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Au/3DOM $La_{0.6}Sr_{0.4}MnO_3$: Highly active nanocatalysts for the oxidation of carbon monoxide and toluene

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ABSTRACT

Three-dimensionally ordered macroporous (3DOM) $La_{0.6}Sr_{0.4}MnO_3$ (LSMO) and its supported gold (xAu/LSMO, $x = 3.4–7.9$ wt%) catalysts were prepared using the polymethyl methacrylate-templating and gas-bubble-assisted polyvinyl alcohol-protected reduction methods, respectively. There were good correlations of surface-adsorbed oxygen species concentration and low-temperature reducibility with the catalytic activity of the sample for CO and toluene oxidation. Among the LSMO and xAu/LSMO samples, 6.4Au/LSMO performed the best, giving $T_{50\%}$ and $T_{90\%}$ values of −19 and 3 °C for CO oxidation and 150 and 170 °C for toluene oxidation, respectively. The apparent activation energies (31–32 and 44–48 kJ/mol) obtained over xAu/LSMO were much lower than those (45 and 59 kJ/mol) obtained over LSMO for the oxidation of CO and toluene, respectively. It is concluded that higher oxygen adspecies concentration, better low-temperature reducibility, and strong interaction between Au and LSMO are responsible for the excellent catalytic performance of 6.4Au/LSMO.

1. Introduction

Catalytic oxidation of carbon monoxide and volatile organic compounds (VOCs) is of considerable interest in the control of environmental pollutants. Since their discovery by Haruta et al., who observed extraordinary catalytic activity of Au/TiO_2 for CO low-temperature oxidation [1], supported gold catalysts have attracted tremendous attention. Apart from the Au particle size, the choice of support also plays a key role in the development of active Au nanocatalysts [2]. To obtain high-performance Au catalysts, some metal oxides (e.g., TiO_2, Fe_2O_3, and CeO_2) are chosen as supports [3–5]. Recently, investigations on gold catalysts have also been focused on the oxidation of VOCs [6–8]. Several authors reported that the activities of the Co_3O_4- and Fe_2O_3-supported gold catalysts were higher than that of Pt/Al_2O_3 for VOC oxidation [9,10], which was due to the enhancement in oxygen mobility of the active support [10,11]. Compared to other precious metals (e.g., Pt, Rh, and Pd), Au is much less expensive and more abundant. Therefore, the use of Au in the removal of CO and VOCs is continuously explored as a substitute for more expensive noble metals.

Perovskite-type oxides (ABO_3) are generally considered efficient catalysts for the oxidation of CO and VOCs [12]. They offer the advantages of low cost, high activity, good anti-poisoning ability, and thermal stability over single-metal-oxide catalysts. Since diffusion is often a problem that limits the overall performance of a bulk catalyst, making a catalyst with a porous structure is expected to greatly increase the number of accessible active sites and ultimately enhance the catalytic efficiency. To the best of our knowledge, only a few reports on the preparation of ABO_3-supported Au catalysts have been seen in the literature. For example, Zhao and co-workers adopted polymethyl methacrylate (PMMA) as a template to generate three-dimensionally ordered macroporous (3DOM) $LaFeO_3$-supported Au (surface area = ca. 32 m^2/g) catalysts and found that Au/3DOM $LaFeO_3$ showed superior performance for the oxidation of soot [13]. Jia et al. observed 100% CO conversion over the nanosized $LaCoO_3$-supported Au (surface area = ca. 14 m^2/g) catalyst at 90 °C and 15,000 mL/(g h) [14]. Up to now, however, there have been no reports on the preparation and use for catalytic VOC oxidation of ABO_3-supported Au nanocatalysts. Hence, it is highly desirable to establish an effective method for the controlled fabrication of Au supported on porous ABO_3 and explore its applications in catalyzing the oxidation of CO and VOCs.

Herein, we report a strategy for preparing 3DOM-structured $La_{0.6}Sr_{0.4}MnO_3$ and its supported Au nanocatalysts, which was

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based on the use of colloidal crystal PMMA as a hard template to generate a 3DOM structure and the gas-bubble-assisted polyvinyl alcohol (PVA)-protected reduction route to obtain supported Au nanomaterials. The aim of this work was to investigate the preparation and catalytic behavior of *x*Au/3DOM-structured $La_{0.6}Sr_{0.4}MnO_3$ ($x = 3.4–7.9$ wt%) for the oxidation of CO and toluene. In addition, the effect of water on the performance of the typical catalyst was also examined.

2. Experimental

2.1. Catalyst preparation

Well-arrayed colloid crystal template PMMA microspheres with an average diameter of ca. 300 nm were synthesized according to procedures described elsewhere [15].

A 3DOM-structured $La_{0.6}Sr_{0.4}MnO_3$ sample was prepared using the surfactant-assisted PMMA-templating strategy. In a typical procedure, stoichiometric amounts of $La(NO_3)_3{\cdot}6H_2O$, $Sr(NO_3)_2$, and $Mn(NO_3)_2$ (50 wt% aqueous solution) were dissolved in 3 mL of poly(ethylene glycol) (PEG, MW = 400 g/mol) and 12 mL of water at 50 °C under stirring for 2 h to obtain a transparent solution. A quantity of 1.0 g of L-lysine was dissolved in a HNO_3 aqueous solution (5 mol/L), and the pH value of this solution was adjusted to ca. 6 for avoiding the formation of metal hydroxide precipitates in the following steps. Then, the L-lysine-containing solution was mixed with the metal nitrate-containing transparent solution under stirring for 1 h to obtain a uniform precursor solution, to which a certain amount of methanol was added to achieve a total metal concentration of 2 mol/L. Circa 2.0 g of the PMMA hard template was soaked in the above precursor solution for 4 h. After being filtered, the obtained wet PMMA template was dried in air at room temperature (RT) for 48 h and then transferred to a ceramic boat, which was placed in a tubular furnace. The obtained powders were subsequently heated in N_2 (200 mL/min) at 300 °C for 3 h, cooled to 50 °C in the same atmosphere, and finally calcined in air (100 mL/min) at 750 °C for 4 h to remove the template, thus generating the 3DOM-structured $La_{0.6}Sr_{0.4}MnO_3$ (denoted as LSMO) catalyst.

