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In situ PMMA-templating preparation and excellent catalytic performance of Co_3O_4/3DOM $La_{0.6}Sr_{0.4}CoO_3$ for toluene combustion

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ABSTRACT

Rhombohedrally crystallized three-dimensionally ordered macroporous (3DOM) $La_{0.6}Sr_{0.4}CoO_3$ (LSCO)-supported Co_3O_4 (x wt% Co_3O_4/3DOM LSCO; $x = 0$, 2, 5, 8, and 10) were prepared using the in situ poly(methyl methacrylate)-templating strategy. Physicochemical properties of the materials were characterized by means of numerous analytical techniques, and their catalytic activities were evaluated for the combustion of toluene. It is shown that the x wt% Co_3O_4/3DOM LSCO samples displayed a 3DOM architecture and a high surface area of 29–32 m^2/g. Among the x wt% Co_3O_4/3DOM LSCO samples, the 8 wt% Co_3O_4/3DOM LSCO sample possessed the highest adsorbed oxygen species concentration and the best low-temperature reducibility. The 8 wt% Co_3O_4/3DOM LSCO sample showed the best catalytic performance for toluene combustion (the temperatures required for toluene conversions of 10, 50, and 90% were 158, 210, and 227 °C at a space velocity of 20,000 mL/(g h), respectively). The apparent activation energies (43–58 kJ/mol) of the x wt% Co_3O_4/3DOM LSCO ($x = 0$–10) samples were lower than those (59–67 kJ/mol) of the 8 wt% Co_3O_4/bulk LSCO and bulk LSCO samples. It is concluded that the excellent catalytic performance of 8 wt% Co_3O_4/3DOM LSCO was associated with its high oxygen adspecies concentration, good low-temperature reducibility, and strong interaction between Co_3O_4 and LSCO as well as high-quality 3DOM structure.

1. Introduction

Volatile organic compounds (VOCs) emitted from industrial and transportation activities caused serious environmental problems. In recent years, a number of researchers have paid much attention to develop kinds of strategies to eliminate the VOCs. Catalytic combustion is one of the most effective techniques and has been widely used all over the world. The key issue of such a technology is the availability of a high-performance catalyst. Many materials, such as supported noble metals [1], single transition metal oxides [2,3], and mixed metal oxides (e.g., perovskite-type oxides) [4] have been used as catalyst to oxidize the VOCs. Although the supported noble metals exhibit excellent catalytic activity for VOC combustion, the expensive cost and easily-poisoned tendency limit their wide applications. The other two kinds of catalysts, however, have the advantages of cheapness and good catalytic activities. For example, Wang and Li [5] prepared octahedral molecular sieve manganese oxide (OMS-2) and sulfate-acidified OMS-2 catalysts, and observed good catalytic activities for the complete oxidation of ethanol and acetaldehyde. Working on the MnO_x/γ-Al_2O_3 catalysts, Tseng et al. [6] claimed that 5 wt% MnO_x/γ-Al_2O_3 catalyst performed well for the oxidative decomposition of trichloroethylene. Our group have investigated the $La_{1-x}Sr_xM_{1-y}Fe_yO_3$ (M = Mn, Co; $x = 0, 0.4$; $y = 0.1, 1.0$) catalysts for the removal of toluene, and found that the partial substitution of manganese and cobalt with iron can significantly improve the catalytic performance of $La_{0.6}Sr_{0.4}MnO_3$ and $La_{0.6}Sr_{0.4}CoO_3$ [7].

