Synthesis of mesoporous Co/Ce-SBA-15 materials and their catalytic performance in the catalytic oxidation of benzene

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Abstract

Cerium-containing SBA-15 mesoporous materials, with different Ce/Si molar ratios, were synthesized by a direct hydrothermal synthesis method and further modified by impregnation with 10, 15 and 20 wt.% Co. Characterizations by powder X-ray diffraction (XRD), N₂ sorption, inductively coupled plasma (ICP) and UV–vis spectroscopy were carried out. The small-angle XRD and N₂ sorption characterizations showed that these Co supported materials have less-ordered mesoporous structures with partial blockage of pores, and their specific surface area, pore volume and pore size were relatively lower than those of unsupported cerium-containing SBA-15. Spinel Co₃O₄ constituted the predominant cobalt phase in the prepared catalysts, and CeO₂ was also detected. All the Co supported catalysts exhibited high catalytic activity in the oxidation of benzene.

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1. Introduction

Periodic mesoporous materials have been widely explored as supports for preparing Co supported catalysts [1–8]. The high surface area and uniform pore-size distribution of mesoporous molecular sieves facilitate the development of higher metal dispersions and better control on the cobalt particle size. Among many kind of mesoporous silicas such as MCM-41, MSU, FSM-16 and SBA-15, etc., SBA-15 has attracted much more attention and been used as support in many catalytic reactions owing to its higher surface area (600–1000 m²/g) and larger pore diameter ranging from 5 to 30 nm [9,10]. Recently, Co supported SBA-15 was prepared and proven to be an effective catalyst for the CO oxidation [4], removal of volatile organic compounds [5] and the Fischer–Tropsch synthesis of hydrocarbons [6–8]. However, studies on the catalytic performance of M–Co (M = metallic element) bimetallic system supported on a mesoporous surface are very limited [2,11].

Cerium-containing materials are powerful one-electron oxidants [12]. Existence of different sites of cerium ions may be important for catalytic activity [13]. Ceria has been widely used as a direct support material or an additive in many oxidation catalysts because of its low temperature reducibility, oxygen storage and release properties. These

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ceria-containing catalysts have been studied in the oxidation of CO [14], water–gas shift reactions [15], elimination of CO and NO_x contaminants from automotive exhaust gases and combustion of hydrocarbons [16].

In a recent work, we synthesized cerium-containing SBA-15 materials by the direct hydrothermal method [9]. These materials possessed the typical hexagonal structure of SBA-15 and displayed a large pore diameter with uniform pore size distribution [9]. It was also observed that the application of the direct hydrothermal method favored the dispersion of CeO₂ on SBA-15, to a greater extent, than the traditional impregnation method—an observation that has been previously reported [17]. Furthermore, these cerium-containing SBA-15 materials have a higher specific surface area than SBA-15 [18]. Thus, it can be predicted that the combination of cobalt with cerium-containing SBA-15 will lead to a good catalytic performance. However, to the best of our knowledge, there has been no published work, on the utilization of cerium-containing SBA-15 as a catalyst support material.

In this study, highly ordered cerium-containing SBA-15 mesoporous materials were synthesized and used as a support to prepare cobalt/cerium bimetallic catalysts. All catalysts were characterized by powder X-ray diffraction (XRD), N₂ sorption, UV–vis spectra analysis and inductively coupled plasma (ICP) analysis. Their catalytic activity was investigated by the catalytic deep oxidation of benzene.

2. Experimental

Cerium-containing SBA-15 materials were synthesized using tetraethyl-orthosilicate (TEOS) and cerium nitrate (Ce(NO₃)₃·6H₂O) as the silicon and cerium precursors respectively. Nonionic triblock copolymer surfactant EO₂₀PO₇₀EO₂₀ (P123, Aldrich) was used as the structure-directing agent. Concentrated aqueous HCl solution was used as the acid source.

