Immobilization of Cu-chelate onto SBA-15 for partial oxidation of benzyl alcohol using water as the solvent

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Abstract Bis(8-quinolinolato)copper(II) complex immobilized onto SBA-15 catalyst has been synthesized through a stepwise procedure. The characterization results indicated that the BET surface area, total pore volume, and average pore width decrease after stepwise modification of SBA-15, while the structure stays intact. Catalytic tests showed that CuQ_2 -SBA-15 catalyzes the oxidation reaction well with 32.5 % conversion of benzyl alcohol and 81.8 % selectivity to benzal-dehyde when water is used as the solvent. In addition, homogeneous catalyst bis(8-quinolinolato)copper(II) exhibits very bad catalytic behavior using water as the solvent.

Keywords SBA-15 · 8-Quinolinol · Copper · Benzyl alcohol · Benzaldehyde

Introduction

The selective oxidation of alcohols is of fundamental importance in synthetic organic chemistry because benzaldehyde is a very important organic intermediate in the perfumery, pharmaceutical, dyestuff, and agrochemical industries [1]. Catalytic oxidation of alcohol with eco-friendly oxidants such as O_2 and H_2O_2 caters to both environmental and industrial needs. Up to now, most efforts have been devoted to metal-catalyzed alcohol oxidations by using transition metals such as titanium [2], vanadium [3], chromium [4], manganese [5], iron [6], cobalt [7], nickel [8], copper

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[9], silver [10], gold [11], ruthenium [12], palladium [13], bimetallic ruthenium-copper [14], palladium–gold [15], and manganese–gold [16]. Thereinto, the metal species as active center were immobilized or anchored onto an appropriate support in order to develop optimized heterogeneous catalysts for alcohol oxidations.

Compared with metal oxides such as TiO_2 , Al_2O_3 , and CeO_2 , mesoporous silicate SBA-15 exhibits specific physical and chemical properties (such as large BET surface area, tunable surface chemistry) and therefore has been used widely as supports in selective oxidation reactions [17–22]. The surface chemistry of SBA-15 is a key factor to their catalytic performance. Usually, the SBA-15 material exhibits large amounts of surface hydroxyl groups, which could be modified and incorporated active sites to efficiently catalyze the target reaction.

Water is an ideal green solvent for the vast mild catalytic transformations from both economic and environmental perspectives, while most organic solvents are corrosive and hazardous in nature and result in much serious pollution and cause wasting in the economy [23]. To meet the increasing demand for benzaldehyde and also satisfy environmental requirements, considerable efforts have been made for producing benzaldehyde using water as a solvent.

In the current work, the bis(8-quinolinolato)copper(II) complex was chelated onto aminopropyl-functionalized SBA-15 for the selective oxidation of benzyl alcohol to benzaldehyde. The effects of parameters, including the types of solvent, the reaction temperature, the reaction time, the amount of H_2O_2 , and the recyclability of the catalyst have been investigated in detail.

Experimental

Materials

SBA-15 was synthesized according to [24]. In a typical synthesis, 2 g (6 mmol) of Pluronic P123 [(EO)20(PO)70(EO)20, Aldrich] was dissolved in 15 ml of H₂O and 60 ml of 2 M HCl, and then 4.68 ml (0.02 mol) of TEOS was added under stirring at 40 °C. The molar composition of the mixture was TEOS:0.017P123: 6HCl:192H₂O. Afterwards, the resultant mixture was maintained under stirring at 40 °C for 24 h, followed by aging under static condition at 100 °C for 24 h. Finally, the solid product was recovered by filtration and washed with distilled water. After being air-dried at ambient temperature overnight, it was calcined at 550 °C for 8 h to remove the template. The obtained sample was denoted as SBA-15.

Aminopropyl-functionalized SBA-15 material APS-SBA-15 was synthesized by post-synthetic grafting method (Fig. 1) [25]. SBA-15 was first dried under vacuum at 100 °C for 5 h. Then, 0.5 g (8.3 mmol) of dried SBA-15 was refluxed in dried toluene with 0.1 ml (0.4 mmol) APTES (3-aminopropyltriethoxysilane) for 10 h. Then the solid was filtered and washed abundantly with several solvents with different polarity (CH₂Cl₂, hexane, and ethanol) to remove the remaining unsupported APTES. The pale solid was dried overnight. The obtained samples were denoted as APS-SBA-15.



