Catalytic combustion of benzene on Co/CeO₂/SBA-15 and Co/SBA-15 catalysts

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ARTICLE INFO

Article history:

Received 1 August 2007

Received in revised form 28 February 2008

Accepted 6 March 2008

Available online 18 March 2008

Keywords:

Benzene

Catalytic combustion

CeO₂/SBA-15 catalysts

Cobalt catalysts

ABSTRACT

Catalytic oxidation of benzene was investigated on Co/CeO₂/SBA-15 and Co/SBA-15 catalysts. These catalysts were characterized by X-ray diffraction, N₂ sorption and temperature programmed reduction (TPR) methods. The results show that Co₃O₄ are not well dispersed on CeO₂/SBA-15. The specific surface area and pore volume of CeO₂/SBA-15 are significantly decreased upon impregnation, which may be ascribed to the serious blockage of channel. Meanwhile, the TPR data show that the reduction of Co₃O₄ to Co⁰ is more difficult on CeO₂/SBA-15 than on SBA-15. Consequently, catalyst Co/CeO₂/SBA-15 shows lower catalytic activity than Co/SBA-15 in the oxidation of benzene.

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1. Introduction

Benzene is a kind of volatile organic compounds (VOCs), which is present in different industries, such as chemical, petrochemical, paint and coating industries and steel manufacture.

Catalytic oxidation is one of the significant technologies to eliminate VOCs. Supported metal oxides or noble metals are the most widely used catalysts in these oxidation reactions [1–8], among which cobalt-supported catalysts are quite promising for the catalytic combustion of VOCs [9–11]. Recently, the use of periodic mesoporous silicas as supports for preparing cobalt-based catalysts has been explored [12,13]. SBA-15 is the most widely used one, which has high surface area and uniform pore-size distribution, allowing for higher dispersions of active phase and better control on the particle size as compared with conventional amorphous silica or MCM-41 [12–16]. In a recent work, we synthesized ordered mesoporous CeO₂/SBA-15 materials by the direct hydrothermal method [17]. It was observed that the application of the direct hydrothermal method favored the preparation of CeO₂/BA-15 with higher specific surface area and better dispersion of CeO₂ on SBA-15 than traditional impregnation method. Furthermore, these CeO₂/BA-15 materials even have a higher specific surface area than SBA-15. Thus, it is presumed that CeO₂/SBA-15 can also be used as support for preparing cobalt catalysts with high activity. However, to the best of our knowledge, few reports on the use of CeO₂/SBA-15 as cobalt support have been published.

Ceria has been employed as a promoter for different alumina/silica-supported metal catalysts and its wide application is attributed to some special properties, such as: (i) excellent thermal and mechanical resistance; (ii) increase of the dispersion of supported metal and (iii) the high oxygen storage capacity [1,7,18–21]. However, the rare-earth element oxides can also cause a negative effect on activity of supported catalysts. It is found that the introduction of Ce⁴⁺ into composition of alumina–palladium catalyst leads to substantial decrease in its activity for carbon monoxide oxidation by oxygen [22].

In this work, we have undertaken a study of the oxidation of benzene on a series of Co/SBA-15 and Co/CeO₂/SBA-15 catalysts. The aim of this work is to investigate the effect of cerium on the dispersion of supported cobalt species, the reducibility of the cobalt species and the catalytic performance for the oxidation of benzene.

2. Experimental

2.1. Chemicals and preparation

Tetraethyl orthosilicate (TEOS) and cerium nitrate (Ce(NO₃)₃ · 6H₂O) were used as silicon and cerium precursors, respectively. Nonionic triblock co-polymer surfactant EO₂₀PO₇₀EO₂₀ (P123, Aldrich) was used as the structure-directing agent. Concentrated HCl aqueous solution was used as acid source.

CeO₂/SBA-15 was synthesized by a hydrothermal method [17]. One gram of P123 and a certain amount of cerium nitrates

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(Si/Ce = 20) were simultaneously dissolved into 35 ml aqueous HCl solution with pH 2.0. Then 2.3 ml TEOS and a little amount of NH_4F (F/Si = 0.03) were put in. 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 washed and dried at 100 °C for 24 h. After it was, the mesoporous sample was finally obtained after calcinations at 550 °C for 6 h. For comparison, pure SBA-15 was also synthesized with a similar method as above.