Cerium-containing SBA-15 was synthesized as follows: 1 g of P123 was dissolved in 35 ml of aqueous HCl solution at pH 2.0, then a certain amount of cerium nitrates was added, followed by the addition of 2.3 ml TEOS and a certain amount of NH₄F (F/Si = 0.03). After stirring at 35 °C for 24 h, the mixture was transferred into an autoclave and aged at 100 °C for 48 h. The resultant solid was filtered and dried at 100 °C for 24 h. The mesoporous samples were finally obtained after calcination at 550 °C for 6 h. The percentage of cerium present was 8, 15 and 25% and expressed as the weight ratio of $W_{\text{cerium}}/W_{\text{Ce-SBA-15}}$. These samples were noted as yCe-SBA-15, where y is the cerium content (wt.%) in the Ce-SBA-15.

The cobalt-loaded Ce-SBA-15 was prepared by the wetness impregnation technique. Different amounts of cobalt nitrate hydrate (Co(NO₃)₂·6H₂O) were dissolved in 10 ml of ethanol, mixed with 0.5 g of Ce-SBA-15, and evaporated at 60 °C. These products were finally calcined at 500 °C for 4 h in static air for the decomposition of impregnated salt to cobalt oxide. The percentage of cobalt tested was 10, 15 and 20% and expressed as the weight ratio of $W_{\text{cobalt}}/(W_{\text{cobalt}} + W_{\text{Ce-SBA-15}})$. The samples were noted as Co-*x*/yCe-SBA-15, where *x* represents the cobalt loading (wt.%).

To study the effect of different supporting materials on catalytic performance, CeO₂/SBA-15 and CeO₂/Al₂O₃, which were prepared by the wetness impregnation method, were also developed to load Co. Using Ce(NO₃)₃·6H₂O as the precursor, Ce was firstly loaded on SBA-15 (BET area, 662 m²/g) and Al₂O₃ (148 m²/g). These cerium-containing materials were then used as supports to prepare Co/CeO₂/SBA-15 and Co/CeO₂/Al₂O₃ catalysts by loading Co through the use of a similar method to the one mentioned above. The cerium and cobalt content in these catalysts was 8 and 10 wt.%, which is similar to that of the Co-10/8Ce-SBA-15 sample.

The metal content in the catalysts was determined by ICP (OPTIMA 2000). Before any measurements were taken, the solid sample was dissolved in dilute HNO₃ solution with a small amount of HF. Wide-angle XRD patterns were measured on a Rigaku powder diffractometer (D/MAX-RB) using Cu Kα radiation ($\lambda = 0.15418$ nm) in the 2θ range of 10–70° with a scanning rate of 4° min^{−1}. Small-angle XRD was recorded on a SIEMENS D5005D powder diffraction system using Cu Kα radiation in the 2θ range of 0.7–6.0° with a scanning step size of 0.02°. The textural properties of the samples were measured by N₂ sorption at liquid N₂ temperature, using a gas adsorption analyzer NOVA 1200. The diffuse reflectance UV–vis spectra were collected on a HITACHI UV3000 scanning spectrophotometer from 190 to 800 nm. The powder sample was loaded into a quartz cell and BaSO₄ was used as reference.

The catalytic activity was investigated in a fixed bed reactor and the temperature of catalyst bed was measured by a thermocouple. To create the stream containing benzene, one stream of pure air was passed through a boat-shaped saturator in an ice bath to produce a mixed gas containing benzene of high concentration, which was further diluted, with another stream of pure air before reaching the reaction bed. The total flow rate was set to be 320 ml min^{−1} with

the concentration of ca. 1000 ppm by adjusting the two flows. In each run, 300 mg of catalyst with 40–60 meshes was tested. The gas hourly space velocity (GHSV) in the tests was kept ca. $39,600 \text{ h}^{-1}$. An on-line gas chromatograph (GC) equipped with a FID detector was used to analyze the concentration of benzene in the inlet and outlet gas.