Fig. 1 Synthetic route for CuQ₂-SBA-15

Bis(8-quinolinolato)copper(II) was synthesized as follows. In a typical synthesis, 1.45 g (10 mmol) of 8-quinolinol ligand was dissolved in 20 ml THF, followed by the dropwise addition of a solution of 1.0 g (5 mmol) $Cu(CH_3COO)_2 \cdot H_2O$ in 10 ml THF at reflux temperature. The resultant solution was stirred and refluxed for 2 h. After cooling, the solid product was separated by filtration and denoted as CuQ_2 .

 CuQ_2 -SBA-15 was prepared by dissolving CuQ_2 (0.1 g, 0.2 mmol) in 10 ml CHCl₃ and by stirring the above APS-SBA-15 (0.1 g) in suspension under reflux conditions for 12 h. The glaucous solid thus formed during stirring was filtered, washed with methanol using Soxhlet, and dried under vacuum (Fig. 1).

For comparison, Cu-SBA-15 was prepared through impregnating SBA-15 with copper acetate precursor and then drying and calcining at 500 °C for 4 h.

Methods

Powder X-ray diffraction patterns (XRD) were obtained on a Rigaku D/max-2200 (0.2° /min) using Cu-K α radiation (40 kV, 40 mA). N₂ adsorption–desorption isotherms were measured with a Micromeritics ASAP 2010 system at liquid N₂ temperature. Before measurements, the sample was outgassed at 130 °C for 6 h. The BET surface area was calculated using the Brunauer–Emmett–Teller (BET) method. Infrared spectra (IR) of the samples were recorded in KBr disks using a NICOLET impact 410 spectrometer. Diffuse reflectance UV–Vis spectra were recorded from 200 to 800 nm on a Shimadzu UV-3600 spectrophotometer using BaSO₄ as a reference. Metal content was estimated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis conducted on a PerkinElmer

emission spectrometer. Elemental analyses of nitrogen were obtained with a VarioEL CHN elemental analyzer.

Catalytic tests

The catalyst (0.05 g), benzyl alcohol (3 ml, 28.8 mmol), 30 % H_2O_2 (4 ml) and solvent (water, acetone, or acetonitrile) (10 ml) were placed into a reaction vessel. The resulting mixture was vigorously stirred at 80 °C under nitrogen. After certain times, the catalysts were separated by filtration. The products were analyzed with a gas chromatography (Shimadzu, GC-8A) equipped with a XE60 capillary column and FID detector.

Results and discussion

The powder XRD patterns of the synthesized SBA-15, APS-SBA-15, and CuQ₂-SBA-15 are shown in Fig. 2. For all of the samples, three well-resolved peaks can be clearly observed, indicating that the prepared materials contain well-ordered hexagonal arrays of one-dimensional channel structure [24]. However, the decrease in the intensity of the (1 1 0) and (2 0 0) peaks for CuQ₂-SBA-15 is observed, suggesting the formation of a less-ordered mesostructure.

 N_2 adsorption-desorption isotherms and pore-size distributions of SBA-15, APS-SBA-15, and CuQ₂-SBA-15 are depicted in Fig. 3. These isotherms are classified as type IV, with a sharp capillary condensation step at high relative pressure and H1 hysteresis loop, which reveals the presence of large channel-like pores in a narrow range of size [25]. The BET surface area, pore volume, and pore diameter of SBA-15, APS-SBA-15, and CuQ₂-SBA-15 are presented in Table 1. The BET surface, the total pore volume area and the average pore width significantly decrease after functionalization of CuQ₂ onto APS-SBA-15.

FT-IR spectra of SBA-15, APS-SBA-15, and CuQ₂-SBA-15 are presented in Fig. 4. In all cases, the typical Si–O–Si bands are observed nearly at 1,080, 802, 464 cm⁻¹ due to the formation of SBA-15 silica framework [26]. The bands around 3,430 and 1,633 cm⁻¹ are mainly aroused by the bend vibration of O–H and physically adsorbed water molecular. After functionalization of SBA-15, peaks centered at 1,627 m (C=C), 1,594 s (C=N), 1,550 vs. (aromatic), 1390 s (C–N), 1087 w (C–O), 819 and 769 m (C–H) were observed suggesting that CuQ₂ has been successfully grafted onto APS-SBA-15.

Figure 5 exhibits UV–Vis spectra of SBA-15, CuQ₂, and CuQ₂-SBA-15. Compared with SBA-15, the absorption bands in the range of 200-400 nm are observed in the hybrid material CuQ₂-SBA-15, which are assigned to $n-\pi^*$, $\pi-\pi^*$ ligand charge transfer [27], suggesting that the bis(8-quinolinolato)copper(II) has been chelated with APS-SBA-15. The d–d transitions at ca. 430 nm are observed for CuQ₂-SBA-15, indicating that bis(8-quinolinolato)copper(II) complexes have been incorporated onto the surface of SBA-15. In addition, compared with the spectrum of the pure CuQ₂ complex, the intensity of absorbance peaks for CuQ₂-SBA-15 becomes weaker, while the two peak positions almost remain unchanged.



