumina. In the presence of 5% CoPc/ γ -alumina, the conversion percentage of cyclohexanol was 87.9% with TBHP as an oxidant. Contrastive experiment results show that cyclohexanol oxidation with TBHP did not occur in the absence of the catalyst under the same reaction conditions. In addition, γ -alumina alone has shown lower catalytic activity than the supported catalyst.

Table 1 Oxidation of cyclohexanol with TBHP in the presence of metallophthalocyanines supported on nano- γ -alumina

Catalyst	Conversion (%)	Selectivity (%)
5% CoPc/ γ -alumina	87.9	100
5% FePc/ γ -alumina	66.4	100
5% MnPc/ γ -alumina	45.6	100
γ -alumina	21.3	100

Reaction conditions: 0.5 g catalyst; cyclohexanol 30 mmol; TBHP 14 mmol; temperature 70 °C; reaction time 8 h

Effect of substrates and oxidants on oxidation

In this study, experiments on various selected alcohols were performed and the comparisons with respect to conversion and product selectivity are represented in Table 2. Higher conversion was obtained for cyclohexanol on 5% the CoPc/ γ -alumina catalyst using TBHP as an oxidant. Table 2 shows that the reactivity of the alcohols toward oxidation with TBHP and H₂O₂ on 5% CoPc/ γ -alumina depends on the particular structure of the substrate and type of oxidant. It shows that TBHP is a more efficient oxidant than H₂O₂ due to weaker O–O bonds. Since the O–O bond of HOOH is 5 kcal/mol stronger than the one in TBHP, an HOO complex is expected to have a higher activation energy for O–O bond cleavage than a TBOO complex and therefore, to have a longer lifetime. The following order has been observed for the percentage of conversions of alcohols: 2° > benzylic > 1°.

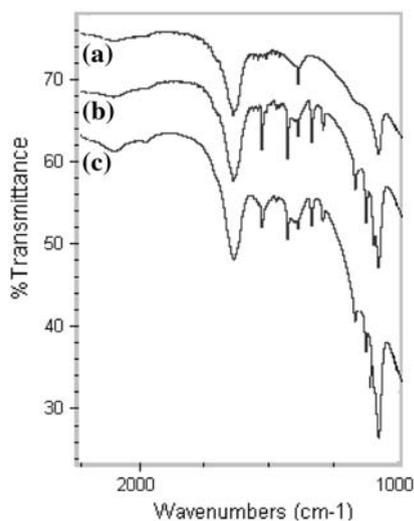
In this regard, it is worth noting that the complexes lose their characteristic color during the course of the reaction with H₂O₂ as reactant. UV–VIS spectroscopy of the recovered catalysts evidenced the degradation of the MPc complexes. This behavior contrasts with that of TBHP which does not produce 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

Table 2 Effect of the 5% CoPc/nano- γ -alumina catalyst in the oxidation of different alcohols

Alcohol	Product	Conversion (%)		Selectivity (%)
		TBHP Oxidant	H ₂ O ₂ Oxidant	
Cyclohexanol	Cyclohexanone	87.9	75.3	100
Benzyl alcohol	Benzaldehyde	65.4	52.7	100
<i>n</i> -Hexanol	Hexanal	48.2	33.6	100

Reaction condition: 0.5 g catalyst; substrate 30 mmol; oxidant 14 mmol; reaction temperature 70 °C; reaction time 8 h

Fig. 4 IR spectra of *a* γ -alumina, *b* freshly prepared 5% CoPc/ γ -alumina and *c* for the 5% CoPc/ γ -alumina catalyst after the reaction was performed. Spectra were taken in KBr plates



confirms that the catalyst is stable, decomposition of MPc was negligible and its reactivity was preserved. Trace (a) in Fig. 4 demonstrates the IR spectrum of γ -alumina and trace (b) is for the freshly prepared 5% of CoPc/ γ -alumina before the reaction test. Trace (c) in Fig. 4 is for the 5% of CoPc/ γ -alumina after the reaction test. The presence of the same relative ratio for the IR peaks in γ -alumina to CoPc/ γ -alumina (i.e. see the signal in 1637 and 1522 cm^{-1} which are for the γ -alumina and CoPc/ γ -alumina, respectively) before and after reaction test clearly prove the stability of the catalyst under our reaction conditions.

At the end of the oxidation with TBHP as the oxidant, the catalyst was recovered by filtration, washed with solvent, and reused. After three consecutive uses, the supported catalyst retained its catalytic activity.

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 under vacuum. Cobalt, iron and manganese phthalocyanines inside nano- γ -alumina pores proved to be active, efficient and reusable catalysts for the oxidation of various alcohols with good conversion percentage and 100% selectivity by using TBHP as the oxidant.

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