3. Results and discussions

3.1. Structural characterization of Co/Ce-SBA-15 catalysts

Fig. 1 displays the small-angle XRD patterns of 8Ce-SBA-15 and Co-*x*/8Ce-SBA-15 catalysts. Three well-resolved diffraction peaks of 8Ce-SBA-15, indexed as the (1 0 0), (1 1 0), (2 0 0) diffractions, reflect the two-dimensional hexagonal mesostructure with a space group of *p6mm* symmetry [9]. After being impregnated, the intensity of the characteristic reflection peaks of Co-*x*/8Ce-SBA-15 is found to be reduced, indicating the loss of long-range order. This may be attributed to the symmetry destroyed by the Co species, which was also found in the ordered mesoporous silica loading with guest matter. This is evident by the decreased diffraction contrast [19]. Furthermore, the prominent peak (1 0 0) of Co-*x*/8Ce-SBA-15 shifts to lower angles compared with 8Ce-SBA-15. The unit-cell parameters (a_0) of cobalt-supported catalysts are provided in Table 1. It can be observed that the a_0 of all the Co-*x*/8Ce-SBA-15 (ca. 11.6–11.8 nm) is larger than that of 8Ce-SBA-15 (11.42 nm). This may be ascribed to the partial incorporation of cobalt into the framework of 8Ce-SBA-15 [20].

The wide-angle XRD patterns of the catalysts are shown in Fig. 2. In all prepared catalysts, the cobalt was present in the form of spinel Co_3O_4 (JCPDS file No. 9-0418). The characteristic peaks of Co-*x*/8Ce-SBA-15 become narrow and sharp with an increase in cobalt loading, indicating an increase of the mean Co_3O_4 crystallite size. There is no obvious difference of Co_3O_4 characteristic peaks for Co-20/yCe-SBA-15 catalysts, except for a slight increase in the mean Co_3O_4 crystallite size with the increase of Ce content in the support. The crystallite size of Co_3O_4 was calculated from the line broadening of the most intense XRD reflections, using the Scherrer equation [21], and shown in Table 1. For all the catalysts, the mean Co_3O_4 crystallite size was in the range of 2.3–10.9 nm, which was smaller than that of bulk Co_3O_4 reported in our previous work [4]. This indicates that Co_3O_4 was well dispersed on the surface of yCe-SBA-15 but its crystallite size increases with increasing cobalt loading. Besides the detection of Co_3O_4 spinel phase, the characteristic diffraction peaks of CeO_2 fluorite structure at $2\theta = 28.5, 33.3, 47.5$ and 56.4° are clearly observed for all

Fig. 1. SAXRD patterns of (a) 8Ce-SBA-15, and its modified catalysts with different cobalt loadings: (b) 10%, (c) 15% and (d) 20%.

Table 1

Physico-chemical property of catalysts

Catalysts	Co content (%)	a_0^a (nm)	S_{BET}^b (m ² /g)	V_p^c (cm ³ /g)	D_p^d (nm)	w^e (nm)	$d_{(\text{Co}_3\text{O}_4)}$ (nm)
25Ce-SBA-15	–	11.52	797.23	1.1	6.5	5.02	–
15Ce-SBA-15	–	11.45	864.46	1.2	6.6	4.85	–
8Ce-SBA-15	–	11.42	912.26	1.2	6.6	4.82	–
CeO ₂ /SBA-15	–	–	594.33	0.78	5.8	–	–
CeO ₂ /Al ₂ O ₃	–	–	113	0.31	10.4	–	–
Co-20/25Ce-SBA-15	19.7	11.62	452.10	0.58	5.28	6.34	10.9
Co-20/15Ce-SBA-15	19.6	11.68	495.97	0.59	5.01	6.67	10.7
Co-20/8Ce-SBA-15	19.6	11.63	529.99	0.63	4.59	7.04	10.6
Co-15/8Ce-SBA-15	14.6	11.81	556.22	0.67	4.52	7.29	6.2
Co-10/8Ce-SBA-15	9.2	11.58	584.37	0.72	4.36	7.22	2.3
Co/CeO ₂ /SBA-15	9.4	–	418.26	0.43	4.29	–	–
Co/CeO ₂ /Al ₂ O ₃	9.2	–	86	0.21	8.7	–	–

^a a_0 calculated by d_{100} , $a_0 = 2 \times d_{100} / \sqrt{3}$.^b BET specific surface areas.^c Total pore volumes were obtained at $P/P_0 = 0.99$.^d Average pore diameters.^e Pore wall thickness = $a_0 - D_p$.

the catalysts. However, there is no other significant diffraction peak found, therefore, it is difficult to identify the existence of the Co–Ce–O compound.