Fig. 2 XRD patterns of a SBA-15, b APS-SBA-15, and c CuQ₂-SBA-15



Fig. 3 N2 adsorption/desorption isotherms of a SBA-15, b APS-SBA-15, and c CuQ2-SBA-15

 Table 1
 Structural and textural parameters of the synthesized materials

Sample	$S_{\rm BET} (m^2 g^{-1})$	D _p (nm)	$V_{\rm p}~({\rm cm}^3~{\rm g}^{-1})$
SBA-15	892	8.9	1.30
APS-SBA-15	697	8.0	0.96
CuQ ₂ -SBA-15	213	5.2	0.47

 $S_{\rm BET}$ surface area, $D_{\rm p}$ average pore width, $V_{\rm p}$ total pore volume



Fig. 4 FT-IR spectra of a APS-SBA-15, b CuQ₂-SBA-15, and c CuQ₂



Fig. 5 UV-Vis spectra of a SBA-15, b CuQ₂, and c CuQ₂-SBA-15

Quantification of the functional group loaded in SBA-15 was performed for the materials using elemental analysis (CHN) and ICP-AES analysis (Table 2). The results show that molar ratio of N/Cu is close to 3/1, which indicating a Cu²⁺ ion chelating one APTES molecule and two 8-quinolinol molecules as shown in Fig. 1.

The catalytic performance of CuQ_2 -SBA-15 was carried out in the selective oxidation of benzyl alcohol with H_2O_2 as an oxidant. For comparison, the catalytic performances of homogeneous catalysts $Cu(CH_3COO)_2$ and CuQ_2 , and heterogeneous-supported catalyst Cu-SBA-15, were also investigated and the reaction data are listed in Table 3. It is obvious that the oxidation reaction cannot be carried out

Sample	С	Н	Ν	Cu
APS-SBA-15	2.86 (3.34)	0.86 (12.04)	1.0 (1)	_
CuQ2-SBA-15	6.19 (7.15)	0.53 (7.35)	1.01 (1)	0.71 (0.34)

Table 2 Elementary analysis and ICP-AES analysis results of APS-SBA-15 and CuQ2-SBA-15

The values in the brackets represent the molar ratio of C, H, N, and Cu

 Table 3
 Catalytic data of the benzyl alcohol oxidation over different catalysts

Catalyst	Conversion (%)	Selectivity (%)		
		Benzaldehyde	Benzoic acid	
No catalyst	Trace	_	_	
Cu(CH ₃ COO) ₂	2.5	60.3	39.7	
CuQ ₂	23.6	62.9	37.1	
Cu-SBA-15	28.5	80.2	19.8	
CuQ ₂ -SBA-15 (1st)	32.5	81.8	18.2	
CuQ2-SBA-15 (2nd)	32.0	81.2	18.8	
CuQ ₂ -SBA-15 (3rd)	32.1	81.3	18.7	

Reaction conditions: catalyst (0.05 g), benzyl alcohol (3 ml), H_2O_2 (4 ml), H_2O (10 ml), reaction time (6 h), and reaction temperature (80 °C)

without catalysts. In addition, the catalytic behavior of $Cu(CH_3COO)_2$ is the worst, over which only 2.5 % conversion can be achieved. Moreover, the catalytic behaviors of homogeneous catalyst CuQ_2 and supported catalyst Cu-SBA-15 are worse than that of CuQ_2 -SBA-15.

In order to get the optimal reaction conditions, different parameters such as reaction media, oxidant amount, reaction time, and temperature were investigated. The influence of reaction media on the catalytic performance was performed by using different solvents (water, acetone, and acetonitrile) and the results are shown in Table 4. It is interesting to note that CuQ_2 -SBA-15 catalyzes the oxidation reaction well when water is used as the solvent, followed by acetonitrile, while only 12.4 % conversion can be obtained when acetone is used as the solvent.

The temperature has a great influence on the catalytic performance. As shown in Table 4, low temperature causes very low benzyl alcohol conversion. For example, only 9.8 % of benzyl alcohol conversion can be achieved at 60 °C. Increasing the reaction temperature could synchronously raise the catalytic activity. However, too high of a reaction temperature might cause deep oxidation and thus increase the selectivity to benzoic acid.

