A Copper(II) Schiff base complex immobilized onto SBA-15 silica for selective oxidation of benzyl alcohol

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Received: 16 November 2013/Accepted: 13 December 2013/Published online: 21 December 2013 © Springer Science+Business Media Dordrecht 2013

Abstract A copper(II) Schiff base complex has been immobilized onto SBA-15 silica through a stepwise procedure and tested as an oxidation catalyst. BET surface area, total pore volume and average pore width of the SBA-15 all decrease after stepwise modification of SBA-15, while the structure of the support remains intact. The molar ratio of Cu²⁺/Schiff base is ca. 1/2 in the synthesized material. Catalytic tests showed that the supported copper complex catalyzes the oxidation of benzyl alcohol with 30 % conversion and 89 % selectivity to benzaldehyde when water is used as the solvent.

Introduction

Selective oxidation of benzyl alcohol has been extensively studied, because benzaldehyde is a very important organic industrial intermediate in the production of perfumes, pharmaceuticals, dyestuffs and agrochemicals [1]. During the past decade, considerable effort has been put into the development of inexpensive, recyclable, highly active and selective metal-based catalysts to realize large-scale production of benzaldehyde. Although homogenous transition metal complexes exhibit high catalytic activity and selectivity in oxidation reactions, many inherent drawbacks hamper their industrial application, such as difficulties in the catalyst regeneration and product separation, deactivation of the catalysts by formation of dimeric peroxo- and μ -oxo species and the need to minimize heavy industrial

waste [2]. With the rapid development of catalyst separation and preparation technology, the encapsulation of various transition metal Schiff complexes on insoluble solid supports to allow for the heterogenization of homogeneous catalysis has become a widely employed method to address these problems [3].

In recent years, there have been a number of reports about the use of Cu-based catalysts for the oxidation of benzyl alcohol to benzaldehyde [4–14]. Ji et al. [5] reported that Ru–Mn–Fe–Cu–O was an efficient heterogeneous catalyst with high selectivity for benzyl alcohol oxidation using O₂ as oxidant. Mahdavi and Mardani prepared a series of Mn(II) bipy complexes with different loadings of Mn²⁺ supported on hexagonal mesoporous silica (HMS) for the oxidation of benzyl alcohol [6]. Spasiano et al. [7] synthesized TiO₂/Cu(II) to convert benzyl alcohol to benzaldehyde by photocatalytic oxidation. Meanwhile, to meet the increasing demand for benzaldehyde and satisfy environmental requirements, considerable effort has been put into the production of benzaldehyde using water as a solvent.

In the current work, a copper(II) Schiff complex was grafted onto SBA-15 for the selective oxidation of benzyl alcohol to benzaldehyde. The effects of various parameters, including the type of solvent, reaction temperature, reaction time, the amount of H_2O_2 and the recyclability of the catalyst, have been investigated.

Experimental

Catalyst preparation

SBA-15 was synthesized according to the literature [15]. In a typical synthesis, Pluronic P123 [$(EO)_{20}(PO)_{70}(EO)_{20}$, Aldrich] (2 g) was dissolved in a mixture of 15 mL of H₂O

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Fig. 1 Synthetic route for Cu-S-SBA-15

and 60 mL of 2 M HCl, and then tetraethoxysilane (TEOS) (4.68 mL, 0.02 mol) was added under stirring at 40 °C. The molar composition of the mixture was thus TEOS: 0.017 P123: 6 HCl: 192 H₂O. Afterward, the resultant mixture was stirred at 40 °C for 24 h, followed by aging under static conditions at 100 °C for 24 h. Finally, the solid product was recovered by filtration and washed with distilled water. After air-drying at ambient temperature overnight, it was calcined at 550 °C for 8 h to remove the template. The resulting sample was denoted as SBA-15 (1.0 g, yield of 83 %).

The Schiff base organosilane reagent was prepared as follows; (3-aminopropyl)triethoxysilane (APTES) (1.33 g, 6 mmol) was refluxed with salicylaldehyde (0.73 g, 6 mmol) in ethanol (10 mL) under N₂ atmosphere at 80 °C for 3 h. The solvent was removed by rotary evaporation under reduced pressure, giving 1.9 g of the Schiff base organosilane product (yield of 92 %).

S-SBA-15 was synthesized by a post-synthetic grafting method. SBA-15 was first dried under vacuum at 100 °C for 5 h. Then, a portion of dried SBA-15 (0.5 g) was refluxed in dried toluene (10 mL) with the Schiff base organosilane (0.14 g, 0.4 mmol) for 10 h. The solid was filtered off and washed with copious amounts of CH_2Cl_2 , hexane and ethanol to remove the remaining unsupported Schiff base organosilane reagent. The resulting yellowish solid, denoted as S-SBA-15, was dried overnight to give 0.45 g of product (yield of 87 %).

Cu–S-SBA-15 was prepared by adding a solution of $Cu(NO_3)_2$ ·3H₂O (0.04 g, 0.17 mmol) in methanol (10 mL) to solid S-SBA-15 (0.122 g) and stirring the suspension at

room temperature for 12 h. The green solid thus formed was filtered off, washed with methanol using a Soxhlet apparatus and dried under vacuum to give 0.11 g Cu–S-SBA-15 (yield of 87 %) (Fig. 1).

