Catalytic Oxidation of Cyclohexene with Hydrogen Peroxide over Cu(II)-Cyclam-SBA-16 Catalyst

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A copper cyclam-type complex was successfully immobilized onto mesoporous silica SBA-16. Characterization by NIR spectroscopy and TGA analysis confirmed that copper cyclam complex is immobilized onto mesoporous SBA-16. The Cu(II)-Cyclam-SBA-16 was proven to be a good catalyst for oxidation reaction of cyclohexene with conversion up to 77.8% after 13 h reaction and providing a high selectivity to cyclohexenol and 3-hydroperoxycyclohex-1-ene. The results suggest that the copper species play a major role as catalyst *via* reversible redox cycles as proven by cyclic voltammetry analysis.

Key Words : Oxidation, Copper, Cyclam, SBA-16

Introduction

Immobilization of homogeneous transition metal complexes and organic functional groups onto inorganic porous material offer merits of high catalytic activity and stability, and several other benefits of catalysis like easy separation and reusability. Various strategies such as encapsulation in zeolites,[1,2] immobilization in porous alumina,[3] immobilization in mesoporous silica[4] and grafting on polymers or porous carbon[5,6] have been developed in terms of heterogenization of homogeneous catalysts. Among various kinds of the reported heterogeneous supports, ordered mesoporous silicas have applied for many applications in the field of heterogeneous catalysis due to their well-defined and highly accessible pore sizes and large surface areas.[7] SBA-16 appears to be one of the best candidates for catalytic support or absorbent applications because of possessing uniformly large pore sizes, high surface area, good thermal stability due to thick wall, economical synthesis with inexpensive silica sources, and three dimensional large pores.[8-10]

Copper-ion based catalysts have received much attention because of wide use in many catalytic reactions.[4,6,11-14] However, up to now, only a few studies have been reported on the utilization of copper cyclam complex immobilized mesoporous silica. The cyclam has been well known as macrocyclic ligand that can accommodate and stabilize various high oxidation state transition metal cations.[15,16] Cyclam type macrocyclics also offer several advantages when applied as ligands such as: (1) enhancing the metal complex kinetic and thermodynamic stabilities compared to its open chain ligand counterpart; (2) giving underlying planar or nearly planar ring system around the metal center; (3) leaving two axial coordination sites relatively free for the substrate molecules or ions; and (4) host for a wide range of transition metals. Moreover, immobilization of metal cyclam complex onto mesoporous silica will give strong interactions preventing leaching of the active centers from the support and simplicity of the catalyst preparation.

Oxidation reaction of hydrocarbons resulting oxygen containing compound is important and useful reaction in the chemical industry.[17,18] Finding of new selective oxidation catalysts is one of the most hot topics in this field in the last few years. In this paper, we report the synthesis of copper cyclam complex immobilized SBA-16 catalyst for oxidation reaction of cyclohexene. Immobilization of copper cyclam complex onto SBA-16 offers some attractive features such as (1) easy separation of the catalyst from the reaction system; (2) minimization of catalyst deactivation by site isolation; (3) minimization of active site lost by covalent grafting on the host; and (4) easy preparation of the catalyst system. Properties of the catalyst were studied by various techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM), UV-Vis-Near-IR spectroscopy (NIR) and surface area measurements. The redox property of the copper ion was investigated using cyclic voltammetry (CV).

Experimental Procedure

Raw Materials. The surfactant F127 triblock copolymer (poly(ethyleneoxide)-poly(propyleneoxide)-poly(ethyleneoxide)/EO$_{106}$PO$_{70}$EO$_{106}$; MW12600; BASF) was used as the template. Sodium metasilicate nona hydrate (Na$_2$SiO$_3$·9H$_2$O; Sigma Aldrich) and 3-chloropropyl triethoxysilane/CPTS (Cl(CH$_2$)$_3$Si(OEt)$_3$; Aldrich) were used as silica and chloropropyl group sources, respectively. CuCl$_2$·6H$_2$O and hydrochloric acid were purchased from Daejung Chemical Company. All the chemicals were used as received without further purification. The tetraazamacrocycle (cyclam) was synthesized according to the reported procedure.[15]

