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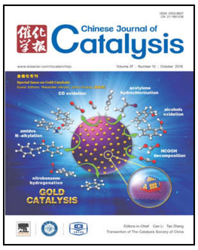

Article (Special Issue on Gold Catalysis)

Enhanced catalytic activities and selectivities in preferential oxidation of CO over ceria-promoted Au/Al_2O_3 catalysts

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The preferential oxidation of CO (CO-PROX) is a hot topic because of its importance in proton-exchange membrane fuel cells (PEMFCs). Au catalysts are highly active in CO oxidation. However, their activities still need to be improved at the PEMFC operating temperatures of 80–120 °C. In the present study, Au nanoparticles of average size 2.6 nm supported on ceria-modified Al_2O_3 were synthesized and characterized using powder X-ray diffraction, nitrogen physisorption, transmission electron and scanning transmission electron microscopies, temperature-programmed hydrogen reduction (H_2-TPR), Raman spectroscopy, and *in situ* diffuse-reflectance infrared Fourier-transform spectroscopy. Highly dispersed Au nanoparticles and strong structures formed by Au–support interactions were the main active species on the ceria surface. The Raman and H_2-TPR results show that the improved catalytic performance of the Au catalysts can be attributed to enhanced strong metal–support interactions and the reducibility caused by ceria doping. The formation of oxygen vacancies on the catalysts increased their activities in CO-PROX. The synthesized Au catalysts gave excellent catalytic performances with high CO conversions (> 97%) and CO_2 selectivities (> 50%) in the temperature range 80–150 °C.

1. Introduction

Proton-exchange membrane fuel cells (PEMFCs) have attracted much attention because of their high current densities, low operating temperatures, and long working lives [1]. However, the Pt-based anode of a PEMFC is prone to poisoning by CO at operating temperatures of 80–120 °C [2,3]. Hopcalite catalysts are generally used for CO removal. Although Cu-based catalysts have the advantages of low cost and high catalytic activities in CO oxidation [4–7], they are not suitable for use in preferential oxidation of CO (CO-PROX) in a H_2-rich stream in the presence of CO_2 and H_2O [8–10]. Au nanoparticles are popular noble-metal catalysts and are used in the water-gas shift reaction [11,12] and CO oxidation [13,14]. Au nanoparticle catalysts show excellent catalytic performance in low-temperature CO oxidation, but the catalytic activities of monometallic Au catalysts are limited to those with competitive oxidation of H_2 at 80–120 °C [15,16]. The development of effective Au catalysts with enhanced catalytic performance in CO-PROX is therefore needed.

This challenge has been addressed using Au catalysts modified with reducible oxides such as TiO_2 [17], MnO_2 [18], FeO_x [17,19], and CeO_2 [17,20]; these catalysts have potential for use in CO-PROX. Ceria is an important catalytic material in heterogeneous catalysis [21,22]. Ceria-based materials enhance catalytic activities because of the oxygen storage capacity (OSC) of

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ceria, which is associated with the formation of oxygen vacancies, and the excellent Ce^{4+}/Ce^{3+} redox reaction [23]. Ceria-doped Al_2O_3 composite materials are promising three-way catalysts [24]. Yuan et al. [25] reported a uniform ceria nanocatalyst stabilized by ordered mesoporous alumina as a catalyst support for Au in CO oxidation; 100% CO conversion was achieved at room temperature. Appropriate supports such as carbon materials [26,27] and mesoporous alumina [28,29] can endow specific catalytic functions by suppressing nanoparticle agglomeration and enhancing the synergistic effects of strong metal–support interactions (SMSIs).

Recently, we reported a K-treated Au–Cu/Al_2O_3 catalyst produced using laboratory-synthesized γ-Al_2O_3 with a controlled morphology; the catalyst was active and stable in CO-PROX even in the presence of CO_2 or H_2O [30]. It was proposed that the introduction of Cu strengthens CO adsorption on the catalyst and K treatment significantly increases the stability of active Cu^+ species. Based on the above results, a series of ceria-doped Au catalysts were prepared and investigated using X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectroscopy, temperature-programmed reduction of H_2 (H_2-TPR), and *in situ* diffuse-reflectance infrared Fourier-transform spectroscopy (DRIFTS). Ceria addition enhanced the reducibility and oxygen activation of the Au catalyst, resulting in improved CO-PROX activity.

