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Article

Catalytic oxidation of styrene to benzaldehyde over a copper Schiff-base/SBA-15 catalyst

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ABSTRACT

The amino-modified mesoporous material SBA-15 (NH₂-SBA-15) was prepared via co-condensation of tetraethylorthosilicate with 3-aminopropyltriethoxysilane in the presence of an amphiphilic triblock copolymer as a pore-directing agent under acidic conditions. The SBA-15-supported Cu Schiff-base complex (Cu-SBA-15) was then synthesized by condensation of salicylaldehyde with NH₂-SBA-15, followed by the addition of a solution of Cu(NO₃)₂. The supported complex was systematically characterized by elemental analysis, inductive coupled high frequency plasma atomic emission spectrometry, powder X-ray diffraction, Fourier transform infrared spectroscopy, ultraviolet-visible spectroscopy, field scanning electron microscopy, transmission electron microscopy, N₂ absorption-desorption, and thermo gravimetric analysis, and was used as the catalyst for the selective oxidation of styrene to benzaldehyde. The influence of the reaction parameters was assessed. The maximum conversion of styrene was 84.4% and the selectivity for benzaldehyde was 83.9%, when the reaction was conducted with a 2:1 molar ratio of H₂O₂:styrene in the presence of 3.8 wt% catalyst at 100 °C for 8 h. The TOF was 261.1 h⁻¹, and the catalyst could be used three times without significant loss of activity. The uniformly sized pore channels, high specific surface area, and well-distributed active centers of the catalyst may contribute to the high activity.

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1. Introduction

Benzaldehyde is an important and valuable fine chemical that has been widely used in the synthesis of several substances, including perfumes, dyes, and pharmaceuticals [1]. Generally speaking, it can be obtained via several routes including benzyl alcohol oxidation, indirect electrochemical oxidation of toluene, benzoic acid hydrogenation, and benzyl chloride hydrolysis [2]. However, these methods suffer from lengthy procedures, expensive starting materials, and the generation of copious and toxic waste, which is environmentally undesirable. The most ideal preparation method is the direct oxidation of toluene with air or oxygen as the oxidant in the presence of a

catalyst. Nevertheless, the lack of an efficient catalyst has curtailed the adoption of this method [3].

Recently, the synthesis of benzaldehyde by styrene oxidation has drawn much attention as the process is simple and environmentally friendly [4,5]. The key to the successful use of this transformation is the design of an active, selective, and recyclable catalyst. Various catalysts, such as metal oxides [6–10], metals [11,12], metal doped zeolites [13,14], solid acids [15,16], and metal Schiff bases or salen complexes [17,18], have been discussed. Among these, the metal Schiff-base complexes demonstrate high catalytic reactivity. However, these homogeneous catalysts are usually difficult to separate from the reaction mixture, making the entire catalytic process unattractive for

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industrial application. Consequently, much attention has been focused on immobilizing the complexes on solid supports such as zeolites [19–22], ordered mesoporous silicates [23–28] or polymers [29–31] to afford heterogeneous catalysts. For example, Islam et al. [29] reported a reusable polymer-anchored Cu(II) complex for the oxidation of styrene to benzaldehyde with TBHP as oxidant. However, the conversion of styrene and the selectivity for benzaldehyde were only 53% and 52%, respectively. Yang et al. [24] prepared a series of SBA-15-supported Cu(II) and V(IV) Schiff-base complexes to study the oxidation of styrene. They found that the supported oxovanadium catalyst showed good selectivity for benzaldehyde using H_2O_2 as the oxidant. The conversion of styrene reached 84.1% and the selectivity for benzaldehyde was up to 83.3%. However, an organic solvent was used. In addition, a post-synthesis grafting method was employed for the surface modification. In summary, although the modified solid support generally maintained the ordered structure of the parent materials, the distribution of amino groups varied, largely depending on the reactivity and concentration of the precursors used as well as the reaction conditions. The result was inferior catalytic activity and recoverability [32–35].

In this paper, we report the direct synthesis of a uniform amino-modified SBA-15 (NH_2 -SBA-15) based on a single-step co-condensation of tetraethylorthosilicate (TEOS) with 3-aminopropyltriethoxysilane (APTES). The condensation reaction took place in the presence of an amphiphilic PEO-PPO-PEO triblock copolymer (P123) as a pore-directing agent. Treatment of the prepared NH_2 -SBA-15 with salicylaldehyde under condensation conditions followed by the addition of a solution of $\text{Cu}(\text{NO}_3)_2$ formed the SBA-15-supported Cu(II) Schiff-base complex (Cu-SBA-15). The immobilized complex was successfully used as a catalyst for the selective oxidation of styrene to benzaldehyde in an aqueous medium.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of NH_2 -SBA-15

NH_2 -SBA-15 was prepared via the co-condensation method described in the literature [36]. P123 (4.0 g, Sigma-Aldrich) was dissolved in 125.0 g aqueous HCl (2 mol/L). After vigorous stirring at 40 °C for 4 h, 7.9 mL TEOS was added dropwise. The resultant solution was pre-hydrolyzed for 1 h before 0.92 mL APTES (Yaohua Chemical Industry, Shanghai, China) was added. After stirring for 20 h, the white solution was transferred into a polypropylene bottle, and aged at 90 °C for 24 h. The solid was collected by suction filtration and dried at 50 °C overnight. The residual P123 was removed by extraction with boiled ethanol (1.0 g of as-synthesized material per 200 mL of ethanol and 10 mL of concentrated HCl) for 24 h. The solid was collected by suction filtration, washed with water and ethanol, and dried at 50 °C overnight. Elemental analysis gave C 8.00%, H 3.27%, N 1.53%. The calculated N content was 1.09 mmol/g.

