Role of metal components in Pd–Cu bimetallic catalysts supported on CeO$_2$ for the oxygen-enhanced water gas shift

Junichiro Kugai[a], Jeffrey T. Miller[b], Neng Guo[b], Chunshan Song[a,*]

[a] Clean Fuels and Catalysis Program, EMS Energy Institute, and Department of Energy and Mineral Engineering, The Pennsylvania State University,
209 Academic Projects Building, University Park, PA 16802, USA
[b] Chemical Technology Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60430-4837, USA

ABSTRACT

Catalytic hydrogen production and CO removal in a post-reforming process are critical for low-temperature fuel cell applications. The present study aims at clarifying the role of metal components in bimetallic catalysts for oxygen-enhanced water gas shift (OWGS), wherein a small amount of O$_2$ is added to H$_2$-rich reformate gas to enhance CO shift. Among CeO$_2$-supported bimetallic catalysts, Pd–Cu and Pt–Cu combinations were found to show strong synergetic promoting effect in OWGS, which leads to much higher CO conversion and higher H$_2$ yield than WGS at low temperature around 250 °C. Temperature programmed reduction (TPR) showed strong interaction between Pd and Cu in Pd–Cu/CeO$_2$ by a single reduction peak in contrast to multiple peaks on monometallic Cu/CeO$_2$. Extended X-ray absorption fine structure (EXAFS) analysis revealed that such bimetallic Pd–Cu and Pt–Cu form alloy nanoparticles, where noble metal is mainly surrounded by Cu atoms. Oxygen storage capacity (OSC) measurements point to higher resistance of Pd–Cu to oxidation indicating that Pd keeps Cu in reduced state in air pulse condition. From kinetic study, Pd in Pd–Cu was found to promote CO shift, rather than CO oxidation by increasing the number of active sites and by suppressing H$_2$ activation (that is inherent to monometallic Pd), which minimizes both the inhibition effect of H$_2$ and the loss of H$_2$ by oxidation in OWGS. Transient response technique revealed that Cu in Pd–Cu enhances desorption of strongly chemisorbed CO$_2$ on catalyst surface in contrast to very slow CO$_2$ desorption from surface of monometallic Pd. Thus, the excellent OWGS activity of Pd–Cu catalyst has been attributed to the complementary roles of the two metals for enhancing CO shift, which is realized by its alloy structure and the accompanying strong interaction between metal components.

© 2011 Published by Elsevier B.V.

1. Introduction

Hydrogen (H$_2$) is considered to be a promising clean energy carrier for use in fuel cells which are intrinsically more energy-efficient for power generation compared to internal combustion systems [1–5]. Catalytic reforming of gaseous and liquid hydrocarbons, biomass-derived liquids, and alcohols is an attractive method for H$_2$ production, especially for fuel cell applications in view of easy handling and safety. One of the drawbacks in this catalytic reforming is the co-production of carbon monoxide (CO) in the H$_2$ stream. As low as 30 ppm of CO concentration in the H$_2$ stream severely poisons anode catalysts of proton-exchange membrane fuel cells [6,7]. Therefore, CO must be removed in the downstream, usually by water gas shift (WGS) and further by preferential oxi-

dation (PROX). Conventional catalysts, Fe–Cr for high temperature shift (HTS) and Cu–Zn–Al for low temperature shift (LTS), have been employed for the WGS in stationary hydrogen plants, but these catalysts are not suitable for fuel cell applications due to (i) their slow kinetics and thus large catalyst volume occupying more than 50% fuel processor system volume and (ii) their pyrophoric nature that requires careful pre-conditioning and/or periodical regeneration [1,5,8].