The cobalt-loaded catalysts were prepared by the wetness impregnation method. A certain amount of cobalt nitrate hydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was dissolved into 10 ml ethanol, mixed with 0.5 g of $\text{CeO}_2/\text{SBA-15}$ or pure SBA-15, and evaporated at 60 °C. In our previous research [23], it is observed that when the cobalt loading is 20%, $\text{Co}/\text{CeO}_2/\text{SBA-15}$ shows a relative high catalytic activity in the catalytic combustion of benzene among all the catalysts tested. Thus we fixed the cobalt loading by 20% in this work and expressed as the weight ratio of $W_{\text{cobalt}}/(W_{\text{cobalt}} + W_{\text{support}})$. These products were calcined at 500 °C for 4 h in static air for the decomposition of impregnated salt to cobalt oxide.

2.2. Catalyst characterization

The metal content in the catalysts was determined by ICP-AES (OPTIMA 2000).

Wide-angle XRD patterns were measured on a Rigaku powder diffractometer (D/MAX-RB) using Cu KR radiation ($\lambda = 0.15418 \text{ nm}$) in the range of 10–70°. Small-angle XRD was recorded on a SIEMENS D5005D powder diffraction system using Cu K α radiation in the range of 0.7–6°.

The textural properties of the support and cobalt-supported catalysts were measured by N_2 sorption at liquid N_2 temperature, using a gas sorption analyzer NOVA1200.

Temperature programmed reduction (TPR) was carried out in a quartz reactor, which was connected with a TCD detector. In each test, 30 mg of catalyst was used, and the temperature was raised from room temperature to 1173 K under a gas flow of 5% hydrogen balanced with nitrogen.

2.3. Oxidation reaction and products analysis

Catalytic oxidation of benzene on $\text{Co}/\text{SBA-15}$ and $\text{Co}/\text{CeO}_2/\text{SBA-15}$ was carried out in a continuous flow fixed-bed reactor of 6 mm i.d. that was placed in a tubular electrical furnace equipped with a temperature programmer under atmospheric pressure. In each test run, 300 mg of catalyst (40–60 mesh) was placed at the center of the reactor, above which a thermocouple was located to monitor the reaction temperatures. To create the steam containing benzene, one steam of pure air was passed through a boat-shaped saturator in an ice bath to make a mixed gas containing benzene of high concentration and then further diluted with another steam of pure air before reaching the reaction bed. And the total flow rate was set to be 320 ml/min with the concentration of ca. 1000 ppm by adjusting the two flow rates. The gas hourly space velocity (GHSV) in the tests was kept ca. 39,600/h. An on-line gas chromatograph equipped with FID detector was used to analyze the concentration of benzene in the inlet and outlet gas. Before each test, the temperature of the catalytic bed was raised to 120 °C under the feed stream and stabilized at that temperature until the concentration of benzene became constant, no conversion of benzene was observed at this temperature. Then the temperature of catalyst bed was raised with a heating rate of 5 °C/min, and the temperature was kept constant for 2 min at each datum point for equilibrium prior to analyzing the benzene concentration of the outlet gas.

3. Results and discussion

The small-angle XRD patterns of $\text{CeO}_2/\text{SBA-15}$ and SBA-15 are displayed in Fig. 1. It can be observed that $\text{CeO}_2/\text{SBA-15}$ has three well-resolved characteristic diffraction peaks centered at $2\theta = \sim 0.8^\circ$, $\sim 1.6^\circ$ and $\sim 1.8^\circ$, which is well in accordance with that of typical SBA-15 [24]. Compared with pure SBA-15, the peak (100) shifts to lower 2θ value and the unit cell a_0 ($a_0 = 2d_{100}/\sqrt{3}$) of $\text{CeO}_2/\text{SBA-15}$ (shown in Table 1) is increased. This increase of a_0 may be attributed to the incorporation of cerium into the framework of SBA-15 [25,26]. After being impregnated, the intensity of the characteristic diffraction peaks of $\text{Co}/\text{SBA-15}$ and $\text{Co}/\text{CeO}_2/\text{SBA-15}$ is found to be reduced (not shown), which is normally observed in the ordered mesoporous silica loading with guest matter and may be attributed to the symmetry destroying by the cobalt species [27].

