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Short Communication

Adsorption synthesized cobalt-containing mesoporous silica SBA-15 as highly active catalysts for epoxidation of styrene with molecular oxygen

Haitao Cui^{a,b}, Ye Zhang^{a,*}, Liangfu Zhao^{a,*}, Yulei Zhu^a

^a State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China
^b Graduate University of Chinese Academy of Sciences, Beijing 100049, PR China

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1. Introduction

The catalytic epoxidation of olefins by O_2 or air without any coreductant has attracted much attention because it is a highly desirable process from both environmental and economic points of view [1]. Cobalt-based catalysts exhibit better catalytic performance in the reaction [2–13]. Tang et al. reported that Co^{2+} which was introduced into NaX and MCM-41 by an ion exchange method showed higher activity in the epoxidation of styrene with O_2 , and the isolated cobalt cations in the molecular sieves were the most active in the reaction [5,10]. In our previous work, we introduced a certain amount of cobalt into SBA-15 by a pH-adjusting method, and found that the cobalt in the mesoporous silica also mainly existed in the single-site Co(II) state and was highly active in the reaction [14]. Therefore, some molecular sieves containing Co^{2+} have aroused great interest of researchers for the reaction.

Aminopropyl-functionalized mesoporous silicas are found to be useful for some based-catalyzed reactions [15], adsorption [16] and separation [17,18]. Wang et al. synthesized highly ordered SBA-15 mesoporous silica that is functionalized with high concentration of amino groups by an improved one-pot method [19]. Recently, we found that the synthesized aminopropyl-functionalized mesoporous silica SBA-15 by the method showed a large adsorption capacity for Co^{2+} . In the present study, we introduced Co^{2+} into the functionalized molecular sieves by an adsorption route. The prepared SBA-15

ABSTRACT

 Co^{2+} was introduced into aminopropyl-functionalized mesoporous silica SBA-15 by an adsorption method. Characterizations with XRD and HRTEM suggested that the prepared material still retained a highly ordered structure, and the cobalt ions were highly dispersed in the molecular sieves. The cobalt-containing SBA-15 was considerably active in the epoxidation of styrene with O₂. Cobalt content, preparation method and oxidant influenced the catalytic performance. The material possessed better stability and recyclability in the reaction.

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containing cobalt was used for the epoxidation of styrene with O₂, and it exhibited high activity in the reaction owing to the effective introduction of cobalt and its suitable state of existing.

2. Experimental

2.1. Preparation of catalysts

Aminopropyl-functionalized SBA-15 was synthesized according to Ref. [19]. In our typical run, 4 g surfactant P123 ($EO_{20}PO_{70}EO_{20}$, $M_{av} = 5800$, Aldrich) was dissolved in 125 g 2.0 M HCl solution, and then a certain amount of tetraethyl orthosilicate (TEOS) was added dropwise into the solution under strong stirring. After prehydrolysis for 2 h at 40 °C, an appropriate amount of aminopropyltriethoxysilane (APTES) was introduced into the sol mixture, followed by vigorous stirring for another 22 h. The molar composition of the mixture was (1-x) TEOS:x APTES:6.1 HCl:0.017 P123:165 H₂O, where x ranges from 0 to 30%. The gel solution was transferred to an autoclave, undergoing hydrothermal reaction at 100 °C for 24 h. The product was filtered and air-dried, followed by template removal by soxhlet extraction with ethanol. After drying at 50 °C, the obtained functionalized samples are designated as SBA-15-x, where x is the molar ratio of APTES in the initial synthesis system.

 Co^{2+} or other transition metal ion was introduced into the functionalized SBA-15 by the following procedures. 5 g of the functionalized sample was immersed in 200 mL of the aqueous solution containing $Co(NO_3)_2$ or one of the other transition metal precursors ($Cr(NO_3)_3$, $MnCl_2$, $Fe(NO_3)_3$, $Ni(NO_3)_2$, $Cu(NO_3)_2$ or Zn $(NO_3)_2$) (0.05–0.15 mol/L, pH of 7.5) for 24 h under stirring. The solid was obtained by filtration, and then it was washed with deionized



^{*} Corresponding authors. Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China. Tel./fax: +86 351 4041526.