Fig. 3 displays the adsorption/desorption isotherms of Co- x /8Ce-SBA-15 and 8Ce-SBA-15 materials. For all samples, the isotherms were of type IV according to the IUPAC classification of adsorption isotherms [22], which is a typical characteristic of mesoporous materials. However, it is easy to observe that the hysteresis loops of Co- x /8Ce-SBA-15 become broader than those of 8Ce-SBA-15. The desorption branch of the isotherm shifts to lower pressure, whereas the adsorption branch is not significantly changed. As suggested by Ravikovitch and Neimark [23], this

Fig. 2. X-ray diffraction patterns for Co- x / y Ce-SBA-15 catalysts: (a) Co-10/8Ce-SBA-15; (b) Co-15/8Ce-SBA-15; (c) Co-20/8Ce-SBA-15; (d) Co-20/15Ce-SBA-15 and (e) Co-20/25Ce-SBA-15. (▲) Co₃O₄; (●) CeO₂.

Fig. 3. Nitrogen adsorption/desorption isotherm of (a) 8Ce-SBA-15, and its modified catalysts with different cobalt loadings: (b) 10%, (c) 15% and (d) 20%.

behavior indicates the coexistence of open and partially closed mesopores. A peculiar two-step behavior is observed on the hysteresis loop of Co supported catalysts. The open mesopores behave as usual and produce the first step hysteresis loop on the desorption branch that ends near $P/P_0 = 0.6$, and the partially blocked mesopores are associated with the second step hysteresis loop which ends near $P/P_0 = 0.4$. The two-step hysteresis loop indicates that cobalt oxide particles have grown in the pores of the 8Ce-SBA-15 [24]. The physico-chemical properties of the investigated catalysts are given in Table 1. For the Co- x /8Ce-SBA-15 samples, an increase in Co loading from 10 to 20%, yielded in a decrease of the specific surface area (S_{BET}) and pore volume (V_p) from 584 to 529 m^2/g and from 0.72 to 0.63 cm^3/g , respectively. This may be attributed to the micropore block by cobalt loading on the mesoporous surface. Comparing Ce-SBA-15 and Co/Ce-SBA-15, it was further found that the cobalt loading significantly reduces the specific surface area and porous size (D_p) but increases wall thickness (w), which further confirms cobalt dispersion on the mesoporous surface. For the Ce-SBA-15 support materials, the S_{BET} decreased from 912 to 797 m^2/g with no obvious changes in V_p and D_p with the increase of cerium content. This indicates that cerium directly influences the microporous structure in framework.

DRS spectra in the UV–vis region of 8Ce-SBA-15 and corresponding cobalt modified catalysts Co-10/8Ce-SBA-15 and Co-20/8Ce-SBA-15 are shown in Fig. 4. The adsorption peaks centered at 300 nm were observed in all the samples. The peak is attributed to the metal charge transfer ($\text{O}^{2-} \rightarrow \text{Ce}^{4+}$) of CeO_2 clusters [25], which is in agreement with the results obtained from XRD patterns. For Co/Ce-SBA-15, there appear to be two new adsorption peaks at 380 and 700 nm, which are indicative of Co_3O_4 clusters [26]. With the increase in cobalt loading, these two peaks become stronger. Characteristic peaks attributing to Co(II) are not observed in Fig. 4, which indicates that Co_3O_4 is the predominant phase when the cobalt loading is high [27]. Besides the previously mentioned peaks, an adsorption peak centered at ca. 230 nm can also be observed for all the samples. According to Ref. [28], the authors have attributed the band to the presence of the NO_3^- ions inside the support pores.