The LSMO-supported gold (*x*Au/LSMO) catalysts were prepared via a gas-bubble-assisted PVA-protected reduction method [16]. The typical preparation procedure is as follows: A desired amount of PVA (MW = 10,000 g/mol) was added to a 100 mg/L $HAuCl_4$ aqueous solution (Au/PVA mass ratio = 1.5:1) at RT under vigorous bubbling for 10 min. After rapid injection of an aqueous solution of 0.1 mol/L $NaBH_4$ (Au/$NaBH_4$ molar ratio = 1:5), one could obtain a dark orange-brown solution (so-called gold sol). A desired amount (theoretical Au loading = 5, 8, or 10 wt%) of the LSMO support was then added to the gold sol, and the obtained suspension was subjected to sonication (60 kHz) for 30 s. A gas-bubble-assisted stirring operation with three bubble outlets in solution was used to further agitate the system, and the suspension was vigorously bubbled with N_2 for 6 h. The solid was collected by filtration, followed by washing with 2 L of deionized water and drying at 80 °C for 12 h, thus obtaining the *x*Au/LSMO catalysts. The results of inductively coupled plasma atomic emission spectroscopic (ICP-AES) investigation reveal that the real Au loading was 3.4, 6.4, and 7.9 wt% for the Au-loaded samples, respectively. All of the above steps were carried out by covering all of the containers with a layer of aluminum foil.

For comparison purposes, the bulk $La_{0.6}Sr_{0.4}MnO_3$ (denoted as bulk LSMO) and 6.2Au/bulk LSMO catalysts were also prepared via the citric acid-complexing [17] and gas-bubble-assisted PVA-protected reduction routes, respectively.

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

2.2. Catalyst characterization

Physicochemical properties of the bulk LSMO, LSMO, *x*Au/LSMO, and 6.2Au/bulk LSMO catalysts were characterized by means of techniques such as X-ray diffraction (XRD), inductively coupled plasma atomic emission spectroscopy (ICP-AES), N_2 adsorption–desorption (BET), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and hydrogen temperature-programmed reduction (H_2 TPR). The detailed procedures are described in the Supplementary data.

2.3. Catalyst evaluation

The catalytic activity was evaluated with the sample charged in a continuous-flow fixed-bed U-type quartz microreactor (i.d. = 4 mm). To minimize the effect of hot spots, the sample (50 mg, 40–60 mesh) was diluted with 0.25 g quartz sands (40–60 mesh). Prior to the test, the sample was treated in O_2 (30 mL/min) at 250 °C for 1 h. After being cooled to a given temperature, the reactant gas containing CO or toluene was passed through the sample bed for 1 h to completely purge the O_2. For CO oxidation, the reactant feed was 1 vol% CO + 20% O_2 + N_2 (balance), giving a space velocity (SV) of ca. 10,000 mL/(g h). In the case of water vapor introduction, certain concentrations (0.5, 2.5, and 5.0 vol%) of H_2O were introduced by passing the feed stream through a water saturator in an isothermal bath at 10, 25, and 50 °C, respectively. Catalytic activities of the samples for CO oxidation at low temperatures (below RT) were measured by immersing the microreactor in an ethanol–liquid N_2 mixture with certain volumetric ratios. Reactants and products were analyzed on line by a gas chromatograph (GC-14C, Shimadzu) equipped with a thermal conductivity detector (TCD), using a 13 X column. For toluene combustion, the total flow rate of the reactant mixture (1000 ppm toluene + O_2 + N_2 (balance)) was 16.7 mL/min, giving a toluene/O_2 molar ratio of 1/400 and a SV of ca. 20,000 mL/(g h). The 500-, 1000-, and 5000-ppm toluene was generated by passing a N_2 flow through a bottle containing pure toluene chilled in an isothermal bath at −15, 0, and 45 °C, respectively. For the change of SV, we altered the mass of catalyst. 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 a Stabilwax@-DA column (30 m in length) for VOC separation and a 1/8 in Carboxen 1000 column (3 m in length) for permanent gas separation. The balance of carbon throughout the investigation was estimated to be 99.5%.

3. Results and discussion

3.1. Real gold content, crystal-phase composition, morphology, pore structure, and surface area

The actual Au content of the *x*Au/LSMO catalysts was determined by the ICP-AES technique; the data are shown in Table 1. It can be seen that the actual Au content of the samples was lower than the initial theoretical values during the preparation processes, indicating that most of the Au in the aqueous solution were deposited on the surface of the LSMO support via the gas-bubble-assisted PVA-protected reduction route.

Fig. 1 shows the XRD patterns of the LSMO and supported gold samples. Compared to the XRD pattern of the LSMO support, the loading of Au did not lead to any changes in perovskite structure. The XRD patterns clearly reveal that the crystal structures of all of the samples could be indexed to the rhombohedral perovskite structure (JCPDS PDF# 82-1152). The calculated grain sizes of LSMO in LSMO and *x*Au/LSMO were 26–27 nm, while those in bulk