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Au/Co_3O_4–TiO_2 catalysts for preferential oxidation of CO in H_2 stream

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ABSTRACT

A series of Au catalysts supported on Co_3O_4–TiO_2 with various Co contents were prepared. Co_3O_4–TiO_2 support was prepared by incipient-wetness impregnation with aqueous solution of $Co(NO_3)_3$ on TiO_2. Gold catalyst was prepared by deposition–precipitation at pH 7 and 65 °C. The catalysts were characterized by ICP-MS, XRD, TEM, HRTEM and XPS. The catalytic performance of these catalysts was investigated by preferential oxidation of carbon monoxide in hydrogen stream (PROX). The reaction was carried out in a fixed bed reactor with feed of $CO:O_2:H_2:He = 1.33:1.33:65.33:32.01$ (volume ratios). Au/TiO_2 catalyst had both high CO oxidation activity and high H_2 oxidation activity. Adding suitable amount of Co_3O_4 on Au/TiO_2 could enhance CO conversion to a higher extent and suppress H_2 oxidation. On Au/TiO_2 catalysts, gold nucleates at oxygen defect sites of anatase TiO_2 and remains highly dispersed and in good contact with the support. The gold atoms directly in contact with TiO_2 are positively charged and highly stable. Doping with cobalt oxide increases the number of oxygen defects on TiO_2, thus leading to a higher concentration of strongly bound gold atoms. The amorphous nature of Co_3O_4 along with TiO_2 not only enhances electronic interaction between Au and Co_3O_4–TiO_2, but also stabilizes the nano-size gold particles, thereby enhancing the catalytic activity of CO towards higher extent.

1. Introduction

Gold-based catalyst has been proved to be effective for CO oxidation at ambient temperature [1] and appears as a promising candidate for CO PROX reaction [2]. Nanoscale gold–oxide systems evaluated in the recent years as PROX catalysts include Au/Al_2O_3 [3], Au/Fe_2O_3 [4,5], Au/TiO_2 [6], Au/Ti-SBA-15 [7], Au/CeO_2 [8], Au/MnO_2–TiO_2 [9] and so on. Schubert et al. [10] found that Au/CeO_2 and Au/Co_3O_4 exhibited high activity in CO PROX. The suitable supports are the reducible metal oxides, such as TiO_2, α-Fe_2O_3, MnO_x, and Co_3O_4 [11–13]. The most intensively studied catalyst for CO oxidation is Au/TiO_2 as neither Au nor TiO_2 is active for CO oxidation but their combination generates surprisingly high catalytic activity. On Au/TiO_2 catalysts, the reaction was observed even at temperature as low as 90 K [14]. A number of catalysts have been investigated for the PROX reaction. Some of the more effective ones include supported-Pt [15–17], Ru [18], and Au [19]. There are two reactions in PROX reactor:

$$CO + 1/2O_2 \rightarrow CO_2 \quad (1)$$

$$H_2 + 1/2O_2 \rightarrow H_2O \quad (2)$$

Both are highly exothermic. Since only limited amount of O_2 was fed into the reactor, how to increase CO conversion and suppress H_2 conversion is the main task, and catalyst plays an important role. Using Au-containing catalysts, it has been reported that the operating temperatures can be lowered to ~80 °C to achieve similar results [20]. Au/Co_3O_4 was more active than Au/TiO_2 catalyst because Co_3O_4 is a more easily reducible support and because the disordered structure facilitated the formation of anion vacancies near gold particles thereby enhancing the catalytic activity. Liu and Vannice [21] have reported that the deposition of TiO_2 on the surface of Au markedly enhances the catalytic activity for CO oxidation. It has been known that the Co/TiO_2 catalyst was considered to have a strong metal-support interaction (SMSI) and showed high activity in CO hydrogenation [22,23]. This interaction is an important factor for determining the properties of Co/TiO_2 catalyst such as cobalt dispersion and reduction behavior [24]. In fact, the synthesis of highly dispersed cobalt on TiO_2 support requires the strong interaction between cobalt and support. However, too strong interaction can produce the Co-support compound as a suboxide at an interface that is high resistant to reduction [25,26].