Synthesis of SBA-16. Mesoporous silica SBA-16 was synthesized according to following procedure: 16.0 g of 10% (w/w) aqueous solution of F127 was poured into 26.6 g distilled water followed by 4.36 g of sodium metasilicate (Na$_2$SiO$_3$·9H$_2$O) with vigorously stirring to get clear solution. Then, 13.0 g of concentrated hydrochloric acid (37.6%)

was quickly added into the solution. The mixture was aged with stirring at 313 K for 1 hour. The obtained gel was subjected to microwave digestion (CEM Corporation. MARS-5) under static conditions at 373 K for 2 h with operating power of 300 W (100%). To remove the template from the crystallize SBA-16. the powder was calcined in the oven at 773 K for 5 h.[19]

Synthesis of Cu(II)-Cyclam-SBA-16. Cu(II)-Cyclam-SBA-16 was prepared by anchoring cyclam to mesoporous silica according to the following procedure: a mixture of SBA-16 and chloropropyl triethoxy silane in toluene was refluxed at 363 K with stirring for 8 h. After filtration and drying. chloropropyl-SBA-16 was added to cyclam and refluxed at 363 K in acetonitrile and triethylamine. Resulting powder was added to CuCl$_2$·6H$_2$O solution in ethanol and refluxed for 8 h. Sample was filtered and washed with ethanol and deionized water to remove excess of CuCl$_2$ (Scheme 1).

Catalytic Reaction. The oxidation of cyclohexene was carried out under vigorous stirring in Pyrex batch reactor in thermal reactor system (Eyela Chemi Station). In a typical run. a mixture of 100 mg catalyst. a 10 mmol olefin, 10 mL of acetonitrile. and 20 (or 40) mmol hydrogen peroxide (35% in water) were introduced to the reaction vessel and heated at 60 °C with constant stirring. The aliquots of the reaction mixture were withdrawn and subjected to GC analysis (Agilent 6890N, HP-5 capillary column. FID detector). GC-MS analysis of the products was performed on a HP 6890N chromatograph equipped with MS 5973N and a 30 m capillary column HP-5MS.

Characterization. The crystallinity of the samples was measured using powder X-ray powder diffraction (XRD) patterns. which were obtained on a Rigaku diffractometer using CuKα radiation (λ = 0.1547 nm). BET measurements including surface area and pore volume were performed using a Micromeritics porosimeter (model ASAP-2400). The samples were degassed at 300 °C for 3 h. UV-Vis-NIR diffuse reflectance spectra were measured with a Solidspec 3700 UV-Vis-NIR spectroscopy. The NIR spectra were recorded in the reflectance mode at room temperature. TGA and cyclic voltammetry (CV) analysis were performed using Bruker AXS TG-DTA2000SA and Epsilon workstation. respectively.

Results and Discussion

Synthesis of copper cyclam complex immobilized SBA-16 was started from the synthesis of pure SBA-16. Micro-

wave irradiation was applied as a heating source throughout the hydrothermal aging treatment in order to achieve the potential advantages of microwave synthesis such as rapid and homogeneous heating, homogeneous nucleation and fast crystallization, phase selectivity. and uniform particle size and morphological control.[20,21] As illustrated in Scheme 1, copper cyclam complex was introduced via covalently bond grafting method to ensure that the complex will not leach out during catalytic application and the copper cyclam complex should be located in the cages of SBA-16. By grafting via cyclam ligand. copper species can allow to stay as single cation in each cyclam macrocyclic and act as single site catalyst rather than bulk catalyst system.