In order to improve the slow kinetics of WGS at low temperatures, our group has been exploring the oxygen-enhanced water gas shift (OWGS) reaction over ceria-supported Pd–Cu bimetallic catalysts, where addition of a small amount of oxygen into WGS feed largely enhanced CO removal from the H$_2$-rich gas stream at relatively low temperatures [9–11]. It was experimentally proven that CO conversion is higher for OWGS than WGS or PROX on this catalyst system [9]. Sekizawa et al. also reported that addition of O$_2$ to WGS of methanol reformate gas over Cu/Al$_2$O$_3$–ZnO enhanced removal of CO through CO oxidation [12]. It was proposed

* Corresponding author. Tel.: +1 814 863 4466; fax: +1 814 865 3573.
  E-mail address: csong@psu.edu (C. Song).

that added O_2 facilitates chemisorption of H_2O to form hydroxyl groups, which is believed to be critical in associative and regenerative mechanisms of WGS over Cu catalysts [13,14], and the heat from exothermic surface reaction activates the reaction sites as well [15,16]. However, O_2 addition to the gas containing water at low temperature resulted in deactivation of Cu. The reaction pathway and the effect of O_2 addition to WGS would also be different on ceria-supported catalysts from alumina-supported Cu catalysts and therefore needs to be clarified.

The ceria-supported Pd–Cu catalysts described in our previous report are considered to be low-pyrophoric and therefore suitable for fuel cell applications. The low-pyrophoric nature originates from the unique redox property of metal-loaded ceria, i.e. ease of reduction at low temperature and high redox capacity [17,18], that leads to low Cu loading required for high activity. During OWGS or WGS reaction, ceria is proposed to participate in the reaction through its redox process, keeping metal oxidation state constant as well as providing oxygen to oxidize CO [19–23]. Metal components also have significant impacts on catalytic performance and pyrophoricity as well. For example, Hilaire et al. compared ceria-supported Pd, Ni, Co, Fe and showed that Pd and Ni have higher WGS activity than Co and Fe [24]. Ceria-supported Pd was shown to be promoted by adding iron as an additive, which was conceived to enhance oxygen transport from ceria to CO chemisorbed on Pd sites [17]. Ceria-supported Pt has been reported to be modified by Re to enhance both WGS activity and stability [25]. The Pd–Cu bimetallic catalysts supported on CeO_2 also exhibit better performance than monometallic Cu or Pd catalysts [9]. By the study on surface and structural properties of Pd–Cu bimetallic system on CeO_2 support, it was found that Pd and Cu form alloy with highly dispersed Pd in Cu which could keep Cu in reduced state, being favorable for WGS and OWGS [11]. However, correlation of structural and chemical properties and OWGS activity with bimetallic composition remains to be clarified and the active sites and role of each metal in Pd–Cu catalysts are yet to be identified.

In this context, the first objective of this study is (i) to identify promising bimetallic catalysts supported on CeO_2 for OWGS from various formulations. The metal loadings of Pd–Cu/CeO_2 system were further optimized for a practical OWGS condition wherein high CO concentration and low O_2 (O_2/CO = 0.14) exist in the feed as well as low Cu loading was sought for lower pyrophoricity. The second objective is (ii) to identify the roles of Pd and Cu in Pd–Cu/CeO_2 for OWGS. For this purpose, reducibility (measured by TPR), oxygen storage capacity (OSC), and local structure (measured by EXAFS) for catalysts with various Pd and Cu loadings were investigated and correlated with kinetic data. The impacts of the presence of H_2 and CO_2 in the feed gas on the rates were also investigated for this purpose.

2. Experimental

The catalysts were prepared by wetness impregnation using aqueous solution of tetra-ammine Pt (IV) hydroxide, Rh (III) nitrate, Ir (III) chloride, Cu (II) nitrate, Co (III) nitrate, Fe (III) nitrate, Mn (II) acetate, acetone solution of Pd (II) acetate on cerium oxide. Co-impregnation was carried out for preparing bimetallic catalysts except Pt–Cu/CeO_2. Sequential impregnation was carried out for preparing bimetallic Pt–Cu (copper first, then platinum) and trimetallic catalysts (Pd–Cu first, then Pt or Ir) because these salts did not dissolve with each other in the solution. A commercial ceria (HSA, Rhodia) with 155 m^2/g of specific surface area was used as the support. The metal loadings were 1 wt% for noble metals and 5 wt% for base metals unless specified otherwise. All the catalysts were calcined at 450 °C for 5 h.