E-mail addresses: yzhang@sxicc.ac.cn (Y. Zhang), lfzhao@sxicc.ac.cn (L. Zhao).

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water and dried at room temperature. The product is denoted as M-SBA-15-x-y, where M is the metal absorbed on the functionalized sample and y is the metal content in the sample. The concentration of the aqueous solution was regulated to control the degree of adsorption and the metal content in the sample.

For comparison, Co/SBA-15 was prepared by a conventional impregnation method [11], and Co-MCM-41-TIE was prepared by the template-ion exchange method according to Ref. [10]. Furthermore, Co-SBA-15₁₀ was also prepared by the pH-adjusting method [14].

2.2. Characterization of catalysts

X-ray diffraction (XRD) patterns were obtained on RIGAKU D/maxrB X-ray diffractometer using Cu K α radiation (40 mA, 40 kV). The textural properties of the samples were derived from N₂ adsorption/ desorption measurement at 77 K on Micromeritics Tristar 3000. Pore size distributions for mesoporous materials were calculated from the desorption isotherms by the BJH method. Metal content in each sample was analyzed with inductively coupled plasma-atom emission spectroscopy (ICP-AES) on a TJA Atomscan 16 spectrometer. High resolution transmission electron microscopy (HRTEM) measurements were carried out on JEOL JEM-2010 operating at 200 kV.

2.3. Catalytic reactions

The epoxidation of styrene with O_2 was performed in a 250-ml three-necked flat-bottomed glass flask equipped with a liquid condenser. Typically, 8 mmol of styrene, 24 g of N,N'-dimethylformamide (DMF) and 0.3 g of catalyst were added to the reactor. The mixture was stirred vigorously by a magnetic stirrer and heated to 100 °C. Then 15 mL/min of O_2 was introduced into the liquid by bubbling at atmospheric pressure. The reactant mixture was stirred vigorously for 6 h. After completion of the reaction, the liquid products were obtained by centrifugation and they were quantitatively analyzed by a gas chromatograph equipped with a capillary column (DB-5, $30 \text{ m} \times 0.25 \text{ µm} \times 0.25 \text{ µm}$) and a FID detector, with bromobenzene as an internal standard. Under the most reaction conditions, the polymerization of styrene was negligible, so polymers in the reaction products were not considered. The conversion of styrene and selectivity of the products were calculated as follows:

Styrene conversion(%) = (*initial moles*-*final moles*) / (*initial moles*) × 100%

The product selectivity(%) = (moles of the product) / (moles of all products) \times 100%.

Recycling tests of Co-SBA-15-20-5.2 were carried out at 100 °C for 6 h. The catalyst was recovered from the reaction mixture by centrifugation, washing with acetone, and drying at 100 °C for 12 h. It was then used in the next run under identical conditions.

3. Results and discussion

3.1. Structural characteristics of catalysts

All the samples showed three well-resolved peaks that can be indexed as (100), (110) and (200) diffractions associated with hexagonal symmetry when the molar ratios of APTES in the initial synthetic system were less than 20% (Fig. 1 (A)). This indicates that the samples still retain a highly ordered hexagonal structure even if higher content of APTES is grafted into the mesoporous silica and a certain amount of cobalt ions is adsorbed onto the surface by amino groups. On the other hand, high-angle XRD patterns for both Co-SBA-15-20-5.2 and Co-MCM-41-TIE merely displayed a broad peak due to the amorphous feature of the framework of SBA-15 or MCM-41 (Fig. 1(B)). However, XRD patterns of Co/SBA-15 showed peaks at 37°,



Fig. 1. XRD patterns of the synthesized samples. (A) Small-angle, (B) high-angle.