2.1.2. Preparation of Cu-SBA-15

NH_2 -SBA-15 (2.35 g) was dispersed in 80 mL methanol, and 20 mL salicylaldehyde/methanol solution (0.2 mol/L, 0.488 g salicylaldehyde) was added to form a light-yellow solution. After stirring at 30 °C for 6 h, the mixture was heated to 50 °C and 10 mL $\text{Cu}(\text{NO}_3)_2$ /methanol solution (0.1 mol/L) was added dropwise to form a green solution. The reaction mixture was stirred for a further 12 h. The solid was then collected by suction filtration, washed with methanol and water, and finally dried at 80 °C overnight. The content of Cu was 0.101 mmol/g (ICP-AES).

2.2. Catalyst characterization

Low-angle X-ray diffraction (XRD) patterns were recorded with a Rigaku X-ray diffractometer with nickel-filtered $\text{Cu } K\alpha$ radiation at 40 kV and 30 mA. The samples were scanned in the range $2\theta = 0.7^\circ$ – 5.0° . The Fourier transform infrared (FT-IR) spectra were collected on a Nicolet IS10 spectrometer (Thermo). Field emission scanning electron microscope (FESEM) images of the samples were obtained with an HITACHIS4800 FSEM and the particle sizes were measured using Adobe Photoshop software. The channel structures were observed on a JEM-2010-UHR transmission electron microscope (TEM) and ultraviolet-visible (UV-Vis) spectra were recorded on a Perkin Elmer UV-Vis spectrophotometer, Lambda 950, in the region of 200–800 nm. A BELSORP II adsorption instrument was used to determine the specific surface area, pore volume, and pore size. The specific surface area (A_{BET}) was calculated by the BET method, the pore volume (V_{total}) was calculated at the relative pressure of 0.99 and the pore size distributions and D_{peak} were measured by the BJH method from the adsorption branch of the isotherms. Thermo gravimetric analysis (TGA) was carried out on a Netzsch STA409 instrument. CHN element analysis was carried out using a Perkin-Elmer 2400 instrument. The content of Cu was measured by inductive coupled high frequency plasma atomic emission spectrometry (ICP-AES) analysis.

2.3. Catalytic activity test

The oxidation of styrene was conducted in a 100-mL stainless-steel high-pressure autoclave (Parr, USA). The catalyst, water, H_2O_2 (30 wt%), and styrene (5.200 g) were added into the vessel and it was then heated to 100 °C with a stirring speed of 800 r/min. After the reaction was complete, the mixture was centrifuged (8000 r/min, 2 min) and the solid was washed with EtOAc. The combined organic phases were dried over anhydrous MgSO_4 , and analyzed on a gas-chromatograph (GC2014, Shimadzu Instruments, Japan) equipped with DB-5 capillary column (30 m $\times$ 0.25 mm $\times$ 0.25 μm). The recovered catalyst was washed with acetone, alcohol, and water, and dried at 100 °C overnight before reuse.

3. Results and discussion

3.1. Catalyst characterization

The low-angle XRD patterns of NH_2 -SBA-15 and Cu-SBA-15

are depicted in Fig. 1(a). The pattern of NH₂-SBA-15 shows an intense diffraction indexed to the (100) plane, which indicates the typical mesoporous structure of SBA-15. The other two small characteristic peaks are not clearly observed, probably because the use of the silane coupling agent negatively affected the formation of micelles and resulted in an irregularity of the pores. FT-IR spectra of SBA-15, NH₂-SBA-15, Schiff-base-SBA-15, and Cu-SBA-15 are shown in Fig. 1(b). The peaks at 467, 799, 1081, and 1230 cm⁻¹ indicate the characteristic absorption of O–Si–O bonds and the peak at 946 cm⁻¹ indicates the existence of Si–OH. The strong peak around 1632 cm⁻¹ in all the samples results largely from the bending vibration of adsorbed water, and the broad band observed between 3700 and 2800 cm⁻¹ is attributed to the –OH stretching vibration of water adsorbed on the surface of the catalyst. The presence of the –NH₂ stretching vibration at 3250 cm⁻¹, the bending vibration at 1510 cm⁻¹ and the N–H bending vibration at 668 cm⁻¹ confirm the incorporation of the amino groups. The absorption

at about 1510 cm⁻¹ can be observed in both Schiff-base-SBA-15 and Cu-SBA-15 but has a low intensity, indicating the occurrence of the condensation of salicylaldehyde with the amino groups on the surface of NH₂-SBA-15. Generally, a weak absorption peak of C=N stretching vibration should occur around 1640–1650 cm⁻¹ for the Schiff-base-SBA-15. However, this peak is overlapped by the stretching vibration absorption of H₂O. Notably, comparison of the IR spectra of Cu-SBA-15 and Schiff-base-SBA-15 indicates the presence of a new adsorption peak around 1387 cm⁻¹ in Cu-SBA-15. This new peak may result from the red shift of the C=N stretching vibration absorption due to coordination to copper ions.

The FESEM image of NH₂-SBA-15 is presented in Fig. 2(a). The sample shows a typical rod-like morphology of SBA-15. As shown in Fig. 2(b), the diameters of most particles are typically in the range of 600–700 nm and the average particle size is 740 nm. The TEM images of NH₂-SBA-15 and Cu-SBA-15 are shown in Fig. 2(c) and (d), respectively,

Fig. 1. (a) XRD patterns of NH₂-SBA-15 and Cu-SBA-15. (b) FT-IR spectra of SBA-15, NH₂-SBA-15, Schiff-base-SBA-15, and Cu-SBA-15.

