

Mild Oxidation of Benzhydrol by *t*-Butyl Hydroperoxide in the Presence of Silica Supported Iron Porphyrin as a Heterogeneous Catalyst

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Abstract: In this study, immobilized Iron (III) complex of *meso*-tetrakis(*p*-chlorophenyl) porphyrin iron(III) [Fe^{III}(TCIPP)] on modified silica gel by 3-aminopropyl group has been used as a heterogeneous catalysts for oxidation of benzhydrol by *t*-butyl hydroperoxide (TBH). The reaction was performed at room temperature to afford benzophenone in high yields and short reaction time. Furthermore, the catalyst can be reused for at least 3 reaction cycles without significant lose of its activity.

Keywords: Silica Supported Iron Porphyrin; Oxidation; Heterogeneous Catalyst; Green Chemistry; *t*-Butyl Hydroperoxide (TBH); Benzhydrol.

Introduction

Over the last 20 years, metalloporphyrins are used as cytochrome p-450 models in oxidation reactions [1]. These complexes are able to catalyze oxidation of different materials such as alkenes, alkanes, alcohols and sulfides [2-5]. However, in these homogeneous catalyst systems, metalloporphyrins may be aggregated by π - π interactions. Therefore, the catalytic activity of them will be reduced. Recently, researchers were introduced some kinds of supports such as alumina, silica, clay, zeolites and resins for immobilization of metalloporphyrins on them. By means of this method, self oxidation and aggregation of porphyrins will be reduced. Furthermore, these new heterogenized catalysts can be easily recovered and reused for several times [6].

Among these different supports, the silica gel as an inorganic support has advantages such as: high stability, good accessibility and good surface attraction towards functional groups of organic molecules [7].

In this work, the catalytic activity of immobilized *meso*-tetrakis(*p*-chlorophenyl) porphyrin iron(III) [$\text{Fe}^{\text{III}}(\text{TCIPP})$] on modified silica gel in oxidation of benzhydrol with *t*-butyl hydroperoxide (TBH) as an oxidant has been studied. The effect of reaction time and amount of the catalysts has also been investigated.

Results and Discussion

Meso-tetrakis(*p*-chlorophenyl)porphyrin iron(III) [$\text{Fe}^{\text{III}}(\text{TCIPP})$], which is prepared by Adler's method [8], 3-aminopropyl group functionalized silica gel (Si-APTE), were added to toluene and stirred at 80 °C for 24 h. Then, after filtration and washing the hybrid material, the heterogeneous catalyst of Si-APTE-Fe(TCIPP) was synthesized (**Fig. 1**).

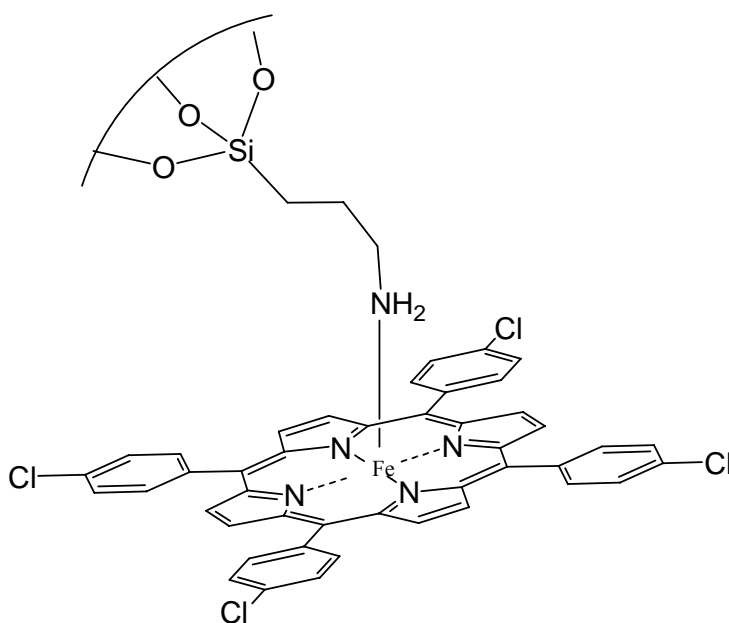


Fig.1 . Schematic structure of Si-APTE-Fe(TCIPP).