2. Experimental

2.1. Catalyst preparation

All reagents were analytical grade and used without further purification. The alumina supports were prepared hydrothermally [31]. In a typical procedure, $KAl(SO_4)_2\cdot12H_2O$ (2.372 g) and $CO(NH_2)_2$ (0.601 g) were separately dissolved in 50 mL of deionized water. The two solutions were mixed and stirred for 0.5 h. The mixture was transferred to a Teflon-lined stainless-steel autoclave and hydrothermal treatment was performed at 180 °C for 3 h. After thorough centrifugation, the product was washed with deionized water and ethanol several times, dried at 80 °C overnight, and calcined at 600 °C in air for 2 h; this product is denoted by Al. A ceria-doped alumina support was prepared using an incipient wetness impregnation method, in which Al was impregnated with a aqueous solution of $Ce(NO_3)_3\cdot6H_2O$ (0.35 mol L^{-1}). The obtained CeO_2/Al_2O_3 composite was dried overnight at 50 °C and calcined at 500 °C for 2 h; this product is denoted by CeAl.

The Au–Cu/CeO_2–Al_2O_3 catalyst was prepared using our recently reported two-step deposition-precipitation (DP) method [30]. The required amount of $Cu(NO_3)_2\cdot9H_2O$ solution (0.1 mol L^{-1}) was added to an aqueous suspension of CeAl and the pH was controlled to ca. 8 by adding $(NH_4)_2CO_3$ solution (0.5 mol L^{-1}). The mixture was stirred at 60 °C for 2 h. The Cu/CeAl catalyst was obtained by centrifugation, and then washed and dried under vacuum. Au was deposited on the Cu/CeAl surface using $HAuCl_4$ solution (7.888 g L^{-1}) as the Au precursor and $(NH_4)_2CO_3$ as the precipitant, as in the first procedure described above. This sample is denoted as Au–Cu/CeAl. For comparison, Au/Al_2O_3 and Au/CeO_2–Al_2O_3 catalysts were prepared using the DP method; these are denoted by Au/Al and Au/CeAl, respectively. A K-doped Au–Cu/CeO_2–Al_2O_3 bimetallic catalyst was prepared using an incipient wetness impregnation method. Typically, the required amount of KNO_3 solution was added to Au–Cu/CeO_2–Al_2O_3 powder with mixing and then aging at room temperature for 1 h. The mixture was dried under vacuum overnight. The obtained K-doped Au–Cu/CeO_2–Al_2O_3 bimetallic catalyst is denoted by Au–Cu/K–CeAl. The Au loading on each catalyst was 1 wt%, and the K loading was fixed at 2 wt%. All the steps described above were performed under light exclusion by covering the round-bottomed flask with Al foil.

2.2. Catalyst characterization

XRD was performed using a Rigaku D/MAX-2400 diffractometer (40 kV, 100 mA) with Cu K_α radiation (λ = 1.54056 Å). Nitrogen adsorption–desorption isotherms were recorded using a Micromeritics Tristar 3000 instrument at −196 °C. The Brunauer–Emmett–Teller surface areas (S_{BET}) and pore size distributions of the prepared catalysts were calculated using the BET and Barrett–Joyner–Halenda method, respectively. The metal loadings on the catalysts were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Optima 2000 DV). TEM images of the Au catalysts were obtained using an FEI Tecnai G220 S-Twin microscope, at an accelerative voltage of 200 kV. High angle angular dark field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDX) were performed using an FEI Tecnai F30 electron microscope at an accelerating voltage of 300 kV. Raman spectra were recorded using a Thermo DXR Raman microscope, at a laser excitation wavelength of 532 nm. H_2-TPR was performed using a Micromeritics Autochem II 2920 instrument equipped with a thermal conductivity detector (TCD) to detect H_2 consumption. Before each H_2-TPR test, the fresh samples were pretreated in an Ar flow at 150 °C for 30 min. After cooling to 40 °C, the gas atmosphere was switched to 8 vol% H_2/Ar at a rate of 50 mL min^{-1} and the catalyst was heated from 40 to 800 °C (10 °C min^{-1}). *In situ* DRIFTS was performed using a Nicolet 6700 FT-IR spectrometer equipped with a mercury cadmium telluride detector and a low-temperature DRIFTS cell (Harrick). Prior to each test, the catalyst was evacuated at 200 °C for 30 min and cooled to room temperature, and the background spectrum was recorded in an He flow at the desired temperature before the introduction of 5 vol% CO/He.

2.3. Catalytic activity measurements

The catalytic performance in CO-PROX was investigated using a fixed-bed flow reactor (i.d. 8 mm) at atmospheric pressure in the temperature range 30–150 °C, at which the water-gas shift reaction is negligible. The reaction temperature was controlled using a thermocouple located at the middle of the catalyst bed. The feed gas, which consisted of 1 vol% CO + 1 vol% O_2 + 40 vol% H_2, and balance N_2, was passed through 100