Alloying Au surface with Pd reduces the intrinsic activity in catalyzing CO oxidation

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ABSTRACT

Various Au-Pd/SiO$_2$ catalysts with a fixed Au loading but different Au:Pd molar ratios were prepared via deposition-precipitation method followed by H$_2$ reduction. The structures were characterized and the catalytic activities in CO oxidation were evaluated. The formation of Au-Pd alloy particles was identified. The Au-Pd alloy particles exhibit enhanced dispersions on SiO$_2$ than Au particles. Charge transfer from Pd to Au within Au-Pd alloy particles. Isolated Pd atoms dominate the surface of Au-Pd alloy particles with large Au:Pd molar ratios while contiguous Pd atoms dominate the surface of Au-Pd alloy particles with small Au:Pd molar ratios. Few synergetic effect of Au-Pd alloy occurs on catalyzing CO oxidation under employed reaction conditions. Alloying Au with Pd reduces the intrinsic activity in catalyzing CO oxidation, and contiguous Pd atoms on the Au-Pd alloy particles are capable of catalyzing CO oxidation while isolated Pd atoms are not. These results advance the fundamental understandings of Au-Pd alloy surfaces in catalyzing CO oxidation.

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1. Introduction

Bimetallic catalysts usually exhibit superior catalytic performances compared with monometallic components [1]. Gold(Au)-palladium(Pd) bimetal catalysts are a representative system and have shown the synergetic effect on catalyzing a variety of reactions, especially in the direct synthesis of H$_2$O$_2$ [2,3], selective oxidation of alcohols [4,5], C—C coupling [6,7], and selective hydrogenation of unsaturated hydrocarbon [8,9]. The catalytic performances of these Au-Pd bimetallic catalysts were found not only to depend on the Au-Pd particle sizes but also on the Au-Pd surface structures [9–13]. For example, the dispersion of Pd atoms on the Au surface strongly affects the catalytic performances of the Au-Pd bimetallic catalysts. Single Pd atoms isolated by Au atoms were reported to promote the catalytic performance in the selective hydrogenation reaction [9] and C—C coupling [6] while contiguous Pd atoms surrounded by Au atoms were reported to benefit for low-temperature CO oxidation [14].

CO oxidation, a popular probe catalytic reaction, has been tested for various Au-Pd bimetallic catalysts. The synergetic effect of Au-Pd structures on low-temperature CO oxidation was proposed on the basis of model catalyst study under ultra-high vacuum condition [14] or density functional theory (DFT) calculation study [13], but the results coming from supported Au-Pd powder catalysts are controversial. CO adsorption on the Au-Pd bimetal surfaces could drive a surface segregation of Pd [11,15–17], making the surface structures of Au-Pd bimetal catalysts sensitively depend on the reaction atmosphere; meanwhile, the supports seemed to strongly affect the catalytic activity of supported Au-Pd catalysts in low-temperature CO oxidation. Ye et al. [18] observed enhanced catalytic activity of Au/SnO$_2$ doped with Pd. The Han's group [19] reported that none of Au-Pd alloys supported on SiO$_2$ exhibited better catalytic activity than pure Au/SiO$_2$. The Chandler's group reported that Au-Pd/TiO$_2$ catalysts were catalytically more active than Au/TiO$_2$ while Au-Pd/Al$_2$O$_3$ catalysts were catalytically more inactive than Au/Al$_2$O$_3$ [16].