Catalyst characterization

Powder X-ray diffraction patterns (XRD) were obtained on a Rigaku D/max-2200 diffractometer $(0.2^{\circ}/\text{min})$ using Cu Ka radiation (40 kV, 40 mA). N₂ adsorption–desorption isotherms were measured with a Micromeritics ASAP 2010 instrument at liquid N₂ temperature. Before measurements, the sample was outgassed at 130 °C for 6 h. The surface area was calculated using the Brunauer–Emmett–Teller (BET) method. SEM photographs were taken on an FE-SEM XL-30 field emission scanning electron microscope. IR spectra were recorded in KBr disks using a NICOLET impact 410 spectrometer. Metal content was estimated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis using a Perkin–Elmer emission spectrometer. Elemental analyses were obtained with a VarioEL CHN elemental analyzer.

Catalytic tests

A mixture of the catalyst (0.05 g), benzyl alcohol (3 mL), 30 % H_2O_2 (4 mL) and solvent (water, acetone or acetonitrile, 10 mL) was vigorously stirred at 80 °C under nitrogen. After the required reaction time, the catalyst was separated by filtration. The products were analyzed with a



Fig. 2 XRD patterns of a SBA-15, b S-SBA-15 and c Cu–S-SBA-15



Fig. 3 SEM image of Cu-S-SBA-15

gas chromatograph (Shimadzu, GC-8A) equipped with a XE60 capillary column and FID detector.

Results and discussion

XRD and SEM characterization

The powder XRD patterns of the synthesized SBA-15, S-SBA-15 and Cu–S-SBA-15 are shown in Fig. 2. For each 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 [15]. However, a decrease in intensity of the (1 1 0) and (2 0 0) peaks for Cu–S-SBA-15 is observed, suggesting the formation of a less ordered mesostructure.

The SEM image of the synthesized Cu–S-SBA-15 (Fig. 3) shows a worm-like structure, indicating that the structure of the SBA-15 support has remained intact [15].



Fig. 4 N₂ adsorption/desorption isotherms of **a** SBA-15, **b** S-SBA-15 and **c** Cu–S-SBA-15



Fig. 5 Pore size distributions of a SBA-15, b S-SBA-15 and c Cu–S-SBA-15

N2 adsorption/desorption studies

N₂ adsorption-desorption isotherms and pore size distributions of SBA-15, S-SBA-15 and Cu–S-SBA-15 are depicted in Figs. 4 and 5, respectively. 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 [15]. The BET surface area, pore volume and pore diameter of SBA-15, S-SBA-15 and Cu–S-SBA-15 are presented in Table 1. The BET surface area and average pore width significantly decrease after functionalization of SBA-15 with the Schiff base and further considerably decrease upon reaction with copper. The total pore volume also decreases after each modification of SBA-15.

Sample	$S_{\rm BET}~({\rm m}^2{\rm g}^{-1})$	$D_{\rm p}$ (nm)	$V_{\rm p} \ ({\rm cm}^3 \ {\rm g}^{-1})$		
SBA-15	892	8.9	1.30		
S-SBA-15	336	4.7	0.51		
Cu-S-SBA-15	304	3.7	0.49		

 $\label{eq:table_$

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



Fig. 6 FT-IR spectra of a SBA-15, b S-SBA-15 and c Cu-S-SBA-15

FTIR studies

FTIR spectra of SBA-15, S-SBA-15 and Cu-S-SBA-15 are presented in Fig. 6. In each case, the typical Si-O-Si bands are observed at ca. 1,080, 802 and 464 cm^{-1} due to the SBA-15 silica framework [16, 17]. The bands around 3,430 and $1,632 \text{ cm}^{-1}$ are assigned to the bending vibration of O-H and physically adsorbed water molecules. After functionalization of SBA-15, the intensity of the O-H stretching bands is markedly weaker, which is attributed to the interaction between the surface Si-OH and the Schiff base organosilane reagent. The presence of C-H vibrations at ca. 2,930 cm^{-1} plus a series of aromatic ring vibrations in the range of $1,350-1,600 \text{ cm}^{-1}$ and C=N stretching vibration at around 1,640 cm⁻¹ are observed for S-SBA-15, indicating grafting of the Schiff base organosilane onto SBA-15 [16, 17]. In addition, the peak in the IR spectrum in Fig. 6c due to the C=N stretching vibration is shifted to $1,626 \text{ cm}^{-1}$, which is attributed to the coordination of the nitrogen with copper(II).

Elemental and ICP-AES analyses

Quantification of the functional group loading on SBA-15 was performed using elemental (CHN) and ICP-AES

Table 2 Elemental and ICP-AES analyses' results (%) for S-SBA-15 and Cu–S-SBA-15

Sample	С	Н	Ν	Cu
S-SBA-15	6.56 (10.3)	0.66 (12.5)	0.74 (1)	_
Cu-S-SBA-15	6.04 (10.2)	0.61 (12.4)	0.69(1)	0.76 (0.53)

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	_	_	
SBA-15	Trace	_	_	
S-SBA-15	Trace	_	_	
Cu-S-SBA-15	30	89	11	

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)

analyses (Table 2). The results show that the molar ratio of N/Cu is close to 2/1, consistent with chelation of two Schiff base ligands to each copper(II) center, as shown in Fig. 1.

