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Mesoporous Co_3O_4-supported gold nanocatalysts: Highly active for the oxidation of carbon monoxide, benzene, toluene, and *o*-xylene

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ABSTRACT

Three-dimensionally ordered mesoporous Co_3O_4 (*meso*-Co_3O_4) and its supported gold (xAu/*meso*-Co_3O_4, x = 3.7–9.0 wt%) nanocatalysts were prepared using the KIT-6-templating and polyvinyl alcohol-protected colloidal deposition methods, respectively. The *meso*-Co_3O_4 and xAu/*meso*-Co_3O_4 samples exhibited a high surface area of 91–94 m^2/g. The Au nanoparticles with a size of 1–5 nm were uniformly deposited inside the mesoporous channels of *meso*-Co_3O_4. There were good correlations of oxygen adspecies concentration and low-temperature reducibility with catalytic activity of the sample for CO or BTX (benzene, toluene, and *o*-xylene) oxidation. Among *meso*-Co_3O_4 and xAu/*meso*-Co_3O_4, the 6.5Au/*meso*-Co_3O_4 sample performed the best, giving the $T_{90\%}$ (the temperature required for achieving a CO or BTX conversion of 90%) of −45, 189, 138, and 162 °C for the oxidation of CO, benzene, toluene, and *o*-xylene, respectively. The apparent activation energies (23 and 45–55 kJ/mol) over 6.5Au/*meso*-Co_3O_4 were much lower than those (48 and 72–92 kJ/mol) over bulk Co_3O_4 for CO and BTX oxidation, respectively. The effects of water vapor, carbon dioxide, and sulfur dioxide on the catalytic activity of the 6.5Au/*meso*-Co_3O_4 sample were also examined. It is concluded that the higher surface area and oxygen adspecies concentration, better low-temperature reducibility, and strong interaction between Au and *meso*-Co_3O_4 were responsible for the excellent catalytic performance of 6.5Au/*meso*-Co_3O_4.

1. Introduction

CO and most of volatile organic compounds (VOCs) emitted from industrial and transportation activities are harmful to the atmosphere and human health. Catalytic oxidation is one of the most effective pathways to eliminate CO and VOCs, in which the key issue is the availability of high-performance catalysts. In the past years, various kinds of catalysts, such as supported noble metals, transition metal oxides, and perovskite-type oxides, have been used for the complete oxidation of CO and VOCs. Currently, the most active catalysts are the supported platinum and palladium materials with the noble metal particles being highly dispersed on the high surface area supports. Due to the high cost, however, wide applications for supported Pt and Pd catalysts are limited. An alternative to the platinum group metal-based catalysts is the use of base transition metal oxides, among which cobalt oxide is one of the most efficient catalysts in the total oxidation of CO and VOCs [1,2]. Co_3O_4 has been reported to show higher catalytic performance than supported noble metals in the oxidation of CO [3]. It is generally believed that catalytic activity is associated with the surface area, oxygen defect, and redox ability of a material. A good approach for increasing surface area is to have a material fabricated in mesoporous structure. Recently, well-ordered mesoporous Co_3O_4 was generated using the nanocasting routes with solid porous materials (e.g., three-dimensionally (3D) ordered mesoporous silica (KIT-6)) as hard template, and the obtained mesoporous Co_3O_4 displayed excellent catalytic performance in the oxidation of CO and VOCs [4,5].

In recent years, supported gold catalysts have attracted tremendous attention owing to the notable discovery by Haruta et al. Although Au is highly active in several catalytic reactions, it is easily sintered at relatively low temperatures, resulting in deactivation of the supported Au catalysts [6]. Dispersion of gold nanoparticles (NPs) on high surface area supports is expected to promote the catalytic activity and stability, because it not only help increasing the gold loading but also improve its dispersion that would be beneficial for the avoidance of sintering of Au NPs [7]. Furthermore, unlike the supported Pt, Pd, or Rh catalysts with the precious metal loading of less 1.0 wt%, the supported Au catalysts usually contain more Au loadings (4–7 wt%), so that they can show improved catalytic performance.

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In recent years, the oxidation of CO and VOCs over the cobalt oxide-supported precious metal catalysts has been widely studied. Palladium or gold over cobalt oxide is active for the catalytic oxidation of CO, methane, and toluene [8–10]. One of the important reasons is the presence of a strong interaction between Au and Co_3O_4. After investigating ordered mesoporous Co_3O_4-supported Pd catalysts for *o*-xylene oxidation, Wang et al. pointed out that the good catalytic performance of Pd/porous Co_3O_4 was associated with the Pd particle size, oxidized Pd species, and oxygen vacancies in Co_3O_4 [8]. Hao and coworkers observed that the morphology of support exerted a significant effect on the catalytic activity of cobalt oxide-supported Au for low-temperature oxidation of trace ethylene and concluded that the catalytic activity was related to the exposed planes of different morphological Co_3O_4 [11]. Moreover, catalytic oxidation of toluene, propane, and CO has been investigated over the Au-deposited partially ordered mesoporous Co_3O_4 catalyst, and the authors found that this catalyst exhibited a high activity for the oxidation of pollutants [12].

