

Synthesis of Copper Porphyrin into SBA-16 Walls as Catalyst for Oxidation Reaction

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Abstract

The SBA-16 was synthesized in acidic medium by F127 as directing agent and Tetraethylorthosilicate as silica source, respectively and then modified by aminopropyltriethoxysilane (APTES). The synthesis of copper tetrakis(4-chlorophenyl)porphyrin (CuTCIPP) immobilized into SBA-16 (CuTCIPP@SBA-16) was performed by using ship-in-a-bottle. The characterization of synthesized materials were identified by FT-IR, UV-vis spectroscopy, XRD, nitrogen adsorption-desorption and SEM. in oxidation of cyclohexene.

Oxidation of cyclohexene with tertiary butyl-hydroperoxide (TBHP) as oxidant efficiently was catalyzed to epoxide, ketone and alcohol in presence acetonitrile as solvent under reflux condition. The obtained products were characterized by using gas chromatography (GC). In addition, leaching and recycling experiments revealed that the catalyst can be repeatedly applied for cyclohexene oxidation for three successive cycles.

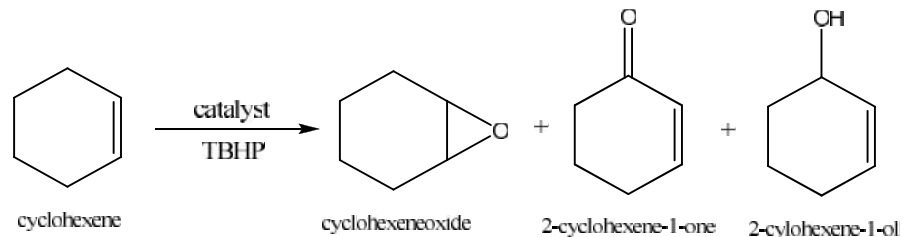
Keywords: TCIPP, Porphyrin, SBA-16, Cyclohexene, Oxidation

1. Introduction

Porphyryns and their derivatives have attracted much attention during the past three decades due to their interesting optical properties and similarities to pigments found in biological organisms. Because of their unique properties, they have been applied for various applications such as dyes in the design solar cells, sensors, catalyse of organic reactions, catalysts for degradation of pollutants etc. Porphyryns are well known for their ability to carry out a wide range of oxidation reactions in homogeneous systems. These compounds have been widely used for homogeneous selective oxidation alkenes [1]. The use of porphyryns as a homogeneous catalyst has disadvantages. Immobilization into the supports enhances catalyst

stability and selectivity and makes possible recycling and reuse of the catalyst. Mesoporous silica materials with their regular channels and pores, high surface area, good hydrothermal stability and rapid mass transport inside the mesostructures are suitable hosts for immobilization of porphyrin macrocycles [2]. Among the mesoporous silicas, SBA-16 is characterized with unique pore size, high hydrothermal and chemical stability. SBA-16 has a body-centered-cubic structure ($Im\bar{3}m$ symmetry) of nearly spherical cages, in which each cage is connected with 8 neighboring cages through small openings, which facilitates diffusion and transport of various species, for these reasons they are promising candidates to be used as support for functionalization of porphyrins [3].

In this study, we have reported synthesis and modify of SBA-16 nanoparticles. Then, incorporation of tetrakis(4-chlorophenyl)porphyrin (TCIPP) into SBA-16 was carried out. Some spectral characterizations were used to identify obtained materials. The results showed that the heterogeneous catalyst has synthesized very well. Oxidation of cyclohexene with tertiary butyl-hydroperoxide (TBHP) as oxidant efficiently was catalyzed to epoxide, ketone and alcohol in presence acetonitrile as solvent under reflux condition (Scheme 1). The obtained products were characterized by using gas chromatography (GC).



Scheme 1

2. Experimental

2.1. Materials and methods

All of the Chemicals used in this work were analytical grade reagents and used without further purification. Deionized water was used to prepare all solutions.

The particle morphologies of the as-prepared powders were observed by a Hitachi scanning electron microscopy (SEM) at 30 kV. The FT-IR analyses were carried out on a Shimadzu FTIR-8400S spectrophotometer using a KBr pellet for sample preparation. The DRS spectra were prepared via a Shimadzu (MPC-2200) spectrophotometer. For investigation of catalytic ability of nanocatalyst, the concentration of obtained oxidation products were determined by using a gas chromatograph (Shimadzu) equipped with a HP-5 capillary column. The reaction products were confirmed by GC-MS (Perkin- Elmer).

2.2. Preparation of catalyst

The immobilized porphyrin (CuTCIPP@SBA-16) used in all the experiments were prepared according to the previously described ship-in-a-bottle procedure [4].