Catalytic properties

The catalytic performance of Cu–S-SBA-15 was evaluated for the selective oxidation of benzyl alcohol with H_2O_2 as oxidant. For comparison, the catalytic performances of SBA-15, S-SBA-15 and a blank test were also investigated, and the reaction data are listed in Table 3. It is obvious that the oxidation reaction cannot be carried out without catalysts. In addition, SBA-15 and S-SBA-15 also cannot catalyze this reaction. It is demonstrated that Cu is the catalytic component for the partial oxidation of benzyl alcohol.

In order to identify the optimal reaction conditions, the effects of varying the reaction medium, oxidant amount, reaction time and temperature were investigated. The influence of solvent on the catalytic performance was investigated for water, acetone and acetonitrile, with the results shown in Table 4. It is interesting to note that Cu–S-SBA-15 catalyzes the oxidation reaction well when water is used as the solvent, followed by acetone, while only 6.8 % conversion was achieved when the solvent was acetonitrile.

The temperature has a great influence on the catalytic performance. As shown in Table 4, low temperatures result in very low benzyl alcohol conversion. For example, only 11 % of benzyl alcohol conversion was achieved at 60 °C. Increasing the reaction temperature increases the catalytic

 Table 4
 Catalytic data of the benzyl alcohol oxidation over Cu–S-SBA-15

Solvent	$H_2O_2 (mL)$	T (°C)	Time (h)	Conversion (%)	Selectivity (%)	
					Benzaldehyde	Benzoic acid
Water	4	80	6	30	89	11
Acetone	4	80	6	10	~ 100	0
Acetonitrile	4	80	6	7	~ 100	0
Water	4	60	6	11	88	12
Water	4	70	6	18	90	10
Water	4	90	6	31	89	11
Water	4	80	2	11	~ 100	0
Water	4	80	4	18	90	10
Water	4	80	8	33	89	11
Water	2	80	6	16	93	7
Water	3	80	6	16	91	9
Water	5	80	6	32	85	15

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

 Table 5
 Reuse of Cu–S-SBA-15 for the selective oxidation of benzyl alcohol

Cycle	Conversion (%)	Selectivity (%)		
		Benzaldehyde	Benzoic acid	
1	30	89	11	
2	29	90	10	
3	29	89	11	

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)

activity. The reaction time also influences on the catalytic behavior. As can be seen from Table 4, the benzyl alcohol conversion gradually increases from 11 to 30 %, while the selectivity for benzaldehyde decreases from ~ 100 to 89 %, when the reaction is increased from 2 to 6 h; while more prolonged reaction times have relatively little influence on the benzyl alcohol conversion, but result in the decrease of selectivity for benzaldehyde.

As shown in Table 4, the conversion of benzyl alcohol remarkably improves from 16 to 30 % after 6 h when the amount of H_2O_2 (30 %) is increased from 2 to 4 mL. Further increases in H_2O_2 have relatively little influence on the conversion, but decrease the selectivity for benzaldehyde.

Mahdavi et al. [6] have investigated the effect of solvents on the oxidation of benzyl alcohol with *tert*-butyl-hydroperoxide (TBHP) in the presence of $[Mn(bipy)_2]^{2+}/$ HMS (HMS: hexagonal mesoporous silica) and found that the best conversion (40 %) was achieved in the aprotic solvent acetonitrile, while the worst conversion (only ca. 8 %) was obtained in the protic solvent ethanol after 8 h reaction. These results are just opposite to our data for Cu–S-SBA-15 catalysis. These differences suggest that the solvent has different influences in different catalytic

systems for the substrate to contact the surface of the catalyst and for the product to depart from the surface of the catalyst.

The recyclability and stability of Cu–S-SBA-15 for benzyl alcohol oxidation with H_2O_2 as oxidant and water as solvent were investigated (Table 5). The solid catalyst was easily recovered by filtration after each reaction cycle; it was then washed thoroughly with acetone and water, dried under vacuum at 60 °C for 12 h and reused for subsequent cycles. The reused catalyst exhibited a negligible decrease in the catalytic activity and selectivity over three consecutive runs.

Conclusions

A heterogeneous catalyst, Cu–S-SBA-15, has been synthesized by covalent anchoring of a copper(II) Schiff complex onto SBA-15 support. The pore structure of SBA-15 remains intact throughout the synthesis. The reaction conditions for the oxidation of benzyl alcohol to benzaldehyde using this catalyst have been determined. Cu–S-SBA-15 exhibits better catalytic performance with water as the solvent, which is attributed to the distinctive pore structure of SBA-15 and synergistic effect between the Cu(II) Schiff base complex and the SBA-15 support.

Acknowledgments This work was supported by the National Natural Science Foundation of China (21303069), Jilin province (201105006) and Specialized Research Fund for the Doctoral Program of Higher Education (20100061120083).

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