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Isolation of Pd atoms by Cu for semi-hydrogenation of acetylene: Effects of Cu loading

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ABSTRACT

Cu-alloyed Pd single-atom catalysts exhibit excellent catalytic performance for the semi-hydrogenation of acetylene; however, the limit of the Cu/Pd atomic ratio for forming the alloyed Pd single-atom catalyst is ambiguous. Herein, silica-supported Cu–Pd bimetallic catalysts with fixed Pd content and varied Cu loadings were synthesized using an incipient wetness co-impregnation method. The X-ray absorption spectroscopy results indicated that Pd formed an alloy with Cu after reduction at 250 °C and that the Pd atoms were completely isolated by Cu for Cu/Pd atomic ratios ≥ 40/1. Notably, increasing the reduction temperature from 250 to 400 °C hardly affected the catalytic performances of the Cu–Pd/SiO_2 catalysts. This finding can be attributed to the similar chemical environments of Pd demonstrated by the X-ray absorption spectroscopy results.

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1. Introduction

Supported nanocatalysts for various important reactions always contain noble metals or alloys. Although they are active under modest reaction conditions, these catalysts are always not selective toward the desired products. In addition, the active sites always cannot be efficiently used. Recently, single-atom catalysts (SACs) with atomic efficiency of the active sites have drawn extensive attention [1–9]. Among the SACs, alloyed SACs with different geometric environments and electronic structures can achieve excellent selectivity toward the target products [10–15]. For example, Sykes *et al.* [10–12] found that the alloying of Pd or Pt single atoms with Cu promoted the dissociation of H_2, thus making the alloyed Pd or Pt single atoms efficient for selective hydrogenation reactions [10–12]. Zhang *et al.* [13,14] anchored Au single atom onto Pd cluster using a colloidal method followed by galvanic replacement, resulting in greatly enhanced catalytic performance for aerobic glucose oxidation compared with the performances of the corresponding monometallic catalysts. In addition, the Au-alloyed Pd SAC obtained by ion exchange on the resin support was efficient and durable for the Ullman reaction of aryl chlorides in water [15].

Selective hydrogenation of acetylene to ethylene in an eth-

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ylene-rich stream is an important process in industry. The ethylene used to produce polyethylene is mainly produced by the cracking of naphtha. During this process, a small amount of acetylene (~1%) is produced, which is poisonous to the catalysts for the polymerization. Therefore, reducing the acetylene concentration in the feed gas to an acceptable level is highly desirable [16–19]. Selective hydrogenation of acetylene to ethylene is the preferred method to eliminate the acetylene. Monometallic Pd catalyst displays high acetylene conversion for this process [20,21]; however, its selectivity to ethylene is extremely low. Great efforts have been made to improve the ethylene selectivity over Pd-based catalysts using, for example, the modification of Pd by other elements (Au, Ag, Cu, Ga, Si, C, S) [22–28]. Although improved ethylene selectivity has been achieved, the results are not satisfactory, especially with increased reaction temperature, a large amount of ethylene in the feed gas is simultaneously hydrogenated to ethane. Moreover, most of the promoters will block the surface of the Pd nanoparticles, resulting in a waste of the active sites. Therefore, the design of a type of novel catalyst that overcomes these deficiencies is highly desirable.

In our previous work, silica-supported Group-IB-metal-alloyed Pd SACs were synthesized and utilized for the selective hydrogenation of acetylene in an ethylene-rich stream [29–31]. Compared with the monometallic Pd/SiO_2 catalyst, the Group-IB-metal-alloyed Pd SACs significantly improved the ethylene selectivity at high acetylene conversions. In particular, for the Cu-alloyed Pd SAC, complete acetylene conversion was accompanied by ~85% selectivity to ethylene [31]. Although the Pd atoms could be isolated and efficiently used when the Cu/Pd atomic ratio was 160/1, an excess of the group IB metal would be employed because of their relatively high loadings. Determination of the optimized amount of both the group IB metal and Pd is thus necessary to reduce the costs of the catalysts.