To the best of our knowledge, however, the preparation and applications of ordered 3D ordered mesoporous Co_3O_4-supported Au nanocatalysts for the oxidation of CO and BTX (benzene, toluene, and *o*-xylene) have not so far been seen in the literature. Hence, it is highly desired to establish an effective method for the controlled preparation of 3D ordered mesoporous Co_3O_4-supported Au NPs and to explore their applications in catalyzing the oxidation of CO and BTX.

In this paper, we report a strategy for preparing 3D ordered mesoporous Co_3O_4 and its supported Au nanocatalysts, which were based on the use of KIT-6 as hard template to control pore structure, and the polyvinyl alcohol (PVA)-protected colloidal deposition processes to generate supported Au nanocatalysts with high performance for the addressed reactions.

2. Experimental

2.1. Catalyst preparation

Mesoporous silica (KIT-6) was synthesized by adopting the procedure described in the literature [13]. Mesoporous Co_3O_4 was fabricated according to the strategy reported previously [14]. In a typical fabrication, 1.0 g of KIT-6 was suspended in 50 mL of toluene. After stirring at 65 °C for 0.5 h, 2.0 g of $Co(NO_3)_2{\cdot}6H_2O$ was added under vigorous stirring. The mixture was further stirred at 65 °C for 3 h. Then, pink powders were obtained after filtration and drying at room temperature (RT). The precursor@silica composite was put in a crucible and then calcined in a muffle furnace at a ramp of 1 °C/min from RT to 600 °C and kept at this temperature for 6 h. The silica template was removed by etching twice with hot NaOH aqueous solution (2 mol/L). The template-free mesoporous Co_3O_4 (*meso*-Co_3O_4) was obtained after centrifugation, washing with deionized water and ethanol, and drying at 80 °C.

The *meso*-Co_3O_4-supported gold (*x*Au/*meso*-Co_3O_4) catalysts were prepared via a PVA-protected colloidal deposition method [15]. 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 stirring for 10 min. After rapid injecting the 0.1 mol/L $NaBH_4$ aqueous solution (Au/$NaBH_4$ molar ratio = 1:5), a dark orange-brown solution (called as gold sol) was obtained. A desired amount of the mesoporous Co_3O_4 support was added to a given amount of gold sol (theoretical Au loading = 4, 7 or 10 wt%) under stirring and kept in contact until complete adsorption (decoloration of the solution) occurred. The solid was filtered, washed with deionized water, dried at 80 °C for 12 h, and calcined in air at 300 °C for 1 h, thus obtaining the *x*Au/*meso*-Co_3O_4 samples. The results of inductively coupled plasma atomic emission spectroscopic (ICP-AES) investigations reveal that the real Au loading (*x*) was 3.7, 6.5, and 9.0 wt% in *x*Au/*meso*-Co_3O_4, respectively.

For comparison purposes, the bulk Co_3O_4 and 6.4Au/bulk Co_3O_4 samples were also prepared via the thermal decomposition of cobalt nitrate at 700 °C for 5 h and colloidal deposition routes, respectively.

2.2. Catalyst characterization

Physicochemical properties of the samples 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), thermogravimetric analysis (TGA), and hydrogen 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 in a continuous flow fixed-bed 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 of quartz sands (40–60 mesh). Prior to the test, the sample was treated in O_2 (30 mL/min) at 250 °C for 0.5 h. After being cooled to a given temperature, the reactant gas containing CO or VOC was passed through the sample bed for 1 h to completely purge the O_2. For CO oxidation, the reactant feed was 1.0 vol% CO + 20% O_2 + N_2 (balance), giving a space velocity (SV) of ca. 60,000 mL/(g h). 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 online by a gas chromatograph (GC-14C, Shimadzu) equipped with a thermal conductivity detector (TCD), using a 13 X packing column. For the oxidation of benzene, toluene, or *o*-xylene, the total flow rate of the reactant mixture (1000 ppm VOC + O_2 + N_2 (balance)) was 16.7 mL/min, giving a VOC/O_2 molar ratio of 1/400 and a SV of ca. 20,000 mL/(g h). The 1000-ppm VOC was generated by passing a N_2 flow through a bottle containing pure VOC chilled in an ice-water isothermal bath. For methane combustion, the reactant feed was 1.0 vol% CH_4 + 20% O_2 + N_2 (balance), giving a SV of ca. 20,000 mL/(g h). In the case of water vapor introduction, 3.0 vol% of H_2O was introduced by passing the feed stream through a water saturator at RT. In the case of CO_2 addition, 10.0 vol% of CO_2 was introduced via a mass flow controller using a high-purity (99.9%) CO_2 cylinder. In the case of SO_2 introduction, 40 ppm SO_2 was introduced via a mass flow controller using a SO_2 cylinder (balanced with N_2). Reactants and products were analyzed online by a gas chromatograph (GC-2010, Shimadzu) equipped with a flame ionization detector (FID) and a TCD, using a stabilwax@-DA column (30 m in length) for VOCs 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%. For the kinetic studies, the turnover frequencies TOF_{Au} or TOF_{Co} were calculated according to the single surface Au site or molar amount of Co in total catalyst, respectively. The amounts of Au sites were estimated according to the procedure reported in the literature [16] and the assumption that the Au particles showed a spherical or hemispherical shape (as confirmed by the high-resolution TEM observations).