Fig. 2. (a) FESEM image of NH₂-SBA-15; (b) Particle size distribution of the sample; (c) TEM image of NH₂-SBA-15; (d) TEM image of Cu-SBA-15.

Fig. 3. UV-Vis spectra of NH₂-SBA-15 and Cu-SBA-15.

and provide a direct visualization of well-ordered hexagonal arrays of 1D mesoporous channels for both types of sample. Some pore walls in the sample have collapsed, which accounts for the absence of the two low-intensity characteristic peaks in the XRD patterns.

Figure 3 shows the UV-Vis spectra of NH₂-SBA-15 and Cu-SBA-15. In contrast to the spectrum of NH₂-SBA-15, a typical metal-ligand band around 390 nm is observed for Cu-SBA-15 [24], indicating the successful anchoring of the Cu(II) Schiff-base complex to the SBA-15 matrix.

As shown in Fig. 4, the N₂ adsorption-desorption isotherm for NH₂-SBA-15 is type IV with an H1-type hysteresis loop, typical for mesoporous materials with cylindrical porous channels. The Cu-SBA-15 sample maintains the characteristics of type IV yet with an H2 hysteresis loop, probably because of a partial blocking of the pores. The size distribution curves show similar peaks at 5.41 nm while the peak for Cu-SBA-15 has a lower intensity and is broader. The textural properties of NH₂-SBA-15 and Cu-SBA-15 are summarized in Table 1. The A_{BET} and pore volumes of Cu-SBA-15 are slightly lower than those of NH₂-SBA-15. We consider that these results reflect the introduction of the Schiff-base-coordinated copper complex on the material, leading to the blockage of some pores.

The TGA results for NH₂-SBA-15 and Cu-SBA-15 are illustrated in Fig. 5. For both NH₂-SBA-15 and Cu-SBA-15, the weight loss below 100 °C is mainly attributed to the loss of adsorbed water. The subsequent weight loss from 200–350 °C

Table 1

Textural properties of NH₂-SBA-15 and Cu-SBA-15.

Sample	$A_{\text{BET}}/(\text{m}^2/\text{g})$	$V_{\text{total}}/(\text{cm}^3/\text{g})$	$D_{\text{peak}}/\text{nm}$
NH ₂ -SBA-15	443	0.54	5.41
Cu-SBA-15	423	0.34	5.41

Fig. 5. TG curves of NH₂-SBA-15 and Cu-SBA-15.

is due to the decomposition of the amino groups and the Schiff bases. The weight loss of Cu-SBA-15 occurs at lower temperatures, relative to NH₂-SBA-15, because of the higher molecular mass of the Schiff-bases compared with that of the amino groups. Finally, the decomposition of the aminopropyl groups caused the weight loss at temperatures above 350 °C.

3.2. Optimization of reaction conditions

3.2.1. Effect of the reaction time

Figure 6(a) shows the effect of reaction time on styrene oxidation at 100 °C using 0.300 g Cu-SBA-15 as the catalyst and 1.5 equiv. H₂O₂ (10 wt% aqueous) as the oxidant. The styrene conversion increased with reaction duration while the selectivity for benzaldehyde declined slowly. The conversion reached 55.4% and the selectivity was 80% after 8 h. The conversion of styrene further increased after 9 h, but styrene then underwent polymerization, resulting in a considerable decrease in selectivity. This behavior is because the H₂O₂ was completely consumed after 9 h, and the residual styrene underwent polymerization under these conditions.

Fig. 4. N₂ adsorption-desorption isotherms (a) and corresponding mesopore size distribution curves (b) of NH₂-SBA-15 and Cu-SBA-15.

3.2.2. Effect of the reaction temperature

Figure 6(b) shows the effect of reaction temperature on styrene oxidation using 0.300 g Cu-SBA-15 as the catalyst and 1.5 equiv. H_2O_2 (10 wt% aqueous) as the oxidant for 8 h. It is clear that the conversion of styrene rapidly decreased with a decrease in the reaction temperature. When the reaction was performed at 80 °C, the conversion of styrene was only 6.8%. However, the selectivity was much higher at a lower reaction temperature because the rate of benzaldehyde oxidation to benzoic acid is also lower. When the reaction was conducted at 100 °C for 8 h, the conversion of styrene reached 55.4% and the selectivity for benzaldehyde was up to 79.3%.

3.2.3. Effect of the amount of H_2O_2

The effect of the amount of H_2O_2 used was investigated by conducting the reactions at 100 °C for 8 h. H_2O_2 (10 wt% aqueous) was used in the presence of 0.300 g Cu-SBA-15 and 17.167 g H_2O . As shown in Fig. 6(c), the conversion of styrene gradually increases with an increase in the amount of H_2O_2 used. When 2 equiv. H_2O_2 was used, the conversion of styrene was 70.6% and the selectivity for benzaldehyde was 79.6%. When 2.5 equiv. H_2O_2 was used, the conversion increased to 84.5%, but the selectivity dropped sharply to 65.4%. A further increase in the amount of H_2O_2 employed resulted in no increase in styrene conversion, and a much lower selectivity. This can be ascribed to the remaining H_2O_2 promoting the further oxidation of benzaldehyde to benzoic acid. Overall, the use of 2 equiv. H_2O_2 for the catalytic oxidation of styrene is suitable.

3.2.4. Effect of the amount of H_2O

Since there is no co-solvent used in the reaction, the amount

of H_2O added in the reaction determines the H_2O_2 concentration. We investigated the effect of H_2O by conducting the reactions at 100 °C for 8 h with various amounts of H_2O in the presence of 0.300 g Cu-SBA-15 and 2 equiv. H_2O_2 . The results are shown in Fig. 6(d). It is obvious that the conversion of styrene is the highest with no extra H_2O added. The addition of H_2O slowed the oxidation process and led to a low conversion.

