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Enhance catalytic activity for CO oxidation over titania supported gold catalysts that dispersed on SiO_2

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ABSTRACT

The enhanced dispersion of gold on TiO_2 was achieved by dispersing TiO_2 onto a high-surface-area SiO_2 powder support. High temperature reduction, at 773–873 K, in hydrogen leads to very active gold nanoparticles on the support surfaces for CO oxidation at room temperature. The surface sol–gel method results better dispersion for both TiO_2 and Au, and higher activity for CO oxidation than that by the conventional impregnation method. Metallic gold with slightly negative charge was evidenced by X-ray photoelectron spectroscopy (XPS) and *in situ* transmission infrared spectroscopy (FTIR) using CO as a probe. The obtained $Au/TiO_2/SiO_2$ catalysts show better stability and higher activities for CO oxidation than that for Au/TiO_2. The promotion effects may origin from the formation of thin layer and small crystalline particles of TiO_2 anchored on SiO_2, leading to a better dispersion of small Au nanoparticles and sinter resisting.

1. Introduction

The interest in studying supported Au catalysts has increased substantially since Haruta and Hutchings showed extraordinary catalytic properties in some reactions [1,2]. Although, Au was reported to be active for CO oxidation on 1925 and 1975 [3,4]. Haruta et al. [1] found that gold nanoparticles deposited on reductive metal oxides exhibit high catalytic activity for low temperature CO oxidation. Hutchings and co-workers [2] found that gold catalysts are catalytically active for hydrochlorination of acetylene to vinyl chloride. Supported gold catalysts have been found to be active for several important reactions like epoxidation of propene [5,6], reduction of nitrogen oxides [7,8], water gas shift reaction [9], low temperature CO oxidation [1,3,4,10–12], and many selective oxidation or hydrogenation of fine chemical [13,14].

Most of the experimental and theoretical studies to date have focused on understanding the origin of the unique activity for low temperature CO oxidation and the issues have been addressed extensively. These studies have concluded that the unique catalytic activity is related to the properties of the metal oxide supports [15], defects on the oxide surface [16,17], quantum size effect with respect to the size of Au nanoparticles [10,18–20], effect of the size of gold particles [11], the structures of the interface of Au nanoparticles and oxide support surfaces [21], and the details in the preparation procedure [22,23]. While how to retain the high activity of Au catalysts remains unsolved, which limits its commercialized applications. It was found that the catalytic activity for CO oxidation on $Au/TiO_2(1\,1\,0)$ decreases sharply within 2 h due to the conglomeration of Au nanoparticles. Such rapid sintering of Au nanoparticles under reaction condition was attributed to quenching of the surface oxygen vacancies on TiO_2 which weakens the binding energy of Au with TiO_2 [10,24].

In order to suppress the sintering of Au nanoparticles under the reaction condition or thermal treatment at high temperature, one of the strategies is to confine them into porous materials forming a core–shell structure [25]. Zheng et al. have recently prepared yolk–shell particles with 6.3 nm Au nanoparticles core and ZrO_2 or TiO_2 mesoporous shell [26]. Another strategy is to find a suitable substrate capable of efficiently stabilizing supported Au nanoparticles through the strong metal support interaction (SMSI). Adding a third component had been found to enhance the catalytic activity significantly [27–42]. Yan et al. [32] experimentally demonstrated that deposition of Au nanoparticles on a nanocrystalline TiO_2 modified with aluminum oxide can enhance stability of supported Au nanocatalysts. The amorphous aluminum oxide layer was found to play an extremely important role in the stabilization of the supported Au nanoparticles without affecting catalytic activities. Huang and co-workers [33] had shown that Au species have a strong interaction with highly dispersive CeO_2 deposited on SiO_2. Goodman et al. [19,34] had reported the stabilization of highly active Au nanoparticles by surface defects via substituting Ti atom for Si in a silica thin film network. A novel design of gold catalysts with enhanced thermal stability by post-modification of Au/TiO_2 by amorphous SiO_2 decoration has been reported [35].

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Studies at ultrahigh vacuum condition showed that the Au bilayer structure deposited on a reduced titania thin film grown on Mo(1 1 2) [20], (Mo(1 1 2)–(8 × 2)-TiO*x*), is exceptionally active. The binding energy of Au and Ti^{4+} is apparently higher than that of Au–Au according to TPD of Au [17], which enables Au nanoparticles to be stable on the support. Inspired from this, one to a few layers of TiO_2 coating on another oxide support surface would be expected to have a stronger interaction with Au atoms. In the present work, we have deposited Au nanoparticles on TiO_2 that dispersed on SiO_2 prepared by a conventional impregnation method and a surface sol–gel method. Such dispersion enhances the stability of Au nanoparticles. Furthermore, the activities for CO oxidation are much higher as compared to that for Au on TiO_2.