3.2. Catalytic testing of Co/Ce-SBA-15

The catalytic performance of Co- x /yCe-SBA-15 catalysts in the oxidation of benzene is listed in Table 2. All the catalysts tested show high catalytic performance and can achieve 90% benzene conversion below 340 °C. For the

Fig. 4. UV-vis adsorption spectra of (a) 8Ce-SBA-15 and Co supported catalysts (b) Co-10/8Ce-SBA-15 and (c) Co-20/8Ce-SBA-15.

Co- x /8Ce-SBA-15 catalysts, the catalytic activities increase with an increase in cobalt loading. Co-10/8Ce-SBA-15 showed the poorest catalytic performance, with T_{10} (the temperature at which the benzene conversion reached 10%) of about 255 °C and T_{90} (the temperature at which the benzene conversion reached 90%) of 340 °C. While for Co-20/8Ce-SBA-15, T_{10} and T_{90} were about 245 and 300 °C, respectively. On the other hand, Co-20/ y Ce-SBA-15 exhibits an obvious enhancement of catalytic activity with an increase in cerium content in the supports, which can be referred in Table 2. Particularly at 280 °C, the conversion of benzene increased significantly from 50 to 95% as shown in Fig. 5. Table 2 also shows the catalytic performance of Co/CeO₂/SBA-15, Co/CeO₂/Al₂O₃ on benzene deep oxidation. It was observed that these catalysts are less active than the Co-10/8Ce-SBA-15 catalysts.

As shown in Table 1, the S_{BET} , V_p and D_p of CeO₂/SBA-15 are much lower than that of 8Ce-SBA-15. This may be ascribed to the blockage of the support pores by CeO₂, which can be observed in the impregnated sample [29]. While for 8Ce-SBA-15 synthesized by the direct hydrothermal method, CeO₂ was better dispersed, which is supported by the XRD patterns in Fig. 6. The S_{BET} , V_p and D_p of CeO₂/Al₂O₃ are the smallest among all the supports tested. By comparing CeO₂/SBA-15, CeO₂/Al₂O₃ and 8Ce-SBA-15, it was found that 8Ce-SBA-15 has a higher specific surface area that makes it an ideal candidate for use as a catalyst support.

The Ce-SBA-15 supported cobalt catalysts showed good catalytic performance in the catalytic deep oxidation of benzene. The increase in cerium content in the support significantly increased the catalytic activity of Co/Ce-SBA-15.

Table 2
Benzene oxidation activities over Co- x / y Ce-SBA-15 catalysts

Catalysts	T_{10}	T_{50}	T_{90}
Co-20/25Ce-SBA-15	220	260	275
Co-20/15Ce-SBA-15	220	265	300
Co-20/8Ce-SBA-15	245	280	300
Co-15/8Ce-SBA-15	245	300	316
Co-10/8Ce-SBA-15	255	319	340
Co/CeO ₂ /SBA-15	270	340	372
Co/CeO ₂ /Al ₂ O ₃	300	355	390

Fig. 5. Conversion curves of benzene oxidation over Ce-SBA-15 supported cobalt oxide catalysts.

Thus, there may exist a synergy effect between the cobalt and cerium ions [4,30]. Taking into consideration previous reported results [31,32], we postulate that this increase in catalytic activity is due to a higher reducibility of cobalt oxides and the increase in the amount of metallic atoms on the surface caused by the increase of cerium added. Detailed investigation of the interaction between the cobalt and cerium is still in progress.

Fig. 6. XRD patterns of (a) CeO₂/SBA-15 and (b) 8Ce-SBA-15 synthesized at pH 2.0.

4. Conclusions

Ce-SBA-15 is used as a support for supported cobalt catalyst for the catalytic deep oxidation of benzene for the first time. On comparing with CeO₂/SBA-15 prepared by an impregnation method, Ce-SBA-15 material synthesized by a direct hydrothermal method appears more suitable for preparing supported cobalt catalysts with high activity. The high surface area and mesoporosity of Ce-SBA-15 favors the dispersion of Co₃O₄. These Co/Ce-SBA-15 catalysts show good catalytic performance in the oxidation of benzene, which is probably due to a synergy effect between the cobalt and cerium ions.

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