The CuTCIPP@SBA-16 were obtained by mixing 2.0 g of SBA-16 and 0.5 g (2.5 mmol) of copper(II) acetate monohydrate in 140 ml of glacial acetic acid and 93 ml of nitrobenzene. To this mixture the corresponding substituted 4-chlorobenzaldehyde (9.5×10^{-3} mol) were added. The temperature was increased to 120 °C and the pyrrole was slowly added (9.5×10^{-3} mol). The reaction continued for 2 h. At the end, all the materials were filtered and Soxhlet extracted sequentially with CH_2Cl_2 , CH_3CN and CHCl_3 , until no porphyrin or precursors were detected in the solution, by UV-vis spectroscopy (72 h). The resulting immobilized sensitizers were dried overnight at 100 °C [5].

2.3. Investigations of Catalytic oxidation reaction

Oxidation reactions were carried out under reflux conditions at atmospheric pressure. At first, a mixture of cyclohexene (10 mmol), acetonitrile (5 cm^3) and heterogeneous catalyst (0.02 g) was added to a flask containing a magnetic stirrer bar. After 5 minutes, TBHP as oxidant (15 mmol) was added. The reaction mixture was heated under stirring at the desired temperature for 6 h. After finishing the time, the catalyst was separated by filtration and the collected products were detected by GC.

3. Result and discussion

3.1. Result of SEM

The SEM image (Fig. 1-A) shows the morphology of synthesized SBA-16. In this image the structure of cubic mesoporous of SBA-16 is visible. Figure 1-B show SEM image of CuTCIPP@SBA-16 catalyst. As can be seen, the fragmentation of mesoporous SBA-16 is observed, due to immobilization of porphyrin into mesoporous silica walls, which leads to smaller particles compared with SBA-16.

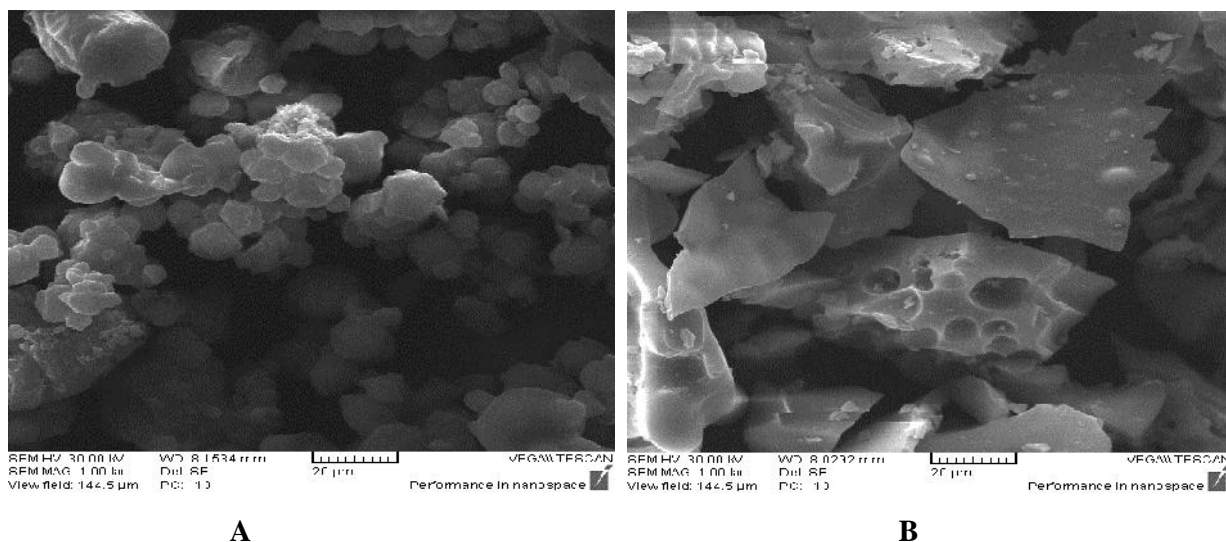


Fig. 1 SEM image of Cr-doped TiO₂ Photocatalyst

3.2. UV-Visible spectra

The UV-vis absorption spectra of the SBA-16 and CuTCIPP@SBA-16 are shown in Fig. 2. This is clear that UV-vis absorption spectrum of pure SBA-16 shows absorption around 400 nm (the sorlet band), followed by several weaker absorptions (Q bands) at higher wavelengths (500–700 nm). In the same regions in UV-vis spectra of SBA-16, any absorption peaks are not observed. While in the CuTCIPP@SBA-16 spectrum, sorlet band and the Q bands are similar to the spectrum of pure CuTCIPP. The intension decreased and encapsulation of CuTCIPP by SBA-16 may cause lowering the intention because porphyrin is now surrounded by interior surface of SBA-16.

