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Catalytic oxidation of toluene and *p*-xylene using gold supported on Co_3O_4 catalyst prepared by colloidal precipitation method

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ABSTRACT

Gold supported on cobalt oxide has been successfully synthesized through a colloidal precipitation method and tested in toluene and *p*-xylene total oxidation. It has been demonstrated that the catalytic activity of Au/Co_3O_4 for toluene and *p*-xylene oxidation is much higher than that of Au/Al_2O_3 and Au/MgO in spite of its lower BET surface area and larger gold crystalline size. The enhanced catalytic activity in toluene and *p*-xylene oxidation has been linked to a high concentration of superficial electrophilic oxygen species and oxygen vacancies, which may be originated from a strong interaction in the colloidal $Au–Co_3O_4$ system.

1. Introduction

Benzene, toluene and xylene (BTX) are major pollutants in indoor and outdoor air, emitted from many industrial processes and transportation activities [1]. They often act as three major categories of greenhouse gases and suspected carcinogens [2]. Therefore, it is an extremely urgent task to reduce the emission of these pollutants. Catalytic oxidation is one of the most effective ways for the elimination of BTX, which operates at relatively low temperatures with respect to the conversional thermal combustion [1]. Furthermore, it provides the potential to destroy BTX totally to carbon dioxide and water [3].

Supported noble metal (Pt and Pd) catalysts [4–9] have been used as catalysts for this reaction due to their high activity at relatively low temperatures and the tolerance to the moisture. Since Haruta's discovery [10] of the remarkably high activity of supported gold catalysts for low-temperature CO oxidation, reports on many practical applications, such as the reduction of NO_x [11], hydrogenation, water–gas shift reaction and complete oxidation of hydrocarbons [12,13], have increased dramatically. The use of supported gold catalysts offers the advantages of both high reactivity and a relatively low price compared with earlier reported supported Pt or Pd catalysts.

Among metal oxides cobalt oxide, in the form of Co_3O_4, has been shown to be one of the most efficient non-noble metal oxides for VOCs elimination, and it seems to be the most active for propane combustion [14] due to its excellent reducibility, high concentration of electrophilic O-species (O_{ads}, O^- or O_2^-) [15] and oxygen vacancies [16]. Furthermore, improved catalytic performance has been associated with the high surface areas and 3D ordered mesoporous structure of the Co_3O_4 [17–19]. In the last years, the complete oxidation of VOCs over gold on cobalt oxide has been widely studied, especially that of alkanes. Gold on cobalt oxide was shown to be active for the catalytic combustion of methane and propane [20,21]. The results suggested that active catalysts were related to the chemical state of gold phase. Recently gold on cobalt oxide has been turned to be highly active for low-temperature oxidation of trace ethylene [22] and it achieves a 76% conversion at 0 °C when mesoporous Co_3O_4 used as support [23]. Furthermore, they found that support morphology has a significant effect on catalytic activity, which is related to the exposed planes of different morphological Co_3O_4 [24]. Moreover, catalytic oxidation of toluene, propane and CO has been investigated on a non-fully ordered nanocast Co_3O_4 deposited by gold, and it exhibits high activity for the pollutants total oxidation [25]. It was proved that the enhanced catalytic activity has been related to both the improved reducibility of Co_3O_4 when gold is added and the simultaneous presence of $Au^{\delta+}$ and Au^0.

In previous paper we reported a highly efficient Au/ZnO catalyst for low-temperature BTX oxidation [26]. Our results confirmed that strong metal-oxide interaction between Au {1 1 1} and ZnO {1 0 1} planes occurs due to the very small lattice mismatch.

In present paper we investigated the properties of Au/Co_3O_4 catalysts prepared by colloidal precipitation method and tested in

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Table 1
structural properties and surface atom ratios of supported gold catalysts.

Catalyst[a]	BET area	Co_3O_4 size average (nm)[b]	Au size average (nm)[c]	Au loading (wt.%)[d]	Au dispersion (%)[e]	Au/M atom ratio (%)	XPS[f] ($m^2\ g^{-1}$)						
							Au^{3+}	$Au^{\delta+}$	Au^0	O_2^-	O_{ads}	O^{2-}	Co^{2+}/Co^{3+}
Au/Co_3O_4	1.6	122	10.6 ± 4.18	1.58	9.43	0.95	0.40	0.39	0.21	0.65	0.23	0.12	1.80
Au/Al_2O_3	205	–	4.2 ± 1.79	1.40	27.55	0.46	0	1.00	0	0	0.88	0.12	–
Au/MgO	44	–	3.3 ± 1.02	1.69	35.07	0.79	0	1.00	0	0	0.63	0.37	–

[a] Calcined at 350 °C.
[b] Calculated by TEM method.
[c] Calculated by HRTEM method.
[d] Calculated from semi-quantitative EDX data.
[e] Calculated by formula: $D_{Au} = 6n_sM_{Au}/\rho_{Au}N_Ad_{Au}$, where n_s is the number of Au atoms at the surface per unit area ($1.15 \times 10^{19}\ m^{-2}$), M_{Au} is the molar mass of gold ($196.97\ g{\cdot}mol^{-1}$), ρ_{Au} is the density of gold ($19.5\ g{\cdot}cm^{-3}$), N_A is Avogadro's number ($6.023 \times 10^{23}\ mol^{-1}$) and d_{Au} is the average Au particle size (determined by HRTEM).
[f] Catalysts before reaction.

the total oxidation of toluene and *p*-xylene, chosen as probe molecules of alkyl aromatic compounds. The results were compared with the analogous series of gold supported on Al_2O_3 (or MgO) with the same preparation procedure and suggested that the amount of chemisorbed electrophilic O-species and oxygen vacancies are the determining factors leading to high activity and stability of the Au/Co_3O_4, which may be originated from a strong metal-oxide interaction between Au and Co_3O_4.