Au/Co_3O_4 was recognized as one of the most active catalyst for methane oxidation, among a series of co-precipitated Au on several transition metal oxides [27]. The structural promotion by CeO_2 of a Co_3O_4 catalyst was observed in methane total oxidation [28,29]. The positive effect was attributed to an improved thermal stability, and an increased dispersion of Au metal. Cobalt is particularly active and possesses a high activity for CO and hydrocarbon oxidation

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[30]. Promotion of Pd with Co results in increased CO and propene oxidation activities under stoichiometric conditions [20].

One of the authors has reported that MnO_2, Fe_2O_3, MgO and CuO are suitable promoters for Au/TiO_2 and Au/CeO_2 catalysts for PROX reaction [9,14,31–39].

There are several literature reports on Au/TiO_2 and Au/Co_3O_4 for PROX reaction, but the results on Au/Co_3O_4–TiO_2 are scarce in literature. In this study, the effects of Co_3O_4 additive on Au/TiO_2 for PROX reaction were investigated. Co_3O_4 is reducible and can be in amorphous state or in hydroxide state, which will provide many hydroxyl groups. It also has strong interaction with Au. Therefore, it was expected to create synergistic effect with Au/TiO_2.

2. Experimental

2.1. Catalyst preparation

Co_3O_4–TiO_2 supports were prepared by incipient-wetness impregnation method. The mixed metal oxides were prepared by varying the molar ratios of metal oxide and titania. $Co(NO_3)_2{\cdot}6H_2O$ was added to distilled water of quantity equal to the pore volume of TiO_2. The solution was added into TiO_2 powder in drops under vigorous grinding and then calcined for 4 h at 300 °C.

Gold catalysts were prepared by deposition–precipitation method. $HAuCl_4$ solution (1 g in 1 l distilled water) was added at a rate 10 ml/min into a solution containing suspended support under vigorous stirring and the precipitation temperature of solution was maintained at 65 °C. Ammonia solution was used to adjust the pH value at 7. After aging for 2 h, the precipitate was filtered and washed with hot water (65 °C) until no Cl^- was detected with $AgNO_3$ solution, and dried at 80 °C for 12 h. The cake was grounded and calcined at 180 °C for 4 h to obtain gold catalysts. The amount of gold loaded on the supported catalysts corresponds to 1 wt.%. The catalyst is denoted as Au/Co_3O_4–TiO_2 (x:y) where x:y is the atomic ratio of Co:Ti in the starting materials.

2.2. Characterization

The catalysts were characterized by inductively coupled plasma-mass spectrometry (ICP-MS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM).

The exact gold content was analyzed with ICP-MS (PE/SCIEX Elan 6100 DRC). The ICP-MS was used for the reduction of plasma-based interferences. The catalysts were first dissolved in hot aqua regia and then microwaved for 15 min. The solution was cooled down and diluted with demineralized water to concentrations within the detection range of the instrument. To release mechanical stress from the inclusion, a small beam size was used to open the inclusion, followed by successive enlargement of the ablation pit. Hydrogen was used as reaction gas for the removal of plasma based interferences when operated at DRC mode. Quantitative results were calculated after calibration of the instrument response using SRM NIST 610 or 612 and a halite for Cl. Al-bulk concentrations, determined by electron microprobe, were used as internal standard in the case of the melt inclusions. The advantage from this gain in sensitivity is shown by the transient signal for a melt inclusion (40 μm diameter) from the Mole Granite. The comparison between standard and DRC operation mode shows an excellent agreement between the concentrations obtained for a series of fluid inclusions.