The wide-angle XRD patterns of $\text{Co}/\text{CeO}_2/\text{SBA-15}$ and $\text{Co}/\text{SBA-15}$ catalysts are shown in Fig. 2. In both catalysts, the cobalt was present in the form of Co_3O_4 spinel (JCPDS file No. 9-0418). Compared with $\text{Co}/\text{SBA-15}$, the diffraction peaks of Co_3O_4 supported on $\text{CeO}_2/\text{SBA-15}$ are more intense and narrower. It suggests that Co_3O_4 particles are better dispersed on SBA-15 with smaller crystallite size than those supported on $\text{CeO}_2/\text{SBA-15}$. The crystallite size of Co_3O_4 was calculated from the line broadening of the most intense XRD reflections, using the Scherrer equation [28] and reported in Table 1. The mean Co_3O_4 crystallite size on SBA-15 was about 7.6 nm, while that on $\text{CeO}_2/\text{SBA-15}$ was increased to 10.6 nm. It should be noted that the characteristic diffraction lines of CeO_2 fluorite structure at $2\theta = 28.5^\circ$, 33.3° , 47.5° and 56.4° are clearly observed for catalyst $\text{Co}/\text{CeO}_2/\text{SBA-15}$. Although it can be speculated that the cerium cation has been incorporated into the framework of SBA-15 based on the increase of a_0 for $\text{CeO}_2/\text{SBA-15}$ [25,26], parts of the cerium still exist in the extra-framework and agglomerate into cerium oxides clusters.

The textural properties of the supports and co-supported catalysts obtained by N_2 adsorption/desorption isotherms are given in Table 1. It can be observed that $\text{CeO}_2/\text{SBA-15}$ has a higher specific surface area ($912 \text{ m}^2/\text{g}$) than that of pure SBA-15 ($672 \text{ m}^2/\text{g}$). This can be attributed to the enhancement in long-range ordering after cerium doping, as also seen in the XRD patterns in Fig. 1. But its total pore volume and average pore diameter are slightly

Fig. 1. The SAXRD patterns of different supports: (a) SBA-15 and (b) $\text{CeO}_2/\text{SBA-15}$.

Table 1

Chemical compositions and textural properties of SBA-15, CeO₂/SBA-15 and their corresponding co-supported catalysts

Sample	Co-content (wt%)	(Si/Ce) solid	S_{BET}^a (m ² /g)	D_v^b (cm ³ /g)	D_p^c (nm)	$d_{(\text{Co}_3\text{O}_4)}^d$ (nm)	a_0 (nm)
SBA-15	–	–	672	1.3	6.7	–	9.5
CeO ₂ /SBA-15	–	32.2	912	1.2	6.6	–	11.4
Co/SBA-15	19.5	–	478	0.84	5.01	7.6	–
Co/CeO ₂ /SBA-15	19.6	32.2	529	0.63	4.59	10.6	–

^a BET specific surface areas.

^b Total pore volumes are obtained at $P/P_0 = 0.99$.

^c Average pore diameters.

^d The crystallite size of Co₃O₄ was calculated using the Scherrer equation.

Fig. 2. X-ray diffraction patterns of different catalysts: (a) Co/SBA-15 and (b) Co/CeO₂/SBA-15. #, Co₃O₄; *, CeO₂.

smaller compared with that of SBA-15, decreasing from 1.3 cm³/g to 1.2 cm³/g and 6.7 nm to 6.6 nm, respectively. After the impregnation by cobalt oxides, a substantial loss in the S_{BET} , D_v and D_p for both supports could be observed in Table 1. The decrease is mainly caused by the partial blockage of the supports pores.

Fig. 3 displays the TPR profile of Co/SBA-15 and Co/CeO₂/SBA-15 catalysts. The reduction of supported cobalt oxide was generally divided into two stages [29,30], namely, the reduction of large crystalline Co₃O₄ particles at lower temperature and the reduction of surface cobalt oxide species that interact with the support at higher temperature. For sample Co/SBA-15, there are two main reduction peaks. The two low-temperature reduction peaks are close to each other with temperature maxima at about 340 °C and 376 °C, respectively. The first peak could be assigned to the reduction of Co₃O₄ to CoO, and the second one to the subsequent reduction of CoO to Co⁰ [31,32]. Besides these two main reduction peaks, a broad reduction peak in the temperature range of 630–770 °C is also observed, suggesting the presence of surface cobalt species that interact with the support at higher temperature [12].

In the case of Co/CeO₂/SBA-15, it can be observed that the reduction process of Co₃O₄ becomes difficult. The first peaks corresponding to the reduction of Co₃O₄ to CoO shifts to higher temperature with a maximum at about 356 °C and the second one corresponding to the reduction of CoO to Co⁰ shifts to 405 °C.

Fig. 3. H₂-TPR profiles of fresh samples: (a) Co/SBA-15 and (b) Co/CeO₂/SBA-15.

Moreover, a strong and broad reduction feature in the temperature range of ca. 672–920 °C is also observed, indicating the formation of hardly reducible cobalt silicates species [12].