The reaction time has some influence on the catalytic behavior. As can be seen from Table 4, the benzyl alcohol conversion gradually increased from 17.2 to 32.5 %, while the selectivity to benzaldehyde decreases step by step from 83.3 to 81.8 % by prolonging the reaction from 2 to 6 h, while further prolonging reaction time has relatively little influence on the benzyl alcohol conversion but results in the decrease of benzaldehyde selectivity.

Solvent	H_2O_2 (ml)	<i>T</i> (°C)	Time (h)	Conversion (%)	Selectivity (%)	
					Benzaldehyde	Benzoic acid
Water	4	80	6	32.5	81.8	18.2
Acetone	4	80	6	12.4	76.2	23.8
Acetonitrile	4	80	6	14.4	81.3	18.7
Water	4	60	6	9.8	84.7	15.3
Water	4	70	6	12.2	82.3	17.7
Water	4	90	6	35.9	70.9	29.1
Water	4	80	2	17.2	83.3	16.7
Water	4	80	4	23.0	82.5	17.5
Water	4	80	8	34.9	77.1	22.9
Water	2	80	6	13.5	85.6	14.4
Water	3	80	6	26.4	83.7	16.3
Water	5	80	6	35.8	72.0	28.0

 Table 4
 Catalytic data of the benzyl alcohol oxidation over CuQ₂-SBA-15

Reaction conditions: catalyst (0.05 g), benzyl alcohol (3 ml)

From the results of effect of different H_2O_2 amount on the benzyl alcohol oxidation in Table 4, it can be seen that the conversion of benzyl alcohol remarkably improves from 13.5 to 32.5 % after 6 h by increasing the H_2O_2 amount from 2 to 4 ml. It is also found that further raising the H_2O_2 amount has relatively little influence on the conversion but results in the reduction of the selectivity to benzaldehyde.

Much research has found that homogeneous catalysts showed high catalytic performance in organic solvent, while few works have focused on using water as the solvent. Actually, according to our results in Table 3, the homogeneous catalyst CuQ₂ shows bad catalytic behavior in water. This might be due to the worse solubility in water than in organic solvent. For example, Mahdavi and Mardani [28] investigated the effect of solvents on the oxidation of benzyl alcohol with TBHP in the presence of $[Mn(bipy)2]^{2+}/HMS$ and found that the best conversion (40.2 %) was achieved in the aprotic solvent acetonitrile, while the worst conversion (only 7.6 %) was obtained in the protic solvent ethanol after an 8-h reaction. In our catalytic system, the efficient synergistic effect between CuQ₂ complexes and the SBA-15 support is one of the reasons for the better catalytic performance CuQ₂-SBA-15 with water as solvent.

The recyclability and stability of CuQ₂-SBA-15 for benzyl alcohol oxidation with H_2O_2 as oxidant and water as solvent were investigated (Table 3). The solid catalyst was easily recovered by filtration after each reaction cycle, washed thoroughly with acetone and water, dried in the vacuum at 60 °C for 12 h, and reused for the subsequent cycles. The reused catalyst exhibited a negligible decrease in catalytic activity and selectivity in three consecutive runs.

Based on our experimental results and other related literature [2, 29, 30], a reasonable reaction mechanism for oxidation of benzyl alcohol with H_2O_2 over



Scheme 1 The mechanism of the conversion of benzyl alcohol to benzaldehyde and benzoic acid over ${\rm CuQ_2-SBA-15}$

 CuQ_2 -SBA-15 has been postulated in Scheme 1. Primarily, the Cu Lewis acid sites react with H_2O_2 to form Cu peroxo complex and the complex further reacts with CuQ_2 -SBA-15 to form Cu–O–Cu species, and then the Cu–O–Cu species oxidizes benzyl alcohol to release one CuQ_2-SBA-15 molecule and give an intermediate that leads to benzaldehyde and regenerate the active sites. The formation of benzoic acid may be caused by deep oxidation of benzaldehyde.

Conclusions

Novel heterogeneous catalyst CuQ_2 -SBA-15 has been synthesized by chelating CuQ_2 complexes onto aminopropyl-functionalized SBA-15. The characterization results demonstrate that the pore structure of SBA-15 remains intact after multiple synthetic procedures. In addition, detailed research was carried out to optimize the reaction conditions of benzyl alcohol oxidation over CuQ_2 -SBA-15. It is found that CuQ_2 -SBA-15 exhibits better catalytic performance with water as the solvent due to its unique pore structure of SBA-15 and efficient synergistic effect between CuQ_2 and the SBA-15 support.

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