In our previous studies, we have used inert SiO$_2$ as the support to successfully demonstrate the structure-intrinsic catalytic activity of Au particles in low-temperature CO oxidation because SiO$_2$ does not directly participate in the catalytic reaction [20–26]. In this paper we applied SiO$_2$ as the support to synthesize a series of Au-Pd/SiO$_2$ catalysts with different Au-Pd ratios. The compositions and structures of Au-Pd/SiO$_2$ catalysts were characterized in detail

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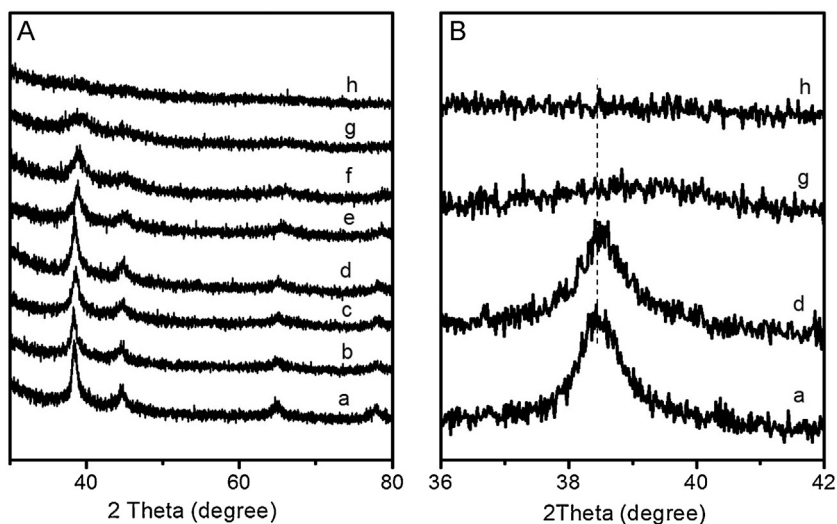
Fig. 1. (A) XRD patterns and (B) the enlarged XRD patterns between 36 and 42° of Au/SiO$_2$ (a), Au-Pd/SiO$_2$-50 (b), Au-Pd/SiO$_2$-20 (c), Au-Pd/SiO$_2$-10 (d), Au-Pd/SiO$_2$-5 (e), Au-Pd/SiO$_2$-2 (f), Au-Pd/SiO$_2$-1 (g) and Pd/SiO$_2$ (h).

and the distributions of Pd atoms on the Au-Pd alloy surfaces were probed by CO adsorption. The catalytic activities of Au-Pd/SiO$_2$ catalysts were also evaluated in CO oxidation. Strong interactions between Au and Pd within the Au-Pd alloy particles were identified but the formation of Au-Pd alloy particles were found to decreases the intrinsic activity of Au surfaces in catalyzing CO oxidation under employed reaction conditions.

2. Experimental section

A series of Au-Pd/SiO$_2$ catalysts with different Au:Pd molar ratios (denoted as Au-Pd/SiO$_2$-x, where x is the Au:Pd molar ratio) were prepared by the traditional deposition-precipitation (DP) method employing HAuCl$_4$·4H$_2$O (Sinopharm Chemical Reagent Co., Ltd., Au content ≥47.8%) and H$_2$PdCl$_4$ (Sinopharm Chemical Reagent Co., Ltd., PdCl$_2$:HCl molar ratio: 1:2) as the precursors and inert SiO$_2$ (40–120 mesh, Qingdao Haiyang Chemicals Co.) as the support. Typically, calculated amounts of HAuCl$_4$ and H$_2$PdCl$_4$ aqueous solution were co-added into a three-neck bottle containing the support and adequately stirred, and then ammonia water was slowly added to adjust the pH between 9 and 10. The system was adequately stirred at 60 °C for 24 h. Then the precipitate was filtered and washed several times, and the resulting powder was dried at 60 °C for 12 h followed by H$_2$ reduction at 200 °C for 4 h. For comparisons, pure Au/SiO$_2$ with 2% weight ratio and Pd/SiO$_2$ catalyst with the same Pd loading as that in Au-Pd/SiO$_2$-1 were prepared with the similar method, and PdO/SiO$_2$ catalyst with the same Pd loading as Pd/SiO$_2$ was prepared by calcining the catalyst precursor at 200 °C for 4 h.