Perovskite-type oxides (ABO_3) are a material whose physicochemical properties can be tailor-made by substituting the A- and or B-site ions with other metal ions. ABO_3 performs well in the combustion of VOCs and possesses outstanding thermal stability. Factors, such as B-site metal nature, reducibility, surface area, oxygen vacancy density, and pore structure, have a great influence on its catalytic activity. Among the ABO_3 catalysts, cobaltites and manganites show good performance in catalyzing VOC oxidation [8]. Due to the high-temperature calcination during the preparation processes, the obtained ABO_3 catalysts usually display large grain sizes and low surface areas (<10 m^2/g) [9]. In order to increase the surface areas and enhance the catalytic activity of ABO_3,

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several strategies have been developed. One is supporting ABO_3 onto porous carriers with high surface areas. For example, Nguyen et al. [10] prepared $LaCoO_3$ well-dispersed on highly ordered mesoporous SiO_2 that exhibited high catalytic performance. Kustov et al. [11] prepared $LaCoO_3$/mesoporous ZrO_2 catalysts by the impregnation method. Recently, much attention has been paid to fabricate porous perovskite catalysts using the template methods. For instance, by adopting the ordered mesoporous silica (KIT-6) as the template, Wang et al. [12] synthesized ordered mesoporous $LaCoO_3$, which showed good catalytic activity for the combustion of methane. Sadakane et al. [13] and Wei et al. [14] generated three-dimensionally ordered macroporous (3DOM) $La_{1-x}Sr_xFeO_3$ using the well-arrayed poly(methyl methacrylate) (PMMA)-templating strategy. Similarly structured $LaMnO_3$ [15] and $LaCo_xFe_{1-x}O_3$ [16] were also obtained via the PMMA-templating route.

The presence of macropores can provide good mass transfer to the reactant molecules and easy accessibility to the active sites. Moreover, 3DOM-structured perovskites possess high surface areas and good thermal stability, thus giving excellent catalytic performance. Therefore, 3DOM-structured perovskites are considered to be one of the most promising catalytic materials [17]. Up to now, some literature has reported metal oxides supported on perovskites. Urasaki et al. [18] prepared the oxides of cobalt and nickel supported on $LaAlO_3$, $SrTiO_3$, and $BaTiO_3$ via an impregnation route using the aqueous solution of $Co(NO_3)_2$ and $Ni(NO_3)_2$, respectively. They found that the $SrTiO_3$- and $LaAlO_3$-supported CoO_x and NiO catalysts showed good activities and thermal stability, whereas the $BaTiO_3$-supported ones exhibited low ethanol conversion and serious carbon deposition. Kaliaguine and coworkers [19] prepared $LaCoO_3$–Cu_2O and $LaCoO_3$–CuO catalysts by grinding $LaCoO_3$ and Cu_2O or CuO at ambient temperature, and observed that the addition of Cu_2O or CuO resulted in the shifting of the reduction peaks to lower temperatures and the copper had a strong effect on promoting the reduction of Co^{3+}. Working on the $Co_3O_4/LaFe_{0.7}Cu_{0.3}O_3$ catalysts derived from the wetness impregnation process, Fang et al. [20] claimed that there was a strong interaction between the Co_3O_4 and the copper ions in $LaFe_{0.7}Cu_{0.3}O_3$.

So far, rare reports on the 3DOM-structured ABO_3-supported transition metal oxide catalysts have been seen in the literature. Recently, our group have generated a number of MO_x (M = Co, Mn, Cr)/3DOM ABO_3 catalysts using the in situ PMMA-templating method. In this paper, we report the preparation, characterization, and catalytic properties of x wt% Co_3O_4/3DOM $La_{0.6}Sr_{0.4}CoO_3$ (x = 0–10) for the combustion of toluene.

2. Experimental

2.1. Catalyst preparation

The well-arrayed hard-template PMMA microspheres with an average diameter of ca. 298 nm were synthesized according to the procedures described elsewhere [21].

