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Catalytic combustion of benzene on Co/CeO_2/SBA-15 and Co/SBA-15 catalysts

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ABSTRACT

Catalytic oxidation of benzene was investigated on Co/CeO_2/SBA-15 and Co/SBA-15 catalysts. These catalysts were characterized by X-ray diffraction, N_2 sorption and temperature programmed reduction (TPR) methods. The results show that Co_3O_4 are not well dispersed on CeO_2/SBA-15. The specific surface area and pore volume of CeO_2/SBA-15 are significantly decreased upon impregnation, which is may be ascribed to the serious blockage of channel. Meanwhile, the TPR data show that the reduction of Co_3O_4 to Co^0 is more difficult on CeO_2/SBA-15 than on SBA-15. Consequently, catalyst Co/CeO_2/SBA-15 shows lower catalytic activity than Co/SBA-15 in the oxidation of benzene.

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 CeO_2/SBA-15 materials by the direct hydrothermal method [17]. It was observed that the application of the direct hydrothermal method favored the preparation of CeO_2/BA-15 with higher specific surface area and better dispersion of CeO_2 on SBA-15 than traditional impregnation method. Furthermore, these CeO_2/BA-15 materials even have a higher specific surface area than SBA-15. Thus, it is presumed that CeO_2/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 CeO_2/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 Ce^{4+} 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/CeO_2/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 ($Ce(NO_3)_3 \cdot 6H_2O$) were used as silicon and cerium precursors, respectively. Nonionic triblock co-polymer surfactant $EO_{20}PO_{70}EO_{20}$ (P123, Aldrich) was used as the structure-directing agent. Concentrated HCl aqueous solution was used as acid source.

CeO_2/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 ($Co(NO_3)_2 \cdot 6H_2O$) was dissolved into 10 ml ethanol, mixed with 0.5 g of CeO_2/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%, Co/CeO_2/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 $W_{cobalt}/(W_{cobalt} + W_{support})$. 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 (λ = 0.15418 nm) in the range of 10–70°. Small-angle XRD was recorded on a SIEMENS D5005D powder diffraction system using Cu Kα 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 Co/SBA-15 and Co/CeO_2/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 CeO_2/SBA-15 and SBA-15 are displayed in Fig. 1. It can be observed that CeO_2/SBA-15 has three well-resolved characteristic diffraction peaks centered at $2\theta = \sim 0.8°, \sim 1.6°$ and $\sim 1.8°$, 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 ($a_o = 2d_{100}/\sqrt{3}$) of CeO_2/SBA-15 (shown in Table 1) is increased. This increase of a_o 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 Co/SBA-15 and Co/CeO_2/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 Co/CeO_2/SBA-15 and Co/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 Co /SBA-15, the diffraction peaks of Co_3O_4 supported on CeO_2/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 CeO_2/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 CeO_2/SBA-15 was increased to 10.6 nm. It should be noted that the characteristic diffraction lines of CeO_2 fluorite structure at 2θ = 28.5°, 33.3°, 47.5° and 56.4° are clearly observed for catalyst Co/CeO_2/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 CeO_2/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 CeO_2/SBA-15 has a higher specific surface area (912 m^2/g) than that of pure SBA-15 (672 m^2/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

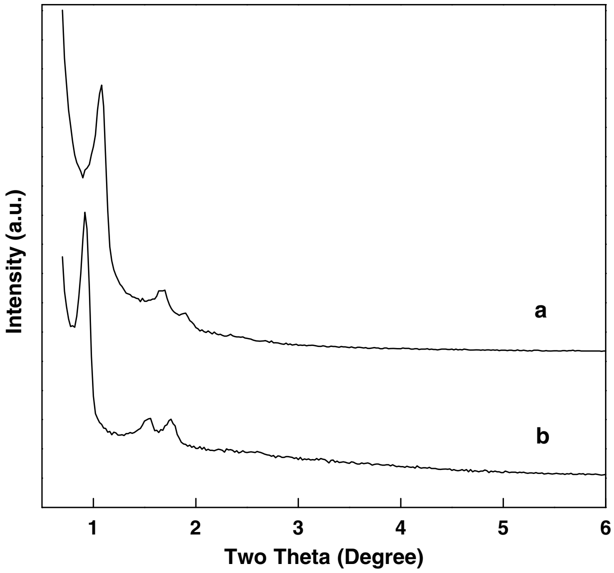

Fig. 1. The SAXRD patterns of different supports: (a) SBA-15 and (b) CeO_2/SBA-15.