Figure 1 illustrates the powder low-angle XRD patterns of SBA-16 and after immobilization of copper cyclam complex. The patterns show a characteristic sharp diffraction peak at low scattering angle 2, corresponding to d100 for typical type of mesoporous silica SBA-16. However Cyclam-SBA-16 samples show a decrease in the ordering peak compared to the pure SBA-16 samples. The diminished peak of the material after immobilization of cyclam is due to some pore blocking. Even though the second peak was diminished, structure of the support was not collapse at all proved by the sharp and high intense d100 plane peak. Further, evidence of high ordered mesostructured was
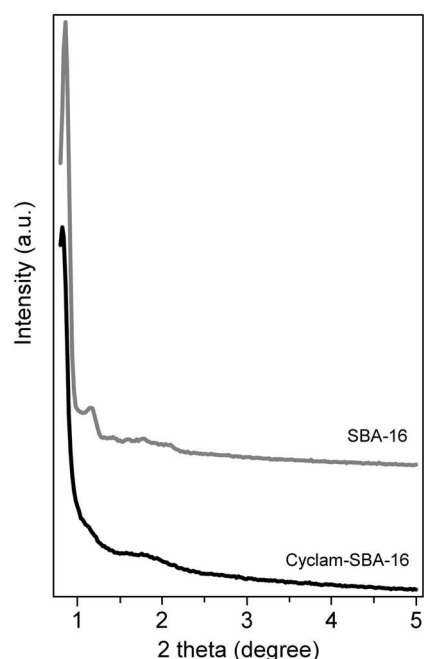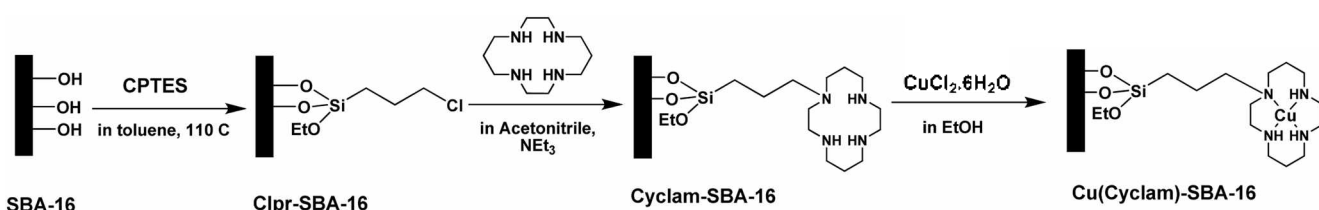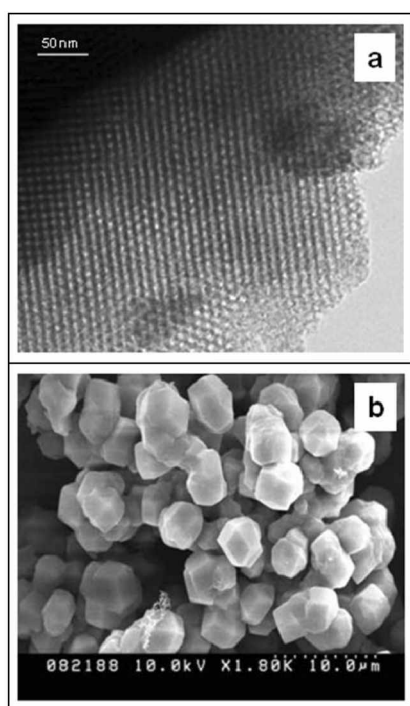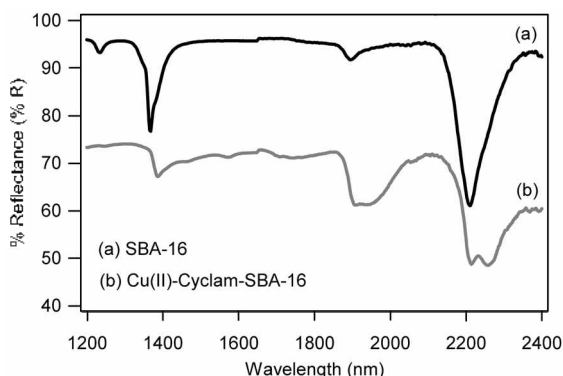

Figure 1. XRD patterns of pure SBA-16 and Cyclam-SBA-16.

Scheme 1. The synthesis route used in preparation of Cu(II)-Cyclam-SBA-16.

Figure 2. (a) TEM image of pure SBA-16; and (b) SEM image of pure SBA-16.

Figure 3. NIR spectra of pure SBA-16 and Cu(II)-Cyclam-SBA-16.

provided by TEM image. Figure 2 shows TEM (a) and SEM (b) images of SBA-16. The TEM image shows that pore structure of the sample can be explained with an *Im3m* cubic structure in good agreement with the XRD data. However, the SEM image revealed that sample is composed of uniformly sized particles and possesses three-dimensional (3D) cubic type morphology.