The x wt% Co_3O_4/3DOM $La_{0.6}Sr_{0.4}CoO_3$ (x wt% Co_3O_4/3DOM LSCO, x = 0, 2, 5, 8, and 10) catalysts were prepared using the in situ PMMA-templating strategy. In a typical procedure, 5.196 g of $La(NO_3)_3{\cdot}6H_2O$ and 1.693 g of $Sr(NO_3)_2$ and the desired amount (5.821, 6.147, 6.636, 7.125, and 7.451 g for the preparation of x wt% Co_3O_4/3DOM LSCO at x = 0, 2, 5, 8, and 10) of $Co(NO_3)_2{\cdot}6H_2O$ were dissolved in 7 mL of deionized water, 3 mL of EG, and 3 mL of methanol at room temperature (RT) under stirring for 2 h to obtain a transparent solution. 0.7 g of L-lysine was dissolved in 2 mL of deionized water, a certain amount of citric acid was used to adjust the pH value of the solution to around 7. Then, the L-lysine-containing solution was mixed with the metal nitrate-containing transparent solution under stirring for 1 h to obtain a precursor solution. 2.0 g of the PMMA template was thoroughly soaked in the precursor solution for 4 h and the excessive liquid was filtered. After the wet template was dried in air at RT for 24 h, the solid was thermally treated in a tubular furnace according to the two steps: (i) first calcined in a N_2 flow of 200 mL/min at a ramp of 1 °C/min from RT to 300 °C, kept at this temperature for 3 h, and cooled in the same atmosphere to RT; and (ii) continuously calcined in an air flow of 200 mL/min at a ramp of 1 °C/min from RT to 800 °C, maintained at this temperature for 2 h, and cooled in the same atmosphere to RT.

For comparison purposes, we also prepared bulk LSCO and 8 wt% Co_3O_4/bulk LSCO samples. The bulk LSCO sample was prepared using the citric acid-complexing method described elsewhere [22]. The obtained solid precursor was first calcined in air at a ramp of 1 °C/min in a muffle furnace from RT to 300 °C and kept at this temperature for 1 h, and then from 300 to 800 °C at the same ramp and maintained at 800 °C for 2 h. The 8 wt% Co_3O_4/bulk LSCO sample was obtained via the incipient wetness impregnation route. The desired amount of $Co(NO_3)_2{\cdot}6H_2O$ was dissolved in 1 mL of deionized water. 0.2 g of bulk LSCO was impregnated with the Co-containing solution for 4 h and then dried at 80 °C in an oven for 12 h. The as-received solid was calcined in an air flow of 200 mL/min at a ramp of 1 °C/min in a tubular furnace from RT to 400 °C and kept at this temperature for 3 h.

All of the chemicals (A.R. in purity) were purchased from Beijing Chemical Reagent Company and used without further purification.

2.2. Catalyst characterization

The physicochemical properties of the samples were characterized by techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected-area electron diffraction (SAED), N_2 adsorption–desorption (BET), X-ray photoelectron spectroscopy (XPS), and H_2 temperature-programmed reduction (H_2-TPR). The detailed procedures are described in the supplementary material.

2.3. Catalytic evaluation

Catalytic activities of the samples were evaluated on a continuous flow fixed-bed quartz microreactor (i.d. = 4 mm). In order to avoid the effect of hot spots, 0.5 g of quartz sands (40 – 60 mesh) were used to dilute the catalyst (0.1 g). The total flow rate of the reactant mixture (1000 ppm toluene + O_2 + N_2 (balance)) was 33.3 mL/min, with a toluene/O_2 molar ratio of 1/400 and a space velocity (SV) of ca. 20,000 mL/(g h). The 1000-ppm toluene was generated by a N_2 flow passing through a bottle containing pure toluene (A.R. grade) chilled in an ice-water isothermal bath. Reactants and products were analyzed on-line by a gas chromatograph (GC-2010, Shimadzu) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD), using Chromosorb 101 column for organic gas separation and a Carboxen 1000 column for permanent gas separation. The balance of carbon throughout the catalytic system was evaluated to be 99.5%.

3. Results and discussion

3.1. Crystal structure

Fig. 1 shows the XRD patterns of the x wt% Co_3O_4/LSCO samples. By comparing to the XRD pattern of the standard $La_{0.6}Sr_{0.4}CoO_3$ sample (JCPDS PDF# 87-1081), one can deduce that the LSCO in the x wt% Co_3O_4/LSCO samples was of rhombohedral perovskite structure, and can be well indexed, as shown in Fig. 1g. With the loading of Co_3O_4, there was the formation of cubic Co_3O_4 (JCPDS PDF#73-1701) phase in the 5–10 wt% Co_3O_4/3DOM LSCO and 8 wt%