The catalytic activity was tested in a quartz fixed-bed down-flow reactor with 4 mm of inner diameter. The catalyst was pelletized and sieved into 0.25–0.50 mm in diameter, and about 0.1 g of the catalyst was packed into the reactor. The aspect ratio was approximately 1.5. The feed gas which modeled a real reformate had a composition of 9.7% CO/22.8% H_2O/6.3% CO_2/37.9% H_2/6.9% air/argon balance. The H_2O/CO ratio was 2.35 and O_2/CO ratio was 0.14. The space velocity was around 64,400 h^{-1} (dry, excluding air and argon). In the case of WGS, air in the feed was replaced by N_2. Prior to the catalytic reaction, the catalyst was reduced in situ in 7.5% H_2/N_2 flow at 260 °C for 1 h. The effluent of the reactor was analyzed using gas chromatograph (Agilent Micro GC 3000A) equipped with dual channels, one with Molecular Sieve 5A and the other with Plot Q, and TCD detectors. For kinetic study, the gas composition of 9.8% CO/23.0% H_2O/6.9% air/N_2 balance was employed and N_2 concentration was adjusted upon a change of gas composition if necessary, so that total flow rate was always constant. The amount of the catalyst used was 0.015 g. It was diluted by SiC particles of the same size to attain 0.065 ml of the catalyst bed volume.

For the WGS reaction with the O_2 pretreatment, the temperature of the catalyst bed comprised of 0.1 g of 1 wt% Pd–5 wt% Cu on CeO_2 was increased in air up to 260 °C, flushed with N_2, and then WGS feed (9.8%CO/23.0% H_2O/N_2 balance) was introduced. The following O_2 and H_2 pretreatments were conducted (before switching to WGS feed gas) in (1) pure air for an hour, (2) 50% H_2/N_2 for an hour, (3) 10% H_2/N_2 for about 12 h, and (4) 6.9% air/22.8% H_2O/N_2 for an hour, respectively.

The temperature-programmed reduction (TPR) experiments were conducted on Micromeritics Autochem 2910 TPD/TPR equipped with a TCD detector using 50 ml/min of 5% H_2/argon flow with the heating rate of 5 °C/min. Oxygen storage capacity (OSC) was measured using the same equipment by pulsing air at 260 °C after the sample was reduced at the same temperature. Ametek Dycor Dymaxion mass spectrometer DM200 M was employed with Autochem 2910 for detection of oxygen pulses.

X-ray absorption measurements were conducted on the insertion-device beam line of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne National Laboratory. The detailed method is described elsewhere [11]. A short description is given here. The measurements were conducted in situ with reduction atmosphere in transmission mode using a continuous-flow EXAFS reactor cell (18 in. long, 0.75 in. diam.). The catalysts were reduced in 4% H_2/He at 250 °C for 30 min followed by purging with He at 250 °C for 30 min to desorb chemisorbed hydrogen and decompose Pd–H. Then the Pd K edge (24.350 keV) or Cu K edge (8.979 keV) spectra were obtained. Spectra of Pd foil and Cu foil were acquired simultaneously with those of Pd–Cu/CeO_2 samples for energy calibration. Experimental phase and amplitude functions were prepared from Pd and Cu foil. Theoretical phase and amplitude functions for Pt–Cu, Cu–Pt, Pd–Cu and Cu–Pd were prepared using FEFF 8 and calibrated to Pt, Pd and Cu foils to determine the appropriate S_o, the Debye–Waller factor and off-set in R.

3. Results and discussion

3.1. Effect of bimetallic catalysts

Fig. 1 shows the CO conversion over CeO_2-supported monometallic catalysts. The metal loadings were 1 wt% for noble metals and 5 wt% for base metals. Fig. 1a presents the measured CO conversion over the catalysts, while Fig. 1b divides CO conversion in OWGS into two parts including the contribution of both CO shift (WGS), and CO oxidation calculated from added