In this work, by applying a fixed Pd content and varied Cu loadings, we synthesized a series of Cu–Pd bimetallic catalysts on silica supports using an incipient wetness co-impregnation method. The interaction between Pd and Cu was analyzed using X-ray diffraction (XRD) and temperature-programmed reduction (TPR) analyses. In addition, the chemical environment of the Pd atoms in all the samples was analyzed using X-ray absorption spectroscopy (XAS). Based on the results of these analyses, the atomic ratio of Cu/Pd for the formation of Cu-alloyed Pd SAC was optimized. Finally, the catalytic performances of the bimetallic catalysts for the semi-hydrogenation of acetylene in an ethylene-rich stream after reduction at different temperatures were evaluated.

2. Experimental

2.1. Catalyst preparation

Cu–Pd/SiO_2 catalysts with different Cu/Pd atomic ratios were synthesized using the incipient wetness co-impregnation method. First, silica gel (Qingdao Ocean Chemical Plant) with a Brunauer-Emmett-Teller (BET) surface area of 463 $m^2 \cdot g^{-1}$ was impregnated with a mixture of $Cu(NO_3)_2 \cdot 3H_2O$ and $Pd(NO_3)_2$ solution to achieve a nominal Pd loading of 523 ppm and varied Cu/Pd atomic ratios. The samples were subsequently dried at 80 °C for 10 h and calcined in air at 400 °C for 2 h. The as-prepared samples are denoted as Cu_xPd/SiO_2 with x referring to the Cu/Pd atomic ratio. Monometallic Cu/SiO_2 and Pd/SiO_2 catalysts, with similar Cu or Pd loading to those of the $Cu_{160}Pd/SiO_2$ catalyst, were also prepared using the same method.

2.2. Catalyst characterization

The actual metal loadings of all the as-prepared samples were determined using inductively coupled plasma spectrometry (ICP-AES; Thermo IRIS Intrepid II XSP). Before the measurement, the samples were first treated with HF to remove the silica support, followed by treatment with aqua regia and dilution to the desired concentration.

TPR experiments were performed on a Micromeritics AutoChem II 2920 automated characterization system. First, approximately 170 mg of the calcined sample was loaded into a U-shaped quartz tube and pretreated with Ar for 10 min. The gas flow was then switched to a gas mixture of 10 vol% H_2/Ar, and the sample was heated to 500 °C at 10 °C·min^{-1}.

XRD patterns were obtained using a PANalytical PW3040/60 X'Pert Pro Super diffractometer, which was operated at 40 kV and 40 mA and equipped with a Cu K_α radiation source (λ = 0.15432 nm). The scanning angle (2θ) ranged from 10° to 80°. Before the experiment, all the samples were reduced at 250 °C for 1 h.

XAS spectra (including the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS)) at the Pd K-edge were recorded at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF), Shanghai Institute of Applied Physics (SINAP), China [32]. Energy selection was performed using a double Si (311)-crystal monochromator. Energy calibration was performed using a Pd foil. The spectra were collected at room temperature under the fluorescence mode using a solid-state detector. Before the experiments, the samples were reduced at 250 or 400 °C for 1 h and then purged by He for another 10 min. After cooling to room temperature, the reactor was evacuated, and the samples were transferred to a glovebox. The samples were then sealed in Kapton films in the glovebox. Data fitting was performed using the Athena software package.

2.3. Catalytic performance evaluation

Selective hydrogenation of acetylene in an ethylene-rich stream was performed in a quartz reactor. Before the experiments, 30 mg of the sample was pretreated with flowing 80 vol% H_2/He (20 mL·min^{-1}) at 250 or 400 °C for 1 h and then purged using He (20 mL·min^{-1}) at the same temperature. After cooling to room temperature, a gas mixture with a space velocity of 60,000 mL·h^{-1}·g^{-1} was introduced into the quartz reactor under the following simulated front-end hydrogenation conditions: 1.0 vol% C_2H_2, 20.0 vol% H_2, and 20.0 vol% C_2H_4 bal-

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