2. Experimental

2.1. Catalyst preparation

A chemical precipitation method was used to synthesize supports of Co_3O_4, Al_2O_3 and MgO. 5 ml of ammonia was gradually added into 10 ml of an aqueous 0.01 M solution of nitrate with continuous stirring. After 2 h, the percolated precipitation was filtered and washed with deionized water. The solids were dried at 80 °C and finally calcined at 500 °C for 2 h for crystallization. The supported gold catalysts were prepared by the colloidal deposition method by using PVA ($M_w = 10{,}000$) as a protecting agent and $HAuCl_4{\cdot}3H_2O$ as the gold precursor [27]. For more details of the preparation procedure, refer to our previous work [26]. The nominal gold loading amount of catalyst is 1.50 wt.%. The resulting catalysts were denoted as Au/Co_3O_4, Au/Al_2O_3 and Au/MgO, respectively.

2.2. Catalysts characterization

The specific surface area was determined by the BET method with N_2 adsorption–desorption measurements at 77 K (Micromeritics ASAP 2020).

The crystalline structure of the catalyst was analyzed by powder X-ray diffraction (XRD, Rigaku D/max-RB) with Cu Kα radiation ($\lambda = 1.54016$ Å) operated at 40 kV and 30 mA. Phases were identified by matching experimental patterns to the JCPDS powder diffraction file.

The morphology and microstructure of the catalysts were observed by the scanning electron microscopy (SEM, JEOL JSM-5610LV) and field emission transmission electron microscopy (FETEM, JEOL JEM-2100F). TEM samples were treated by sonicating in absolute ethanol for several minutes and then a few drops of the resulting suspension were deposited onto a holey-carbon film supported in a copper grid, which was dried naturally.

The chemical composition and metal content of the catalysts were analyzed by the energy-dispersive X-ray spectroscopy analysis (EDX, OXFORD INCA).

The atomic percentage and chemical state of surface element in the catalysts were measured by X-ray photoelectron spectroscopy (Perkin-Elmer, ESCA PHI 5400) using a monochromatic Mg Kα X-ray source. Gold catalysts (calcined at 350 °C in air for 4 h) before and after use in catalytic oxidation were pressed into a pellet and transferred to a test chamber with the vacuum below 5×10^{-5} Torr. The binding energies were calibrated by referencing the C1s at 284.6 eV.

2.3. Activity measurement for toluene and p-xylene oxidation

The catalytic activity of supported gold catalysts in toluene and *p*-xylene oxidation was measured in a fixed tubular quartz reactor under atmospheric pressure. The reactant and product mixtures were analyzed by an on-line gas chromatograph equipped with a hydrogen flame ionization detector and a HP-5 column. The following conditions were chosen: catalyst volume 0.082 cm^3, inlet toluene concentration 0.6 $g\ m^{-3}$ (146 ppmv) and *p*-xylene concentration 0.40 $g\ m^{-3}$ (85 ppmv) in synthetic gas (O_2, 10 vol.%; N_2, balance), volume hour space velocity 14,690 h^{-1}, the temperature range 50–300 °C. The primary products were CO_2 and H_2O only analyzed by GC–MS and FTIR. Thus, the catalytic activity was expressed as a degree of the conversion of hydrocarbon. The conversion of toluene (or *p*-xylene) was calculated as following:

$$\text{Conversion}\,(\%) = \frac{[\text{Reactant}]_{in} - [\text{Reactant}]_{out}}{[\text{Reactant}]_{in}} \times 100\%$$

3. Results and discussion

3.1. Structural and textural properties

The N_2 adsorption–desorption isotherm and pore size distribution of Au/Co_3O_4 are shown in Fig. S1. The Au/Co_3O_4 gives an isotherm characteristic of macroporous material with a hysteresis loop of type III (Fig. S1a). The BET surface area and single-point total pore volume of Au/Co_3O_4 are 1.6 $m^2\ g^{-1}$ and 0.0043 $cm^3\ g^{-1}$, respectively. Besides, the BJH desorption average pore diameter is determined to be 59.7 nm (Fig. S1b). In contrast, the BET surface area measured for Au/Al_2O_3 and Au/MgO are significantly higher than that of Au/Co_3O_4. Table 1 summarizes the textural parameters of supported gold catalysts, alongside with the Au loading, average Au particle size, Au dispersion and surface atom ratio.

The phase composition and structural characterization of supported gold catalysts were examined by powder X-ray diffraction (PXRD) as shown in Fig. S2. It can be observed that the Au/Co_3O_4 is cubic Co_3O_4 ($a = 8.056$ Å) in crystal structure [space group: Fd3m (2 2 7)] by comparing the XRD pattern of the standard cobalt oxide sample (JCPDS PDF 65-3103). Moreover, a new peak centered at 38.2° related to metallic Au^0 can be roughly identified in the sample containing Au. The result indicates that, regardless of the low