 45° , 59° and 65° , ascribed to the crystalline Co_3O_4 . The results indicate that the cobalt introduced by the adsorption method and templateion exchange method is highly dispersed in the molecular sieves. The HRTEM observations (the best one we obtained) showed that the pores of the cobalt-containing mesoporous silica were hexagonally arranged, and no large particles were located outside the mesopores for Co-SBA-15-15-3.6, even if 15% of APTES was added into the initial system during its synthesis and 3.6 wt.% of cobalt was introduced (see Fig. 2).



Fig. 2. HRTEM image of Co-SBA-15-15-3.6.

| Samples | Co content (wt.%) | Surface area (m^2/g) | Pore volume (cm ³ /g) | Pore diameter (nm) | Styrene conversion (%) | Epoxide selectivity (%) |
|------------------|-------------------|------------------------|----------------------------------|--------------------|------------------------|-------------------------|
| SBA-15 | - | 608 | 1.2 | 8.2 | - | - |
| Co-SBA-15-10-2.1 | 2.1 | 511 | 0.66 | 5.2 | 69.5 | 62.8 |
| Co-SBA-15-15-3.6 | 3.6 | 490 | 0.49 | 4.0 | 81.7 | 64.0 |
| Co-SBA-15-20-5.2 | 5.2 | 468 | 0.36 | 3.1 | 92.4 | 63.2 |
| Co-SBA-1510 | 3.6 | 292 | 1.01 | 13.8 | 93.9 | 65.5 |
| Co-MCM-41-TIE | 5.2 | 689 | 0.52 | 3.0 | 53.6 | 58.5 |
| Co/SBA-15 | 5.2 | 506 | 0.81 | 6.4 | 47.8 | 54.7 |

Textural properties of Co-containing SBA-15 materials and their catalytic performance in epoxidation of styrene with O2.

Reaction condition: styrene, 8 mmol; DMF, 24 g; catalyst, 0.3 g; temperature, 100 °C; time, 6 h and flow rate of O2, 15 mL/min.

3.2. Content of cobalt introduced and changes in textural properties after APTES and cobalt introduction

Table 1 summarizes the content of cobalt in the samples. Clearly, pure silica SBA-15 showed no adsorption ability for Co^{2+} because of no amino groups. The cobalt content in Co-SBA-15-20-5.2 was 5.2 wt.%, higher than that in Co-SBA-15-10-2.1, indicating that more grafted amino groups show a better adsorption performance when equilibration of adsorption takes place.

The textural properties for the synthesized samples are listed in Table 1. Compared with pure silica SBA-15, functionalization with APTES and cobalt introduction made surface area, pore volume and pore diameter obviously decrease, due to the space occupied by the aminopropyl chains bound on the inner surface of the mesopores and a certain amount of cobalt introduced. All of the parameters gradually decreased with the increase of amino groups and cobalt content.

3.3. Investigations of epoxidation of styrene with O_2 over synthesized catalysts

Table 1 lists the catalytic performance of various cobalt-based catalysts in the epoxidation of styrene with O_2 . The pure silica was nearly inert in the reaction. For the cobalt-containing mesoporous silica, styrene conversion increased obviously with the rise of cobalt content in the samples. This suggests that catalytic activity of the catalyst depends on the number of cobalt sites. And the increase of cobalt content relies on the rising of the grafted amino groups. On the other hand, cobalt content in the samples made no difference to epoxide selectivity.