The presence of the tethered cyclam was proved by NIR spectroscopy (Fig. 3). The NIR spectrum of Cu(II)-Cyclam-SBA-16 showed three strong bands at around 2214, 1900, and 1370 nm. corresponding to the vibrational transitions of surface hydroxyl groups.[22] Absorption bands at 1945 (as a shoulder) and 1456 nm (as a shoulder) could be assigned to the adsorbed H_2O on the SBA-16 surface. Absorption bands at around 2265-2350 and 1736 nm could be assigned to the combination ($\nu + \delta$) bands of the CH_2 moiety stretching vibration (ν) and bending (δ) mode and the first overtone band of CH_2 moiety stretching vibration. respectively. The
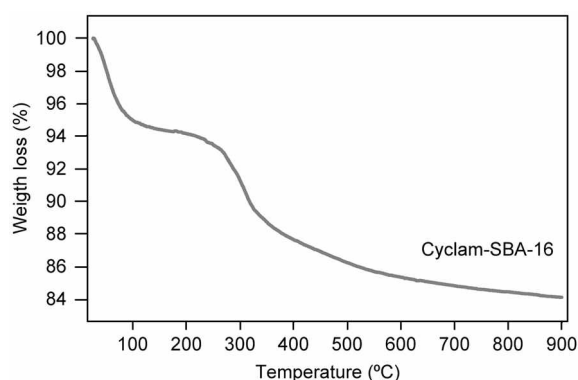
Figure 4. TGA profile of the Cyclam-SBA-16.

chemical bonding of cyclam with chloro groups was confirmed with the appearance of the absorption band for the secondary amine of cyclam at 1572 nm.[23] The amount of tethered Cyclam in the SBA-16 was estimated by TGA measurements. The TGA profile of Cyclam-SBA-16 is illustrated in Figure 4. The weight loss at temperatures below 393 K would be attributed to the loss of adsorbed water. However. the weight loss at 473-773 K can be assigned to the decomposition of Cyclam and the anchoring groups. By calculating the weight loss on second region, the value of the grafted cyclam is 0.42 mmol g^{-1}. Further, we can also calculate the number of active sites. Since one copper cation interacts with one molecule of cyclam, the amount of active site is found to be 0.42 mmol g^{-1}.

The nitrogen adsorption isotherms and BJH pore size distribution of the pure SBA-16 and Cu(II)-Cyclam-SBA-16 are shown in Figure 5. These isotherms had the "hysteresis loop" resembling the type IV isotherm, typical in mesoporous silica materials having large cage and small opening pore. BET surface areas measured from these isotherms were 634 and 415 m^2/g for SBA-16 and Cu(II)-Cyclam-SBA-16. respectively. However. the pore volume of SBA-16 and Cu(II)-Cyclam-SBA-16 were 0.58 and 0.23 cm^3/g. The decreasing of surface area and pore volume is due to the presence of Cu(II)-Cyclam complex in the mesopore. The physicochemical characteristics are listed in Table 1.
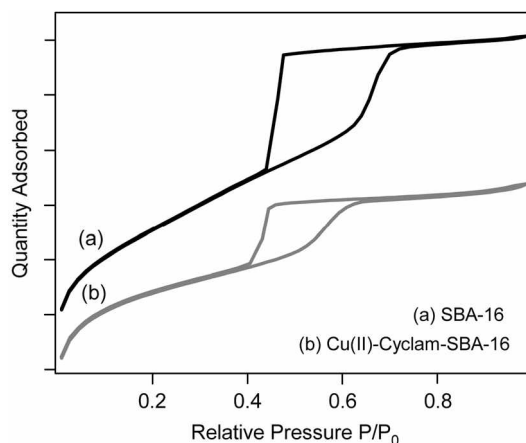

Figure 5. Nitrogen adsorption-desorption full isotherms for pure SBA-16 and Cu(II)-Cyclam-SBA-16.