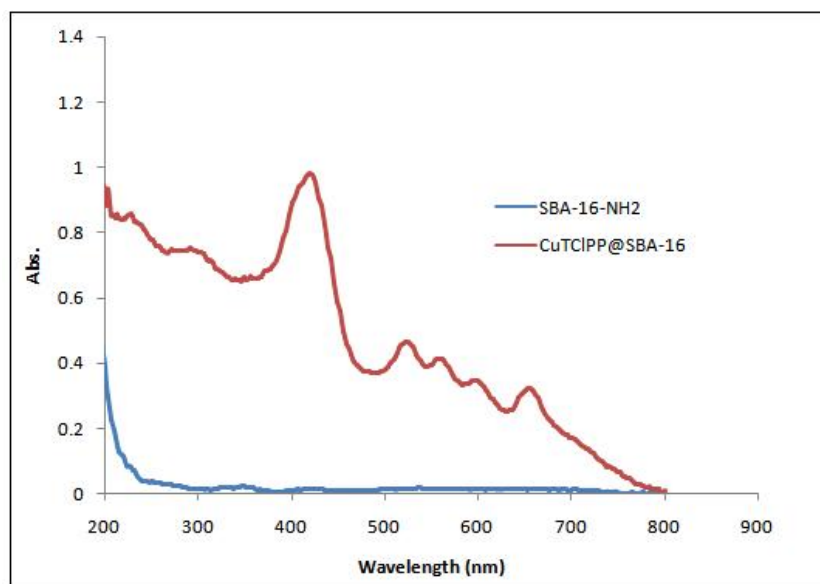


Fig. 2. The UV-vis spectra of SBA-16 and CuTCIPP@SBA-16

3.3. Nitrogen adsorption-desorption

Structural characteristics of the solid materials are listed in Table 1. A decrease of specific surface area from 400 m²/g to 328 m²/g corresponding to a decrease of the pore volume from 0.3 cm³/g to 0.26cm³/g may indicate a successful incorporation of porphyrin to the walls of SBA-16. Therefore, there is enough space for oxidizing the organic compounds via formation of active species.

Table 1. Structural Properties of the Mesoporous Silica SBA-16-NH₂ and CuTCIPP@SBA-

16

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (Å)
SBA-16-NH ₂	400	0.3	4.5
CuTCIPP@SBA-16	328	0.26	4.1

3.4. Photocatalytic activity

The results of oxidation of cyclohexene using TBHP as oxidant and acetonitrile as solvent in the presence of the resultant catalysts are summarized in Table 2.

Table 2. Catalytic oxidation of cyclohexene by TBHP in the presence of supported metalloporphyrin catalysts

Catalyst	Cyclohexene Conversion ^c /%	Epoxide selectivity /%	Ketone selectivity/%	Alcohol selectivity /%
SBA-16-NH ₂	-	-	-	-
CuTCIPP@SBA-16	76	5.9	93	1.1

The blank experiment with pure support (SBA-16) did not show any oxidation products. This obviously indicates that metalloporphyrin complexes encapsulated in SBA-16 play the main role in the catalytic activity. The catalyst displayed significant activity on cyclohexene oxidation reactions. According to the data of Table 2, allylic oxidation favors over epoxidation and 2-cyclohexene-1-one appears as the main product which points to the high selectivity. This is a remarkable and multifaceted substance with good application in the synthesis of variety of chemical products like pharmaceuticals and perfumes. The selectivity pattern expresses that attack to the activated C-H bond is more preferable than C=C bond under our reaction conditions. Also on the basis of reported literature [6], it shows the metalloporphyrin species are almost immobilized into the internal pore wall surface of SBA-16.

4. Conclusions

Porphyrins are the most widely studied catalysts for homogeneous selective oxidation alkenes. An important area of research into their catalytic properties is associated with immobilization of the porphyrin onto a solid support, in order to make the catalyst easier to handle and to separate from the reaction medium, as well as possibly stabilize and/or modify the catalytic performance.

Acknowledgements

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References

- [1] H. Liu, X.B. Shao, M.X. Jia, et al. *Tetrahedron* 61 (2005) 8095.
- [2] V. Meynen, P. Cool, E.F. Vansant, *Microporous and Mesoporous Materials* 125 (2009) 170–223.
- [3] T.W. Kim, R. Ryoo, M. Kruk, K.P. Gierszal, M. Jaroniec, S. Kamiya, O. Terasaki, J. *Phys. Chem. B* 108 (2004) 11480.
- [4] F. Bedioui, *Coord. Chem. Rev.* 144 (1995) 39–68.
- [5] M. Silva, M.E. Azenha, M.M. Pereira, H.D. Burrows, M. Sarakha, C. Forano, M.F. Ribeiro, A. Fernandes, J. *Applied Catalysis B*. 100 (2010) 1-9.
- [6] Serwicka EM, Mokaya R, Poltowicz J, Jones W (2002) *Chem Phys Chem* 3:892