2. Experimental

2.1. Catalyst preparation

A commercial high-surface area silica (specific surface area = 400 m^2/g) was used as a support. The silica support was cleaned by soaking overnight in 30% HNO_3 solution, washed with distilled water, then dried at 110 °C and calcined at 550 °C for 2 h before use. TiO_2/SiO_2 mixed oxides were prepared by a surface sol–gel (SSG) process and a conventional impregnation method. The procedure of SSG for coating monolayer to multilayer titanium oxide and other metal oxide films onto a silica surface was developed according to the method described by Kunitake and co-workers [43], which is similar to grafting titanium alkoxides on SiO_2 [44]. In the present work, 10 g of the pre-cleaned high-surface area SiO_2 powder sample was dried in flowing Ar at 130 °C for 11 h, and then loaded into a reflux bottle. Subsequently, a solution of tetrabutyl titanate (11 mL), Ti-(O-n-Bu)$_4$, in anhydrous toluene (110 mL) was added, following vigorous reflux at the boiling temperature of toluene (112 °C) for 4 h. Then the sample was filtered, washed several times with anhydrous ethanol and toluene respectively, and dried at 130 °C for 2 h, hydrolyzed with steam at 80 °C, and finally dried at 130 °C for 2 h again. In order to cover the silica surface with TiO_2 completely, the procedure of grafting was repeated several times. The final TiO_2/SiO_2 samples were calcined in air at 500 °C for 2 h. Here after the obtained samples were denoted as T-*N*-S, in which *N* stands for the repeating number. In the second method (a conventional impregnation method, IMP), silica was immersed in certain amount of $TiCl_3$–HCl solution for 12 h, then dried and calcined at 500 °C for 2 h. The obtained samples were described as *x* wt% TS according to the TiO_2 loading. For comparison, TiO_2/SiO_2 was also prepared by IMP method using $Ti(OC_4H_9)_4$ as a precursor.

Au was deposited onto the above prepared supports by an IMP method using chloroauric acid ($HAuCl_4$) as a precursor. The paste was dried at ~323 K first, at 373 K then for overnight. The obtained precursor was then reduced in hydrogen at temperature between 523 and 973 K. The catalysts after reduction were purged by helium, then directly exposed to CO:O_2:He (1:1:98) mixture without exposing to air. Space velocity is controlled at 600,000 mL per g-catalyst per hour.

2.2. Catalytic testing

The CO oxidation reaction was carried out in a U-tube quartz reactor with a water bath to better control the reaction temperature. Typically, 10 mg of catalyst was used. Samples were reduced in a vertical fixed-bed quartz reactor using high-purity H_2. Then the catalyst was transferred into the U-tube reactor under the protection of high-purity He. Reaction gas of 1 vol.% CO and 1 vol.% O_2 balanced with He, pre-purified by a liquid N_2 trap, was flowed at an ambient pressure through the catalyst at a rate of 30 mL/min. The reaction products were analyzed using a gas chromatograph (GC) equipped with a methanation convertor and a flame ionization detector (FID).

2.3. Catalyst characterization

The diffusion reflectance UV–vis (DR-UV–vis) spectra were taken on a Varian Cary-5000 spectrometer equipped with a diffuse-reflectance accessory. The spectra were collected with dehydrated $BaSO_4$ as a reference and recorded in the diffused reflectance mode (*R*) and transformed to a Kubelke-Munk function (*F*(*R*)).

The powder X-ray diffraction (XRD) patterns for the structure determination were measured on a Phillips Panalytical X'pert Pro diffractometer equipped with a graphite monochromator. Cu K_α radiation (40 kV and 30 mA) was used as the X-ray source.

The X-ray photoelectron spectroscopy (XPS) was measured with a PHI Quantum 2000 Scanning ESCA Microprobe equipment (physical Electronics) using monochromatic Al K_α radiation ($h\nu$ = 1486.6 eV). The background pressure in the analysis chamber was lower than 1×10^{-7} Pa. The X-ray beam diameter was 100 μm, and the pass energy was 58.7 eV for each analysis. All binding energies were referenced to the C 1s hydrocarbon peak at 284.6 eV.

Nitrogen physisorption at 77 K was carried out with a Micromeritics Tristar 3000 surface area and porosimeter analyzer to examine the surface area and the porous property of each sample. The samples were pretreated at 573 K in vacuum for 3 h before N_2 adsorption. The specific surface area was calculated following the BET method. The pore diameter distribution was evaluated by the BJH method according to the desorption isotherm branch.

The prepared fresh and used catalyst samples were characterized using X-ray photoemission spectroscopy (XPS, Quantum 2000), transmission electron microscope (TEM, FEI Tecnai 300 kV), and *in situ* Fourier transmission infrared spectroscopy (FTIR, Nicolet Nexus 870) combined with home-made *in situ* IR cell [45].

3. Results and discussion

3.1. Catalyst performance

The catalytic activities for CO oxidation over 2 wt% Au supported on TiO_2/SiO_2 prepared by the surface sol–gel (SSG) and conventional impregnation (IMP) methods as a function of the reduction temperature were compared with that on TiO_2 in Fig. 1. It clearly shows the significant effects of the reduction temperature on the

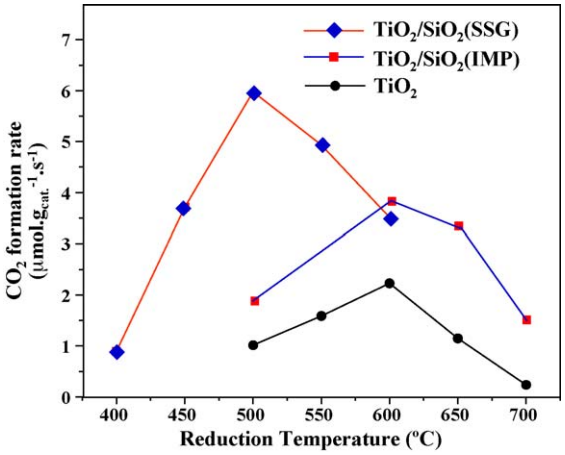

Fig. 1. Catalytic activities for CO oxidation over 2 wt% Au/TiO_2 and Au/TiO_2/SiO_2 prepared both by the SSG and IMP as a function of the reduction temperature.