XRD experiments were performed using a Siemens D8-A powder diffractometer. The XRD patterns were collected using Cu $K\alpha_1$ radiation (1.5405 Å) at a voltage and current of 40 kV and 40 mA, respectively. The sample was scanned over the range $2\theta = 20$–70° at a speed of 3°/min to identify the crystalline structure. The samples for XRD were prepared as thin layers on a sample holder.

Temperature programmed reduction (TPR) was performed on each of the sample. First the sample was treated in 100 ml/min argon at 100 °C for 1 h to remove any adsorbed gases or water. Then 25 ml/min 5% H_2 in Ar was flowed through the sample while the temperature was ramped from 25 to 720 °C at a rate of 10 °C/min. During each of these steps the process was monitored using a thermal conductivity detector (TCD), and the resulting current was plotted to quantify the consumption of H_2.

The morphologies and particle sizes of the samples were determined by transmission electron microscopy (TEM) on a JEM-2000 FX II (JEOL) operated at 120 kV and 160 kV. HRTEM on a JEOL JEM-2010 was operated at 160 kV. The samples were ground, suspended in methanol at room temperature and dispersed with ultrasonic agitation; then, an aliquot of the solution was dropped on a 3 mm diameter carbon film supported on lacey copper grid. The average particle size (ds) of the Au particles was calculated by the following equation: $ds = \sum n_i d_i^3 / \sum n_i d_i^2$, where d_i is the diameter measured directly from the TEM micrographs; and n_i is the number of particles having the diameter d_i. From each catalyst, about 200 Au particles were measured in order to determine a statistically justified average particle size and size distribution.

XPS spectra were recorded with a Thermo VG Scientific Sigma Prob spectrometer. The powder samples were pressed onto a special sample holder, which was then placed in a vacuum chamber. The XPS spectrometer was equipped with a hemispherical electron analyzer and an Al Kα X-ray radiation source ($h\nu = 1486.6$ eV) powered at 20 kV and 30 mA. The residual pressure in the chamber was below 5×10^{-9} Torr. The base pressure in the analyzing chamber was maintained in the order of 10^{-9} Torr. The spectrometer was operated at 23.5 eV pass energy. The intensities of the peaks were estimated by calculating the integral peak after subtracting an S-shaped background and fitting the experimental peak to a combination of Lorentzian/Gaussian lines of variable proportions. The binding energy of XPS was corrected by contaminant carbon ($C_{1s} = 284.5$ eV) in order to facilitate the comparisons of the values among the catalysts and the standard compounds.

2.3. Catalytic activity

Catalytic reaction tests were performed in a similar manner as reported previously [9,31]. The catalytic measurements of CO oxidation in hydrogen stream were carried out in a downward, fixed-bed continuous-flow, pyrex glass-tubular reactor loaded with 0.1 g of catalyst. The reactant gas containing 1.33% CO, 1.33% O_2 and 65.33% H_2, and He for balance was fed into the reactor with a total flow rate of 50 cm^3/min. The reactor was heated with a temperature regulated furnace with a heating rate of 1 °C/min and the temperature was measured by a thermocouple placed inside the catalyst bed. The outlet gas was analyzed by a gas chromatograph (China Chromatography 8700T) equipped with MS-5A column and thermal conductivity detector. Calibration of the gases was done with a standard gas containing known concentration of the components. The influent and effluent gases were analyzed by a six-port auto-sampling valve in an on-line gas chromatograph, which was equipped with a packed Carbosphere column (80/100 mesh and 10 ft 1/8 in.) and a thermal conductivity detector (TCD). Since the change of hydrogen concentrations in the stream was very little, one was not able to measure it by gas chromatograph. The selectivity of oxygen reacting with hydrogen was calculated by O_2 consumption and CO consumption. The CO and O_2 conversion calculations were based on the CO and O_2 consumption, respectively. The selectivity of oxygen reacting with CO (CO selectivity) was calculated by the ratio of O_2 consumption for the CO oxidation reaction