3.2.5. Effect of catalyst loading

Figure 6(e) shows the influence of catalyst loading. The conversion of styrene and the selectivity for benzaldehyde were 84.4% and 83.9%, respectively, when the reaction was conducted at 100 °C for 8 h with 2 equiv. H_2O_2 and 0.200 g Cu-SBA-15. An increase in the amount of catalyst used has little effect on the reaction. However, when the amount of the catalyst was reduced to 0.150 or 0.100 g, the reaction mixture became viscous after 8 h, probably because of the formation of styrene oligomers. A high loading of the catalyst is required to accelerate the rate of the oxidation process and prevent styrene polymerization.

Based on the above results, we obtained the optimum conditions as follows: the reaction should be carried out at 100 °C for 8 h using 2.0 equiv H_2O_2 (30 wt% aqueous) and 3.8 wt% Cu-SBA-15 catalyst. The conversion of styrene obtained was up to 84.4%, and the selectivity for benzaldehyde was 83.9%. The TOF of the catalyst was 261.1 h^{-1} . Benzoic acid was the only by-product and the formation of styrene oxide was not observed. At the optimum conditions, we found that this heterogeneous catalyst gave competitive results compared with other reported catalysts in terms of conversion and selectivity and, in addition, a high TOF was obtained (Table 2). When

Fig. 6. Effect of reaction time (a), temperature (b), amount of H_2O_2 (c), weight of H_2O (d), and the amount of catalyst (e) on the oxidation of styrene to benzaldehyde. Other reaction conditions: (a) 100 °C, $n(\text{styrene}):n(\text{H}_2\text{O}_2) = 1:1.5$, 10 wt% H_2O_2 , 0.3 g catalyst, 800 r/min; (b) 8 h, $n(\text{styrene}):n(\text{H}_2\text{O}_2) = 1:1.5$, 10 wt% H_2O_2 , 0.3 g catalyst, 800 r/min; (c) 100 °C, 8 h, 10 wt% H_2O_2 , 0.3 g catalyst, 800 r/min; (d) 100 °C, 8 h, $n(\text{styrene}):n(\text{H}_2\text{O}_2) = 1:2$, 0.3 g catalyst, 800 r/min; (e) 100 °C, 8 h, $n(\text{styrene}):n(\text{H}_2\text{O}_2) = 1:2$, 30 wt% H_2O_2 , 800 r/min.

Table 2

Activity of the supported metal complex catalysts.

Catalyst	Conversion (%)	Selectivity (%)		TOF (h ⁻¹)	Oxidant	Solvent	Reference
		Benzaldehyde	Styreneoxide				
Cu-SBA-15	84.4	83.9	0	261.1	H ₂ O ₂	H ₂ O	this work
VO-Salen-SBA	84.1	83.3	11.9	67.4	H ₂ O ₂	CH ₃ CN	25
Cu-Salen-SBA	96.9	45.2	13.5	134.6	H ₂ O ₂	CH ₃ CN	25
Co-[H ₄]Salen-SBA	78.5	43.6	54.1	196.0	Air	CH ₃ CN	28
SBA-Fe(acac: salen)	45.0	99.0	0	0.24	H ₂ O ₂	CH ₃ CN	26
SBA-VO(acac)	84.0	96.0	0	9.5	H ₂ O ₂	CH ₃ CN	27
PS-NH ₂ -Cu-Sal	53.0	52.0	48.0	12.6	TBHP	CH ₃ CN	29
Polymer supported cobalt complex	100	89.0	11.0	50.0	H ₂ O ₂	H ₂ O	30

acetonitrile was used as a solvent under these conditions, the conversion of styrene reached up to 96.7%, while the selectivity for benzaldehyde was only 58.3% because of the formation of several by-products including benzoic acid (16.7%), phenylacetaldehyde (15.8%) and phenylethylene glycol (9.2%).

3.3. Catalyst recycling

Recyclability is one of the most important benefits of supported catalysts and makes them attractive for commercial applications. We therefore investigated the recovery and recyclability of the supported catalyst used. The results are summarized in Table 3 and show that the Cu-SAB-15 catalyst could be successfully used three times without significant loss of the activity. The main product and by-product were benzaldehyde and benzoic acid, respectively, and no styrene oxide was detected in any of the cases. The slight decrease in selectivity for the recovered catalyst is probably due to residual organics on the catalyst impeding the desorption of benzaldehyde from the catalytic centers, leading to over-oxidation to benzoic acid.

3.4. Mechanism of styrene oxidation

Styrene can generally be oxidized to benzaldehyde via two distinct pathways using a copper(II) Schiff-base complex as a catalyst (Scheme 1) [27]. The first path involves a radical mechanism. One molecule of H₂O₂ adsorbed on the catalyst first decomposes to two hydroxyl radicals. These radicals then add to the C=C bond of styrene to form phenylethylene glycol, which then undergoes oxidative cleavage to form benzaldehyde and formaldehyde. Benzaldehyde is readily oxidized to benzoic acid. Alternatively, styrene first reacts with the active H₂O₂ molecule to form styrene oxide, which may further transform

Scheme 1. Plausible reaction mechanism of styrene oxidation.

to a hydroxyl-hydroxylperoxystyrene intermediate upon nucleophilic attack by another molecule of H₂O₂. Carbon bond cleavage of this unstable intermediate then produces benzaldehyde and formaldehyde. Since the intermediate styrene oxide was not detected during the course of the reaction, we concluded that the catalytic oxidation of styrene with Cu-SBA-15 follows the first pathway. In addition, as can be seen from the reaction mechanism, 2 equiv. H₂O₂ is required for styrene oxidation to benzaldehyde. This is in good agreement with our experimental results, which showed that the conversion was generally low when less than 2 equiv. of H₂O₂ was used, while a high conversion of styrene was observed, with decreased selectivity if more H₂O₂ was employed.