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Table 1. Physicochemical properties of the pure SBA-16 and Cu(II)-Cyclam-SBA-16

| Sample	S_{BET} (m^2g^{-1})	Pore volume (cm^3g^{-1})	Pore size[a] (nm)
SBA-16	634	0.58	3.61
Cu(II)-Cyclam-SBA-16	415	0.23	3.18

[a]Pore size distributions were calculated from the desorption branch by using BJH method.
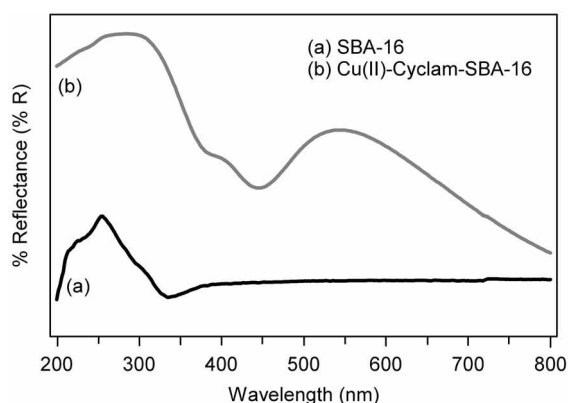
Figure 6. UV spectra of pure SBA-16 and Cu(II)-Cyclam-SBA-16.

Diffuse reflectance UV-vis spectroscopy was used to characterize the effectiveness of loading of copper species and to observe the chemical nature and coordination state of the copper ions. The UV-vis spectra of copper cyclam complex are shown in Figure 6. The spectra were recorded in diffuse reflectance (DRS) mode. The copper cyclam complex anchored SBA-16 catalyst consisted of typical of square planar copper complexes, as it exhibits a absorption at λ_{max} 547 nm in an intense charge-transfer band, which corresponds to the low-energy part of the three unresolved d-d transitions $d_{xy} \leftarrow (d_{yz}, d_{xz}, d_{z^2})$.[24] The observed d-d transitions are in the range expected for Cu^{2-} species in an axially distorted octahedral (Jahn Teller Effect) environment.

To study redox behavior of entrapped Cu species in the copper cyclam complex immobilized SBA-16, cyclic voltammetry analysis was carried out. These cyclic voltammetry measurements were carried out using carbon paste electrode modified with Cu(II)-Cyclam SBA-16 sample. The electrolyte used in this measurement was 0.1 M LiClO₄ solution in acetonitrile. The oxidation step was recorded first followed by reduction step. The sample showed two reversible redox peaks at 0.28 and −0.17 V vs. SCE, which correspond to the Cu(III)/Cu(II) and Cu(II)/Cu(III) peaks, respectively (Fig. 7). Cu(II)-Cyclam SBA-16 sample showed a high intensity which means that copper species in this sample can be easily oxidized and reduced (reverse). These reversible changes of Cu oxidation states are important in the catalytic oxidation reactions because oxidation reaction catalyzed by metal ions mainly depend on the ability of the ion to be oxidized and reduced.

The catalytic activity of the obtained Cu(II)-Cyclam-SBA-16 was investigated for oxidation of cyclohexene with hydrogen peroxide as the oxidant. The copper-catalyzed
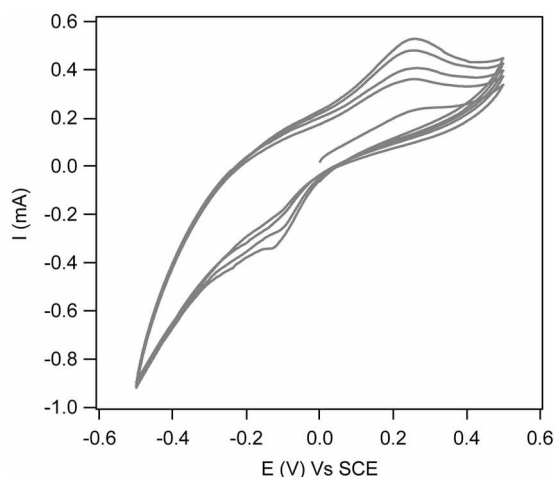

Figure 7. Cyclic voltammogram of the carbon paste electrode modified with Cu(II)-Cyclam-SBA-16.