Powder X-ray diffraction (XRD) patterns were acquired on a Philips X'Pert PRO SUPER X-ray diffractometer with a Ni-filtered Cu Kα X-ray source operating at 40 kV and 50 mA. High resolution X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 high performance electron spectrometer using a monochromatized Al Kα excitation source (hν = 1486.6 eV). The binding energies in the XPS spectra were referenced to the Si 2p binding energy in SiO$_2$ at 103.3 eV. Transmission electron microscopy (TEM) measurements were performed on JEOL-2010 and JEOL-2100F high-resolution transmission electron microscopes. The Au L$_{III}$-edge and Pd K-edge X-ray absorption near-edge structure (XANES) spectra were measured in a transmission mode with an energy step of 0.5 eV at the BL14W1 beamline of Shanghai Synchrotron Radiation Facility (SSRF).

Operando diffuse reflectance infrared spectroscopy (DRIFTS) measurements were performed on a Nicolet 6700 FTIR spectrometer equipped with an *in-situ* DRIFTS reaction cell (Harrick Scientific Products, INC) at RT. Prior to the measurements, 10 mg catalyst precursor was loaded onto the sample stage of the reaction cell and reduced by H$_2$ at 200 °C for 4 h, then purged with Ar (flow rate: 20 mL/min) and cooled down to RT to prepare the catalysts. Then the gas stream consisting of 1% CO and 99% Ar was admitted and the DRIFT spectra were measured in the series mode with 64 scans and a resolution of 4 cm^{-1} using a MCT/A detector. The DRIFTS spectrum of the freshly-prepared catalyst purged with Ar at RT was taken as the background spectrum.

The catalytic activity was evaluated on a fixed-bed flow reactor. Prior to the catalytic activity evaluation, 100 mg catalyst precursor in the catalytic reactor was reduced by H$_2$ at 200 °C for 4 h and then cooled to RT in Ar (flow rate: 20 mL/min) to prepare the catalysts. Then the reaction gas consisting of 1% CO and 99% dry air was fed at a rate of 20 mL/min. The composition of the effluent gas at the steady state was analyzed with an online GC-14C gas chromatograph equipped with a TDX-01 column (T = 80 °C, H$_2$ as the carrier gas at 30 mL/min). The CO conversion was calculated from the change in CO concentrations in the inlet and outlet gases.

3. Results and discussion

In our Au-Pd/SiO$_2$ catalysts, the loading of Au in the catalysts was fixed with a Au:SiO$_2$ weight ratio of 2% and the Au:Pd molar ratio varied between 50 and 1. Fig. 1A displays the XRD patterns of Au/SiO$_2$, Pd/SiO$_2$ and various Au-Pd/SiO$_2$ catalysts. Au/SiO$_2$ displays clear diffraction patterns well indexed to Au while Pd/SiO$_2$ exhibits no diffraction patterns. This suggests the formation of Au particles but highly dispersive palladium species on SiO$_2$ under the employed catalyst preparation recipes. Similar to Au/SiO$_2$, all Au-Pd/SiO$_2$ catalysts only show diffraction patterns arising from Au; however, as shown in Fig. 1B, comparing that of Au/SiO$_2$, the Au (1 1 1) diffraction peak of Au-Pd/SiO$_2$ catalysts shifts to higher diffraction angles and broadens with the Pd loading. The standard positions of Au (1 1 1) and Pd (1 1 1) diffraction peaks are respectively located at 38.2 and 39.9° respectively corresponding to lattice spacing of 2.36 and 2.25 Å. The (1 1 1) lattice spacing were calculated to be 2.36, 2.36, 2.35, 2.35, 2.34, 2.33 and 2.32 Å in Au/SiO$_2$, Au-Pd/SiO$_2$-50, Au-Pd/SiO$_2$-20, Au-Pd/SiO$_2$-10, Au-Pd/SiO$_2$-5, Au-Pd/SiO$_2$-2 and Au-Pd/SiO$_2$-1, respectively. The decrease of the