As Table 1 shows, the preparation methods play a great impact on the performance of the catalysts. Co-SBA-15-20-5.2 and Co-SBA-15₁₀ exhibited the similar catalytic performance. The catalytic activity in the epoxidation of styrene by O₂ decreased in the sequence Co-SBA-15-20-5.2>Co-MCM-41-TIE>Co/SBA-15 with the same cobalt content of 5.2 wt.% under the identical reaction conditions. The cobalt in Co-MCM-41-TIE and Co-SBA-15₁₀ mainly existed in the single-site Co(II) state [10,14], whereas Co/SBA-15 basically contained Co₃O₄,

Table 2

Table 1

Epoxidation of styrene with O_2 catalyzed by various metal ions based on aminopropyl-functionalized SBA-15.

| Catalyst | Styrene | Product selectivity % | | | |
|------------------|----------------|-----------------------|---------|-------------------|--------------------|
| | conversion (%) | Bena ^a | Epoxide | Phea ^b | Other ^c |
| Co-SBA-15-20-5.2 | 92.4 | 15.6 | 63.2 | 7.9 | 13.3 |
| Cr-SBA-15-20-5.2 | 12.6 | 27.2 | 47.4 | 8.2 | 17.2 |
| Mn-SBA-15-20-5.2 | 3.1 | 48.3 | 35.5 | 7.7 | 8.5 |
| Fe-SBA-15-20-5.2 | 20.7 | 22.1 | 55.9 | 8.4 | 13.6 |
| Ni-SBA-15-20-5.2 | 5.5 | 47.8 | 38.3 | 8.3 | 5.6 |
| Cu-SBA-15-20-5.2 | 0 | - | - | - | - |
| Zn-SBA-15-20-5.2 | 4.5 | 21.9 | 56.6 | 8.1 | 13.4 |

Reaction condition: styrene, 8 mmol; DMF, 24 g; catalyst, 0.3 g; temperature, 100 $^\circ C$; time, 6 h and flow rate of O2, 15 mL/min.

^a Benzaldehyde.

^b Phenylacetaldehyde.

^c Includes benzoic acid, phenylacetic acid, etc.

as indicated by XRD. Through comparison, the adsorbed Co^{2+} on the aminopropyl-functionalized SBA-15 and the cobalt species in Co-SBA-15₁₀ are the most active for the epoxidation of styrene with O₂.

Table 2 shows the catalytic performance of different metal ions based on aminopropyl-functionalized SBA-15. Among the various transition metal-containing SBA-15 materials, Co-SBA-15-20-5.2 exhibited the best catalytic performance. Both the highest styrene conversion and epoxide selectivity were obtained over this catalyst. Other metal ions were all inferior to Co^{2+} in the reaction when they were adsorbed onto the aminopropyl-functionalized mesoporous silica. The reason for this might be the differences of their performance for activation of molecular oxygen. A few previous researches indicated that the reaction solvent (DMF) could coordinate to cobalt(II), and such coordination affected the ability of O₂ to bind to the Co(II) as well as their redox potential, which led to the activation of O₂ in the epoxidation [10,20]. However, other transition metal ions cannot effectively activate O₂. This may explain why cobalt ions are superior to other metals in the reaction.

Table 3 summarizes the catalytic performance of Co-SBA-15-20-5.2 in the epoxidation of styrene with various oxidants. No styrene conversion was observed when the reaction was carried out under Ar or N₂ without any oxidants. The catalyst showed similar features under O₂ and air, and the best catalytic performance was obtained with the two oxidants. When H₂O₂ was used, the styrene conversion was 48.8%, much lower than that with O_2 or air, probably ascribed to the rapid decomposition of H_2O_2 into O_2 at the initial stage. The catalyst showed the lowest activity if TBHP was used, and the polymerization of styrene was a serious problem. In fact, the two homogenous oxidants (H₂O₂ and TBHP) can be decomposed under the reaction conditions. Reaction activity of the catalyst had some improvement (62.7% of conversion) when H₂O₂ was added in several portions over the reaction course, but it was still lower than that when O_2 or air was used as oxidants. By comparison, O_2 or air is an appropriate oxidant in the epoxidation of styrene over the cobaltbased catalyst.