4. Conclusions

We prepared NH₂-SBA-15 using a one-pot co-condensation method, and anchored the copper(II) Schiff-base complex to afford a solid catalyst, Cu-SBA-15, for the selective oxidation of styrene to benzaldehyde. The highest conversion of styrene reached 84.4%, the selectivity for benzaldehyde was up to 83.9%, and the TOF of the catalyst was 261.1 h⁻¹. The catalyst could be used three times without significant loss of activity. The distribution of amino groups on the material prepared by the one-pot co-condensation method may be better than is the case with a post-synthesis grafting method. Therefore, the active species could be well distributed on the surface of the prepared Cu-SBA-15 catalyst, leading to a higher catalytic activity.

Table 3

Experimental results on the recycling of Cu-SBA-15.

Cycle	Styrene Conversion ^a (%)	Selectivity ^b (%)		
		Benzaldehyde	Benzoic Acid	Styrene oxide
1	84.4	83.9	16.1	0
2	86.9	81.6	18.4	0
3	85.7	81.2	18.8	0

^a Styrene conversion calculated via GC analysis.^b Product selectivity calculated via GC analysis.

Graphical Abstract

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Catalytic oxidation of styrene to benzaldehyde over a copper Schiff-base/SBA-15 catalyst

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A Cu-SBA-15 catalyst was prepared by immobilizing a copper Schiff-base complex onto an amino-modified mesoporous material SBA-15, synthesized via a one-pot co-condensation method. The catalyst was used for the oxidation of styrene to benzaldehyde in an aqueous medium.

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SBA-15负载的Cu(II)席夫碱配合物催化的苯乙烯氧化反应制备苯甲醛

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摘要: 采用一步法将原硅酸四乙酯与3-氨丙基三乙氧基硅烷在表面活性剂P123作用下, 酸性共水解制备出氨基功能化的介孔分

子筛SBA-15 (NH_2 -SBA-15), 再利用其中氨基与水杨醛的缩合反应制备SBA-15固载的席夫碱, 该席夫碱与 $\text{Cu}(\text{NO}_3)_2$ 溶液反应最终制成固定于SBA-15的 $\text{Cu}(\text{II})$ 席夫碱配合物多相催化剂Cu-SBA-15. 采用X射线衍射、红外光谱仪、紫外可见分光光度计、场发射电镜、透射电镜、 N_2 吸附-脱附、元素分析、原子发射光谱和热重分析对催化剂进行了表征, 并将此催化剂用于无有机溶剂条件下催化氧化苯乙烯制备苯甲醛, 考察了反应时间、反应温度、 H_2O_2 用量、水的用量、催化剂用量对反应的影响. 当反应温度为 $100\text{ }^\circ\text{C}$, 反应时间8 h, H_2O_2 与苯乙烯的摩尔比为2:1, 不额外添加溶剂, 且催化剂用量为3.8 wt%时, 苯乙烯的转化率最高为84.4%, 苯甲醛选择性为83.9%, 催化剂的TOF值为 261.1 h^{-1} , 并且重复使用3次后活性没有明显下降. 规则的孔道、较大的比表面积以及分布均匀的活性中心可能是催化剂活性提高的原因.

关键词: 铜席夫碱配合物; 氨基功能化; SBA-15; 苯乙烯氧化; 苯甲醛; 杂相催化

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1. 前言

苯甲醛是一种重要的有机化学中间体, 广泛应用于香料、医药、染料等^[1]. 现今工业上制备苯甲醛的工艺主要有苯甲醇氧化法、间接电化学氧化法、苯甲酸加氢还原法和苯叉二氯水解法^[2]. 这些方法步骤过长, 成本较高, 污染腐蚀较大. 甲苯在催化剂作用下以空气或者氧气进行气相氧化制备苯甲醛是一条最为绿色环保的路线, 但是有效催化剂的缺乏制约其发展和应用^[3].

近年来, 以苯乙烯为原料催化氧化制备苯甲醛的方法, 因其过程相对简单, 污染较小而广受人们关注^[4,5]. 其关键在于开发具有高效率、高选择性的催化剂. 目前已报道的催化剂主要有金属氧化物^[6–10]、金属^[11,12]、掺杂金属的分子筛^[13,14]、固体酸^[15,16]和金属席夫碱配合物^[17,18]. 其中, 金属席夫碱配合物是一种活性较高的均相催化剂, 但因难以从产物中分离回收循环使用而限制了其工业应用. 将金属席夫碱配合物固载于分子筛^[19–22]、介孔硅材料^[23–28]或聚合物^[29–31]等固体材料中有望克服这一问题. Islam等^[29]对聚苯乙烯进行氨基改性后, 制备了固定有Cu席夫碱的PS- NH_2 -u-Sal催化剂, 以TBHP为氧化剂, 但是苯乙烯的转化率仅为53%, 苯甲醛选择性为52%, 同时副产大量的环氧苯乙烷. Yang等^[24]采用嫁接法以3-氨丙基三乙氧基硅烷(APTES)改性SBA-15后, 在其上固定了一系列Cu和V的席夫碱络合物, 并研究了其对苯乙烯氧化的催化活性. 结果表明, 在以 H_2O_2 为氧化剂时, VO-Salen-SBA催化剂对苯乙烯氧化制苯甲醛有较好的选择性, 苯乙烯转化率可达84.1%, 苯甲醛选择性为83.3%, 但是反应需要在有机溶剂中进行. 上述研究均采用将含氨基的硅烷偶联剂与材料表面的羟基反应进行嫁接. 这种方法制得的载体虽然能保持规整的孔道结构, 但其表面氨基的分布受硅烷偶联剂的浓度和反应条件影响较大^[32–35], 可能是导致催化活性

不高以及回收使用后活性显著下降的原因.