oxidation of cyclohexene with hydrogen peroxide can promote either the oxidation of the double bond to produce epoxides or the allylic oxidation leading to allylic hydroperoxides.[25] The selectivity and activity results of Cu(II)-Cyclam-SBA-16 catalyst on the oxidation of cyclohexene with H₂O₂ have been given in Table 2. As shown in the Table 2, the conversion of cyclohexene reached 47.3% with 38.2% selectivity to the hydroxy-cyclohexene after 4 h of reaction time and the other products were found to be epoxide, cyclohexenol and cyclohexenone. As comparison, the reaction over homogeneous Cu-cyclam complex catalyst has been carried out. The similar result could be observed. It means catalytic properties of Copper cyclam complex are same ven in homogeneous condition or in the heterogeneous condition. However, when the copper cyclam complex homogeneous catalyst was used, the separation of the catalyst from the mother liquor is quite difficult and could not be recycled. It also proved the advantages of anchoring copper cyclam onto mesoporous channel of SBA-16. In Figure 8, cyclohexene conversion and selectivity is plotted as function of reaction time. It can be seen that cyclohexene conversion increases with time while the selectivity to alcohol decreases. According to our previous study,[18] the redox reaction of cyclo-olefin substrates with the copper-cyclam-SBA-16 proceeded through a one-equivalent change in the oxidation state of the Cu(III) to Cu(II), generating a HOO free-radical intermediate. The resulting Cu(II) species

Table 2. Products distribution of cyclohexene oxidation with hydrogen peroxide over Cu(II)-Cyclam-SBA-16

Entry	H_2O_2 ratio	Time (h)	Conversion (%)	Product distribution (%)			
				-OOH	-OH	=O	epoxide
1	2:1	4	21.3	31.7	38.2	2.9	8.2
2	2:1	13	41.5	33.4	34.9	3.4	4.7
3	4:1	4	47.3	38.2	26.4	4.1	3.6
4	4:1	13	77.8	37.6	13.7	7.3	1.3
5[a]	2:1	4	45.1	36.3	31.4	4.2	4.5

[a]Cu-Cyclam complex (homogeneous) was used as catalyst.
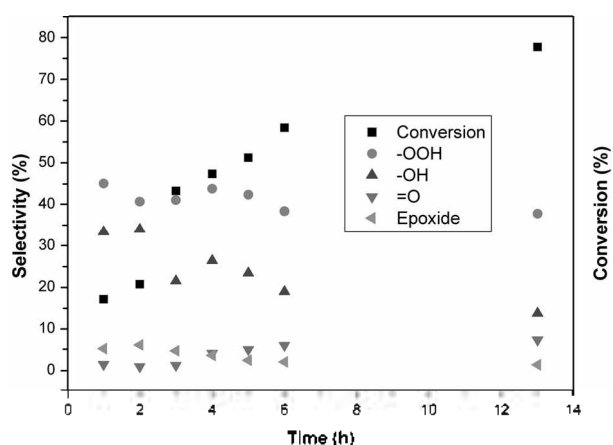
Figure 8. Effect of reaction time on conversion and product distribution on the cyclohexene oxidation with H_2O_2 over Cu(II)-Cyclam-SBA-16.

subsequently form a complex with the resulting HOO· through the formation of Cu(III) hydroperoxo complex. facilitating the reaction between cyclo-olefins and the HOO·. The reaction between the resulting Cu(cyclam)OOH complex and the cycloolefins could occur *via* two routes. hydrogen abstraction and hydroperoxy radical addition to the double bond, producing allylic radicals and β-hydroperoxy-alkyl radicals. respectively. The allylic radicals reacted with the Cu(cyclam)OOH complexes to yield allylic hydroperoxides, whereas the β-hydroperoxyalkyl radicals followed by the unimolecular decomposition gave epoxides and hydroxyl radicals. Ji *et al.* proposed that hydroperoxy product as major product in this reaction is formed mainly *via* further oxidation of the epoxide and alcohol.[26] This phenomenon was also observed by putting different ratio of hydrogen peroxide. By increasing the H_2O_2 ratio, the conversion of cyclohexene increased from 21.3% to 47.3% as shown in Table 2. Moreover, on increases in H_2O_2 ratio resulted an increase selectivity of hydroperoxy and decrease in the alcohol and epoxide product. It proved that hydroperoxy product is formed mainly *via* further oxidation of the epoxide and alcohol. Further. a leaching test was also performed. In the leaching test. catalyst was separated after 4 h of reaction and washed with acetonitrile. Right after washing. the same reaction was conducted. The catalyst showed similar activity (41% conversion) which indicates no significant loss of the active sites during reaction process.

Conclusions

The Cu(II)-Cyclam has been successfully immobilized onto the porous SBA-16 which showed a high catalytic activity in the oxidation of cyclohexene with hydrogen peroxide. The reaction provided gave high selectivity to cyclohexenol and 3-hydroperoxycyclohex-1-ene with conversion up to 77.8% after 13 h reaction.

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