| Table 3 |
|---|
| Epoxidation of styrene with various oxidants over Co-SBA-15-20-5.2. |

| Oxidant | Styrene | Product selectivity % | | | | |
|----------|----------------|-----------------------|---------|-------------------|--------------------|--|
| | conversion (%) | Bena ^a | Epoxide | Phea ^b | Other ^c | |
| None | 0 | - | - | - | - | |
| 02 | 92.4 | 15.6 | 63.2 | 7.9 | 13.3 | |
| H_2O_2 | 48.8 | 21.4 | 60.3 | 2.8 | 15.5 | |
| TBHP | 37.3 | 20.3 | 70.8 | 8.9 | 0 | |
| Air | 91.9 | 17.4 | 62.4 | 8.2 | 12.0 | |

Reaction condition: styrene, 8 mmol; DMF, 24 g; catalyst, 0.3 g; temperature, 100 $^\circ$ C; time, 6 h; oxidant amount, O₂, 15 mL/min; H₂O₂, 10 mmol; TBHP, 10 mmol and air, 40 mL/min.

^a Benzaldehyde.

^b Phenylacetaldehyde.

^c Includes benzoic acid, phenylacetic acid, etc.



Fig. 3. Recycling investigations of Co-SBA-15-20-5.2 in epoxidation of styrene with O^a, (■) styrene conversion, and (▲) epoxide selectivity. ^aReaction condition is the same as that in Table 2.

Catalyst recycling experiments were performed with repeated use of Co-SBA-15-20-5.2 at 100 °C for 6 h. The styrene conversion slightly decreased after the first cycle, and a small part of cobalt ions in the catalyst was lost (Fig. 3). But the catalytic performance changed little from the second cycle. The styrene conversion and epoxide selectivity were kept more or less constant (88.0% and 63.0% respectively). Any visible amount of cobalt in the solution was not detected by the chemical analyses, indicating little leaching of Co²⁺ from the catalyst. This suggests the stability and recyclability of the catalyst.



Fig. 4. Proposed mechanism for epoxidation of styrene with O₂ over Co²⁺ catalyst. L in DMF-LCo²⁺ means SBA-15-x-y.

3.4. Reaction mechanism

Based on our studies and other researchers' work [6,9,10], a proposed mechanism for epoxidation of styrene with molecular oxygen over the Co²⁺ catalyst is illustrated in Fig. 4. DMF molecules were coordinated to the cobalt cations which are adsorbed on the surface of aminopropyl-functionalized SBA-15, forming DMF-LCo(II). The resultant cobalt complex was coordinated to molecular oxygen to form a cobalt superoxo complex DMF-LCo(III)OO• I, which led to oxidative addition to the CC double bond of styrene molecules to give the styrenic olefin II. Through migratory insertion, II was rearranged into the intermediate III. III then collapsed to the cyclic peroxide radical IV and the cobalt catalyst DMF-LCo(II) was regenerated. The intermediate IV could react via two different pathways. One is that IV underwent thermal decomposition to benzaldehyde and formaldehyde, and the other reaction is that IV could react with another molecule of styrene to generate epoxide and by-products (isomeride, over-oxidation product). In the catalytic reaction, formaldehyde was not detected in the obtained liquid products. However, we introduced the tail gas into water to trap the possibly escaped formaldehyde with the unreacted oxygen, and formaldehyde was detected in the water after reaction. Clearly, this confirmed the presence of formaldehyde.

4. Conclusions

Cobalt-containing SBA-15 was prepared by the adsorption method. The prepared material still retained highly ordered structure. The cobalt introduced was highly dispersed in the aminopropylfunctionalized mesoporous silica. The cobalt ions that were adsorbed onto the functionalized SBA-15 showed excellent catalytic performance in the epoxidation of styrene with O_2 . O_2 or air was a suitable oxidant over the catalyst. The catalyst possessed better stability and recyclability in the reaction.

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