本文采用原硅酸四乙酯(TEOS)与APTES共水解的方法制备氨基功能化的介孔分子筛SBA-15 (NH_2 -SBA-15), 然后通过缩合反应和配位反应制得 $\text{Cu}(\text{II})$ 席夫碱配合物多相催化剂Cu-SBA-15, 并研究了该催化剂在无有机溶剂条件下催化氧化苯乙烯反应制备苯甲醛的反应.

2. 实验部分

2.1. 催化剂的制备

2.1.1. NH_2 -SBA-15的制备

NH_2 -SBA-15的制备方法与文献[36]类似, 将4.0 g P123 (Sigma-Aldrich)于 $40\text{ }^\circ\text{C}$ 与125.0 g稀盐酸(2 mol/L)在500 mL的三口烧瓶中剧烈搅拌4 h后, 逐滴加入7.9 mL TEOS. 滴加完毕后, TEOS于 $40\text{ }^\circ\text{C}$ 下预水解1 h, 然后移取0.92 mL硅烷偶联剂KH550迅速加入到烧瓶中. TEOS和KH550 (上海耀华化工厂)共水解20 h后, 将得到的乳白色液体转移至聚丙烯的塑料小瓶中, 并于 $90\text{ }^\circ\text{C}$ 下老化24 h. 对所得的混合物抽滤, 并将滤饼于 $50\text{ }^\circ\text{C}$ 烘箱中干燥过夜. 乙醇萃取回流24 h除去 NH_2 -SBA-15中残留的模板剂P123 (每克固体约需200 mL乙醇与10 mL浓盐酸)后, 用去离子水和乙醇洗涤数次, 放入 $50\text{ }^\circ\text{C}$ 烘箱中干燥过夜. 元素分析结果显示, NH_2 -SBA-15中各元素含量为(%): C 8.00, H 3.27, N 1.53. 经计算得其表面氨基的含量为 1.09 mmol/g .

2.1.2. Cu-SBA-15的制备

将2.35 g干燥的 NH_2 -SBA-15悬浮于80 mL的无水甲醇中, 逐滴加入20 mL的0.2 mol/L的水杨醛甲醇溶液(0.488 g水杨醛), 水杨醛与氨基缩合, 反应液变为黄色. 在 $30\text{ }^\circ\text{C}$ 反应6 h后, 将水浴温度升至 $50\text{ }^\circ\text{C}$, 随后逐滴加入0.1 mol/L的 $\text{Cu}(\text{NO}_3)_2$ 甲醇溶液10 mL, 此时悬浮液中由于Cu的配位而渐渐变为浅绿色. 反应12 h后将固体过

滤,并用甲醇和去离子水先后洗涤数次至滤液无色.将制得的催化剂于80 °C烘箱中干燥过夜.经原子发射光谱法检测得Cu元素含量为0.101 mmol/g.

2.2. 催化剂表征

采用Rigaku公司X射线衍射仪(XRD)测定催化剂的结构,Cu靶 K_{α} 射线,管电压40 kV,管电流30 mA;采用小角度XRD分析Cu-SBA-15的结构,扫描步长0.02°,每步扫描0.5°/s.采用美国Thermo公司Nicolet iS10型红外光谱仪(FT-IR)表征样品,KBr压片制样,扫描范围500–4000 cm^{-1} .用HITACHIS4800型场发射电镜(FESEM)观察样品的表面形貌.采用JEL-200CX型透射电子显微镜(TEM)观察样品的孔道结构.用PerkinElmer公司Lambda950型紫外可见分光光度计(UV-Vis)表征催化剂,扫描范围为200–800 nm. N_2 吸附-脱附等温线在BELSORP II型体积吸附仪上测定,吸附温度为–196 °C, N_2 吸附前,样品在200 °C真空条件下处理3 h;采用BET方程计算样品的比表面积 A_{BET} ,根据相对压力为0.99时 N_2 的吸附量计算样品的总孔体积(V_{total}),根据 N_2 等温线的吸附分支用BJH方法计算样品的介孔孔径分布及峰值孔径 D_{peak} .样品的热重分析(TGA)在Netzsch公司STA409型同步热分析仪上进行,以 Al_2O_3 坩埚装载样品,空气气氛,升温速率10 °C/min. CHN元素分析在Perkin Elmer 2400上进行. Cu含量通过等离子体发射光谱(ICP)仪测定.

2.3. 催化剂评价

苯乙烯的氧化反应在100 mL不锈钢高压反应釜(美国Parr公司)中进行.先在反应釜中加入一定量的催化剂,再称取一定质量的去离子水、30 wt%的 H_2O_2 和5.200 g苯乙烯混合后倒入釜中将搅拌速度调节至800 r/min,当温度升至100 °C反应开始计时.反应结束后,将产物离心分离(离心机转速8000 r/min,时间2 min),并用乙酸乙酯洗涤催化剂.将所得的所有液体倒入梨型分液漏斗中静置分层,取上层有机相加入无水硫酸镁干燥后进行气相色谱分析.气相色谱分析在岛津GC-2014上进行,色谱柱为DB-5弹性毛细管MS柱(30 m $\times$ 0.25 mm $\times$ 0.25 μm),进样口温度为260 °C,检测室温度为260 °C,柱温为90 °C保持8 min,以20 °C/min升温至200 °C保持10 min.反应后的催化剂用丙酮、乙醇和去离子水先后洗涤数次,放入100 °C烘箱中干燥过夜以回收.