The catalytic oxidation of benzene over Co/SBA-15 and Co/CeO₂/SBA-15 catalysts is illustrated in Fig. 4. It is observed that the products originated from the oxidation of benzene are CO₂ and H₂O, there is no other VOCs can be detected by GC (not shown). Co/SBA-15 shows an excellent catalytic performance, exhibiting a sharp conversion curve and being capable of achieving the complete oxidation of benzene at about 260 °C. In contrast, Co/CeO₂/SBA-15 is less active with a higher T₁₀₀ (the temperature for 100% conversion of benzene) at about 320 °C. The catalytic activity of Co (20 wt%)/CeO₂/SBA-15 with other Si/Ce molar ratios are also evaluated (not shown). Although there exhibits an obvious improvement of catalytic activity in the whole reaction temperature range upon increasing cerium addition, all the tested Co/CeO₂/SBA-15 catalysts do show lower catalytic activity than pure SBA-15 supported cobalt catalyst.

According to Li's report [23], large surface area favors better dispersion of the supported cobalt oxide species, thus enhancing the catalytic activity. While in the present work, it seems that the higher surface area of CeO₂/SBA-15 does not make the cobalt oxides better dispersed on them. It is presumed that the presence of CeO₂ fluorite existing in the extra-framework inhibits the dispersion of cobalt nitrate on the surface of CeO₂/SBA-15 and makes them easily aggregate, forming large Co₃O₄ crystallites (ca. 10.6 nm) when calcined at 500 °C. These Co₃O₄ particles significantly block the support mesopores and make the total pore volume of CeO₂/SBA-15 decreased drastically from 1.2 to 0.63 cm³/g with a D_v loss about 50% as shown in Table 1. While on SBA-15, cobalt nitrate are well diffused and transform into better-dispersed Co₃O₄ crystallites with little particle size (ca. 7.6 nm) after calcinations. From Table 1, it could be observed that the D_v loss of SBA-15 after impregnation is only about 35%, indicating a less blockage of mesopores induced by better dispersed Co₃O₄.

The reducibility of supported active species is an important parameter that influences the catalytic performance of supported catalysts. In this work, we propose that the reducibility of the supported cobalt oxide is an important factor that determines the activity of the Co supported catalysts. It is widely believed that Mars–van Krevelen mechanism is involved in catalytic oxidation

Fig. 4. Conversion of benzene over different catalysts: ■, Co/CeO₂/SBA-15 and ▲, Co/SBA-15.

reactions of hydrocarbons. This mechanism is characterized by a surface redox cycle: the metal oxide oxidizes the hydrocarbons and become less oxidative, and then the reduced metal oxide species was re-oxidized by oxygen again for next oxidation reaction cycle. Thus the reactivity of the oxygen species of metal oxide might determine the activity of the catalysts, and the reactivity of the oxygen species can be reflected by the reducibility of the active oxide phases [23]. According to TPR results shown in Fig. 3, it is observed that the reduction peak corresponding to the Co₃O₄ to Co⁰ shifts to higher temperature for Co/CeO₂/SBA-15. This means that the Co₃O₄ dispersed on the surface of CeO₂/SBA-15 is more difficult to be reduced than those on the surface of SBA-15. At the same time, it can be found that the area of reduction peak corresponding to the Co₃O₄ to Co⁰ on CeO₂/SBA-15 is smaller than that on SBA-15, indicating that there are fewer amounts of readily reducible Co₃O₄ particles dispersed on the CeO₂/SBA-15. The presence of a strong and broad reduction peak at ca. 672–920 °C on Co/CeO₂/SBA-15 can also indicate that large amount of Co₃O₄ strongly interact with the CeO₂/SBA-15 and show poor reducibility. Above all may be an interpretation of the lower catalytic activity of Co/CeO₂/SBA-15 than Co/SBA-15 in the catalytic oxidation of benzene.

4. Conclusion

XRD and N₂ adsorption/desorption analyses indicate that the Co₃O₄ are not well dispersed on CeO₂/SBA-15. Here, we speculate that CeO₂ presenting in the extra-framework hinders the diffuse of Co₃O₄ on CeO₂/SBA-15 and make them aggregated. The larger

Co₃O₄ particles readily block the mesopore, which make the total pore volume of CeO₂/SBA-15 significantly decreased upon impregnation. Compared with Co/SBA-15, Co/CeO₂/SBA-15 shows poorer catalytic performance in the oxidation of benzene. According to the TPR results, the difficult reduction of Co₃O₄ to Co⁰ on CeO₂/SBA-15 and less amount of reducible Co₃O₄ may be an explanation for the poor catalytic performance of Co/CeO₂/SBA-15. Further research is in progress.

Acknowledgments

National Basic Research Program of China (2004CB719500), High Technology Research and Development Program of China (2006AA06A310) and National Science Fund for Distinguished Young Scholars (20725723) are gratefully acknowledged.

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