The obtained heterogeneous catalyst of Si-APTE-Fe(TCIPP) was characterized by solid state UV-Vis, EDX and ICP. As shown in **Fig. 2**, by comparison of Solid state UV-Vis of Si-APTE-Fe(TCIPP) and heterogeneous catalysts (Si-APTE-Fe(TCIPP)), immobilization of catalyst on the silica support was confirmed.

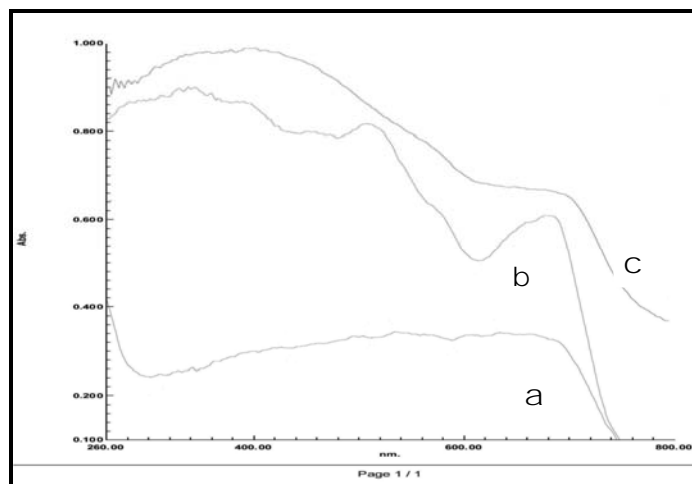
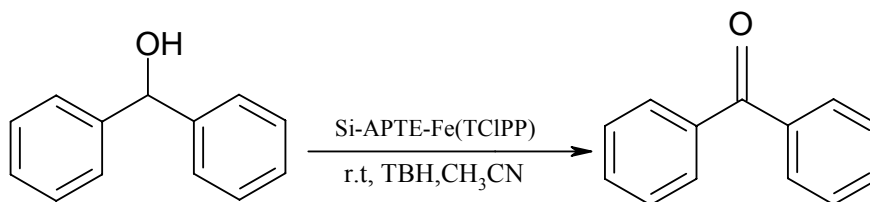


Fig. 2. UV-Vis. solid state spectra of Si-APTE (a), Fe(TCIPP) (b) and Si-APTE-Fe(TCIPP)(c).

After characterization of Si-APTE-Fe(TCIPP) catalyst, it was investigated for oxidation of benzhydrol by TBH in different solvents such as CH_2Cl_2 , *o*-dichlorobenzene and CH_3CN (**Scheme 1**). Interestingly, the best result with respect to the catalyst durability was obtained in CH_3CN as solvent.



Scheme 1. Oxidation of benzhydrol by TBH in the presence of Si-APTE-Fe(TCIPP).

A mixture of benzhydrol (1 mmol), TBH (1 mmol) and Si-APTE-Fe(TCIPP) (0.2 g) was added to a flask containing magnetic stirring bar in CH_3CN (10 mL) at room temperature. For obtaining the optimized reaction time, the analysis of the reaction mixture was performed by GC after different periods of time. As the results show in **Fig. 3**, the obtained yield after 3 hours was the best (76%). No significant improvement in the reaction yield was observed even after 24 h. Comparison of the optimized yield in this study with homogeneous catalytic systems shows that the required reaction time of this heterogeneous catalyst is longer than the analogous non-supported metalloporphyrin [9]. However, the reusability of this system makes it cost-effective.