3. 结果与讨论

3.1. 催化剂的表征

图1(a)为 NH_2 -SBA-15和Cu-SBA-15的XRD谱.可以看到主峰明显,所制材料具有SBA-15的结构,但是后2个小衍射峰并不明显,这是由于硅烷偶联剂的加入影响了胶束的形成,使得材料的孔隙规整度发生了变化.图1(b)为SBA-15, NH_2 -SBA-15, Schiff-base-SBA-15和Cu-SBA-15的FT-IR谱.位于467, 799, 1081和1230 cm^{-1} 处的吸收峰表明其中存在着O–Si–O键,而在946 cm^{-1} 处的吸收峰证明了Si–OH的存在.所有样品在1632 cm^{-1} 左右的较强的吸收峰均是由催化剂吸附的水分子产生,而在2800–3700 cm^{-1} 左右出现的强吸收峰是由其自身表面上的羟基以及其吸附的水分子的羟基产生的伸缩振动引起.在3250和1510 cm^{-1} 处的吸收峰分别由 $-\text{NH}_2$ 的伸缩振动和弯曲振动产生,而668 cm^{-1} 处的小峰则由N–H的弯曲振动产生,表明 NH_2 -SBA-15中存在 $-\text{NH}_2$ 基团.在Schiff-base-SBA-15和Cu-SBA-15样品中也在1510 cm^{-1} 附近出现吸收峰,但是强度明显减弱,表明催化剂表面的 $-\text{NH}_2$ 基团与水杨醛发生了缩合反应,形成席夫碱结构.由于通常C=N双键伸缩振动在1640–1450 cm^{-1} 处产生较为微弱吸收,与 H_2O 分子的伸缩振动产生的红外吸收处于同一区域而被其掩盖,所以C=N键特征峰并不明显.比较Schiff-base-SBA-15和Cu-SBA-15的FT-IR谱,发现后者在1387 cm^{-1} 处出现了一个新吸收峰,这可能是由于Cu和席夫碱配位引起了C=N键吸收的红移.

图2(a)为 NH_2 -SBA-15的FESEM照片.发现该样品呈短棒状,是SBA-15典型形貌.图2(b)为 NH_2 -SBA-15的粒径分布图,其粒径大多在600–700 nm,平均粒径为740 nm.图2(c)与(d)分别为 NH_2 -SBA-15及Cu-SBA-15的TEM照片.可以看出,两者的孔道结构均为规整的六方形孔道,但是其中有少量发生了局部孔道坍塌.这与XRD谱中显示的小衍射峰不明显相一致.

图3为 NH_2 -SBA-15和Cu-SBA-15的UV-Vis谱.可以看出,相比于 NH_2 -SBA-15, Cu-SBA-15于 $\lambda = 390$ nm处有一个吸收峰,由配体向过渡金属的电荷转移产生^[24],证明铜的席夫碱络合物成功负载于SBA-15表面.

图4为 NH_2 -SBA-15和Cu-SBA-15的 N_2 吸附曲线和孔径分布图.可以看出, NH_2 -SBA-15的 N_2 吸附脱附等温线均为IV型,其滞后回环为H1型,而Cu-SBA-15中的等温线虽仍为IV型,但其滞后回环变为H2型,表明负载后有部分孔道发生了堵塞.另外,两者孔径分布峰值虽均为5.41 nm,然而负载后的Cu-SBA-15的强度降低,孔径分布发生了宽化.两者的比表面积、孔体积和孔径见表1.

相比于NH₂-SBA-15, Cu-SBA-15的比表面积和孔体积略有减小. 这可能主要是由于负载过程中, 铜席夫碱的引入使得部分通道口变小或发生堵塞.

图5为NH₂-SBA-15和Cu-SBA-15的TGA结果. 可以看到, 在温度低于100 °C时出现的重量损失对应于催化剂表面物理吸附的水, 200–350 °C左右质量的减少为氨基和席夫碱配合物的分解所致. 由于席夫碱络合物的质量大于氨基的质量, 故在Cu-SBA-15上的质量减少比NH₂-SBA-15快. 在350 °C后催化剂质量继续减少, 归属于三甲基硅烷基团的分解.

3.2. 反应条件的优化

3.2.1. 反应时间的影响

图6(a)为在反应温度为100 °C, H₂O₂用量为1.5倍当量且浓度为10 wt%, 催化剂用量0.300 g的条件下, 苯乙烯的转化率与产物苯甲醛的选择性随时间的变化规律. 由图可见, 随着反应时间的延长, 苯乙烯的转化率提高, 苯甲醛的选择性缓慢下降, 至8 h时, 转化率达到55.4%, 选择性在80%左右; 但延长至9 h时, 苯乙烯发生聚合, 苯乙烯的转化率提高, 但产物选择性大大降低, 这可能是由于时间过长时, 釜中的H₂O₂已完全消耗, 苯乙烯无法再被氧化而在高温下发生聚合所致.

3.2.2. 反应温度的影响

在H₂O₂用量为1.5倍当量, 浓度为10 wt%, 催化剂用量0.300 g, 反应时间为8 h条件下, 对反应温度的影响进行了考察, 结果见图6(b). 降低反应温度使苯乙烯转化率迅速下降; 如80 °C时苯乙烯转化率只有6.8%. 但是反应的选择性在温度较低时较高, 这是由于该条件下苯甲醛氧化成苯甲酸的速度也相对较慢. 当于100 °C反应8 h, 苯乙烯的转化率为55.4%, 苯甲醛的选择性为79.3%.

3.2.3. H₂O₂用量的影响

固定反应时间为8 h, 反应温度为100 °C, 水量为17.167 g以及催化剂用量为0.300 g, 对H₂O₂的用量进行了考察, 结果见图6(c). 可以看出, 随着H₂O₂用量的增加, 苯乙烯的转化率逐渐增加, 当H₂O₂用量为2倍当量时转化率为70.6%, 苯甲醛选择性为79.6%; 至2.5倍当量时, 虽然转化率提高至84.5%, 但选择性迅速下降为65.4%. 这是由于H₂O₂用量的增加虽加快了反应, 但是也使得苯甲醛发生进一步氧化变为苯甲酸, 故选择性下降. 所以, 当H₂O₂用量为2倍当量时相对较好.

3.2.4. H₂O用量的影响

由于反应中不添加有机溶剂, 苯乙烯直接与H₂O₂进行两相反应, 故水量的多少间接影响着H₂O₂的浓度. 在

反应时间为8 h, 温度为100 °C, H₂O₂用量为2倍当量, 催化剂用量为0.300 g条件下, 我们考察了反应中H₂O量对反应的影响, 结果如图6(d)所示. 可以看出, 当原料中不额外添加H₂O时, 反应的转化率最高; 随着H₂O量的增加, 反应的转化率明显下降. 因此H₂O的引入不利于反应进行, 反应中无需再加入额外的H₂O.

3.2.5. 催化剂用量的影响

图6(e)考察了在反应时间为8 h, 温度为100 °C, H₂O₂用量为2倍当量且不额外添加水的条件下催化剂用量的影响. 当催化剂用量为0.200 g时, 苯乙烯的转化率可达到84.4%, 苯甲醛选择性为83.9%, 继续提高催化剂的用量对反应的影响不大. 但是降低催化剂的用量至0.150和0.100 g时, 产物中出现了少量高粘度物质, 可能为低聚合度的聚苯乙烯. 所以较多的催化剂有利于促进氧化反应的进行, 阻止苯乙烯的聚合.

综上, 以制得的Cu-SBA-15为催化剂, H₂O₂为氧化剂得到苯乙烯的转化率最高为84.4%, 苯甲醛选择性为83.9%, 副产物仅为苯甲酸, 无环氧苯乙烷的生成. 最优反应条件为反应温度100 °C, 反应时间8 h, H₂O₂与苯乙烯的比例为2:1, H₂O₂浓度为30 wt%且不额外加水稀释, 催化剂用量为0.200 g, 此时催化剂的TOF为261.1 h⁻¹. 在最佳工艺条件下, 催化剂的TOF高于文献中以直接嫁接法合成的金属席夫碱催化剂, 且取得了与使用有机溶剂条件下相近的转化率与选择性(见表2). 值得指出的是, 在该条件下加入乙腈作为共溶剂, 苯乙烯的转化率虽然提高至96.7%, TOF达299.2 h⁻¹, 但是苯甲醛选择性, 仅为58.3%, 且副产物除了苯甲酸外(16.7%), 还有苯乙醛(15.8%)和苯基乙二醇(9.2%).

3.3. 催化剂的循环使用

催化剂的循环利用实验(表3)表明, 在使用3次之后活性无明显变化. 反应主要产物均为苯甲醛, 同时生成少量苯甲酸, 未检测到有环氧苯乙烷生成. 利用回收的催化剂时, 苯甲醛的选择性略微降低, 可能是催化剂回收时未完全洗涤干净, 有少量残余的有机物滞留于催化剂表面导致苯甲醛未及时脱附而过度氧化. 总体上催化剂活性未发生明显变化, 催化剂可重复循环使用.

3.4. 苯乙烯的氧化反应机理

在Cu席夫碱配合物催化下, 苯乙烯的氧化反应可能通过两种反应路径生成苯甲醛^[27], 如图式1所示. 第一种为自由基氧化机理, H₂O₂分子在催化剂表面吸附, 在固定于SBA-15表面的Cu席夫碱配合物作为催化剂的活

性中心作用下分解为羟基自由基,后者加成到扩散进入孔道的苯乙烯分子的C=C双键上加成形成苄基羟亚甲基自由基,该自由基继续和羟基自由基反应生成1-苯乙醇-1,2-二醇,然后通过氧化裂解生成苯甲醛和甲醛,苯甲醛易被过度氧化生成苯甲酸。另一条路线为,苯乙烯与活化的 H_2O_2 分子直接发生氧化反应生成氧化苯乙烯,后者继续被氧化生成羟基-过氧苯乙烯,因不稳定而易分解为苯甲醛和甲醛。在反应进程中,并未检测到环氧苯乙烷的生成,故当使用该Cu-SBA-15为催化剂时,苯乙烯的氧化可能遵循的是第一种反应机理。因此若要苯乙烯完全反应变成苯甲醛,理论需消耗2倍当量的 H_2O_2 。所以,当 H_2O_2 用量较少时,反应的转化率不高;而当

H_2O_2 用量远远超过2倍当量时,苯甲醛越容易过度氧化生成苯甲酸,所以反应的选择性迅速下降。

4. 结论

以一步共水解法制得的 NH_2 -SBA-15为载体,在其上嫁接Cu的席夫碱络合物,用于无溶剂条件下催化苯乙烯氧化制苯甲醛的反应中,苯乙烯的转化率最高为84.4%,苯甲醛选择性为83.9%,催化剂的TOF达261.1 h^{-1} ,且催化剂重复使用3次活性不下降。该催化剂活性高于以液相嫁接法合成的。这是由于,一步法制得的载体表面氨基分布更均匀,使得固定在催化剂表面的金属络合物活性中心分布较好所致。