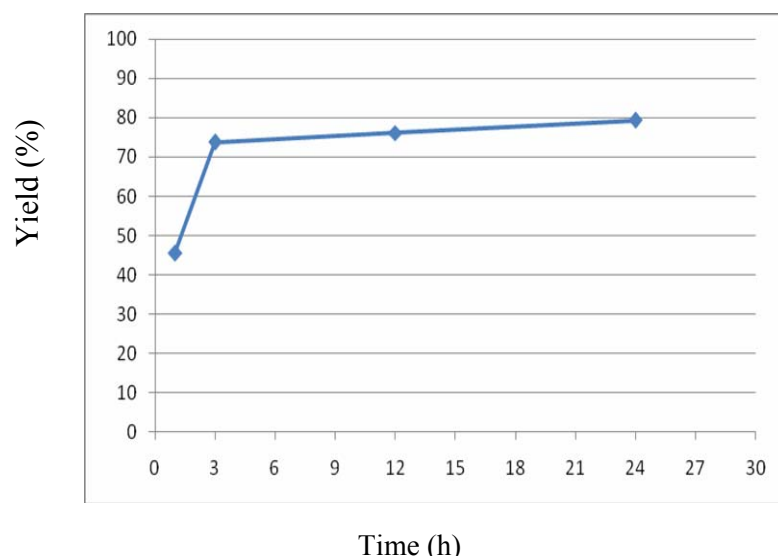


Fig. 3. Effect of different reaction time on the oxidation of benzhydrol in the presence of Si-APTE-Fe(TCIPP).

Another important parameter which optimized in catalytic reactions is the amount of catalyst. Therefore, the effect of different amount of catalyst on the oxidation of benzhydrol by TBH was also investigated. The results show that by increasing the amount of catalyst to 0.1 g, the optimal yield is obtained (**Table 1**).

Table 1. The effect of different catalyst loading on the oxidation of benzhydrol by TBH in the presence of Si-APTE-Fe(TCIPP)^a

| Entry | Catalyst Loading (g) | Yield (%) ^b |
|-------|----------------------|------------------------|
| 1 | 0.02 | 23 |
| 2 | 0.05 | 67.4 |
| 3 | 0.1 | 71.6 |
| 4 | 0.2 | 76 |

^a Benzhydrol (1 mmol), TBH (1 mmol) and Fe(TCIPP) and CH₃CN (10 mL), 3 h.

^b yields obtained by GC

On the other hand, the reusability of the catalyst was also investigated. The obtained results showed that the catalyst can be used at least 3 cycles without significant loss of its activity.

Conclusions

We have presented a new heterogeneous catalysts by immobilization of Iron(III) complex of *meso*-tetrakis(*p*-chlorophenyl)porphyrin, [Fe^{III}(TCIPP)], on modified silica gel Si-APTE for oxidation of benzhydrol at room temperature by *t*-butyl hydroperoxide (TBH) with high yield. The important advantages of our method are: short reaction time, reusability of catalyst for at least 3 cycles without significant lose of reactivity and mild conditions.

Experimental

General

Meso-terakis(*p*-chlorophenyl) porphyrin was prepared by Adler's method [8]. Insertion of Iron into this organometallic complex was performed according to the previous reports [10]. Silica gel (Merck, 60/70-250) was activated at 250 °C under vaccum. Another substances and solvents were obtained from Merck and Aldrich and used without further purification. IR spectra were recorded on a Shimadzu FT-IR-8400S spectrometer and performed by using KBr pellets. Gas chromatography (GC) experiments were performed with a Shimadzu GC-16A instrument equipped with a FID detector and Capillary column (length 30 m). The yields were obtained by calibration curve obtained with using internal standard.

Typical experimental procedure for immobilization of Fe(TCIPP) on the modified silica gel (Si-APTE):

The modified silica (Si-APTE) was prepared according to the reported procedure [11]. In a round bottom flask, a mixture of silica gel (5 g), 3-Aminopropyltriethoxysilane (5 mL) and toluene (70 mL) were degassed and sealed under nitrogen. Then suspension was refluxed at 80 °C during 24 h. The product was filterated and exhaustively washed in a soxhlet extractor with anhydrous ethanol for 24 h. Then the solid was dried at 80 °C under vaccum for 24h. Functionalizing of silica gel with 3-Aminopropyltriethoxysilane was characterized by FT-IR. Then, in a round bottom flask, FeTCIPP (0.3 g) and Si-APTE was added in toluene (80 mL). The mixture was vigorously stirred at 80 °C for 24h. After cooling, the solid was filtered and washed with dichloromethane, methanol and ether and dried in vaccum at room temperature for 12 hours [12].

Typical experimental procedure for oxidation of benzhydrol:

A mixture of benzhydrol (1 mmol), TBH as an oxidant (1 mmol) and Si-APTE-Fe(TCIPP) (0.1 g) was added to a flask containing a magnetic stirring bar in CH₃CN (10 mL).

The progress of the reaction was monitored by thin layer chromatography (TLC). Then, the catalyst was separated by filtration and the reaction mixture was analyzed by GC. The yields were calculated from standard curve by using internal standard.

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