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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 $\geq 40/1$. Notably, increasing the reduction temperature from 250 to 400 °C hardly affected the catalytic performances of the Cu–Pd/SiO₂ 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 H₂, 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/SiO₂ 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/SiO₂ 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 m²·g^{−1} was

impregnated with a mixture of Cu(NO₃)₂·3H₂O and Pd(NO₃)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/SiO₂ with *x* referring to the Cu/Pd atomic ratio. Monometallic Cu/SiO₂ and Pd/SiO₂ catalysts, with similar Cu or Pd loading to those of the Cu₁₆₀Pd/SiO₂ 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% H₂/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% H₂/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% C₂H₂, 20.0 vol% H₂, and 20.0 vol% C₂H₄ bal-

anced with He. The purities of the gases were as follows: H₂ (UHP, 99.999%), He (UHP, 99.999%), C₂H₂ and C₂H₄ (mixture of 4.76 vol% C₂H₂ in C₂H₄ with 50 ppm C₂H₆ and 10 ppm CH₄ impurity from Dalian Special Gases Co., Ltd.). Mass flow controllers were employed to control all the gas flows. The reaction temperature was held constant for 25 min before ramping to the next temperature point. The gas components from both the microreactor inlet and outlet were analyzed using on-line gas chromatography (GC, Agilent Technologies 6890N) and a flame ionization detector.

Consistent with our previous studies [29–31,33–35], the only C₂ products detected by GC were C₂H₄ and C₂H₆. Because of the short contact time, the oligomer amount formed during the hydrogenation process was negligible. Based on the volume ratios of the inlet and outlet gas composition, the following equations were used to calculate the conversion and selectivity:

$$\text{Conversion} = (\text{C}_2\text{H}_2(\text{feed}) - \text{C}_2\text{H}_2) / \text{C}_2\text{H}_2(\text{feed}) \times 100\% \quad (1)$$

$$\text{Selectivity} = [1 - (\text{C}_2\text{H}_2 - \text{C}_2\text{H}_6(\text{feed})) / (\text{C}_2\text{H}_2(\text{feed}) - \text{C}_2\text{H}_2)] \times 100\% \quad (2)$$

3. Results and discussion

3.1. Reducibility and crystallinity

TPR characterization was used to analyze the reducibility of the catalysts. Fig. 1 presents the TPR profiles of the Cu–Pd/SiO₂ bimetallic catalysts with different Cu/Pd atomic ratios (Table 1). The reduction peak for the monometallic Pd/SiO₂ catalyst was hardly detectable, which might be due to the low Pd content. However, the reported reduction temperature for the Pd/SiO₂ catalyst is approximately 100 °C [36]. A broad reduction peak from 200 °C to higher than 350 °C was observed for the monometallic Cu/SiO₂ catalyst. The reduction peaks appeared for both CuO_x and PdO over the catalysts with relatively high Cu loadings. For the Cu₁₆₀Pd/SiO₂ catalyst, reduction peaks at approximately 100 °C and from 150 to ~300 °C were detected. The former was attributed to the reduction of PdO [36], and the latter was attributed to the reduction of CuO_x [37]. With decreased Cu loading, the reduction peak for PdO shifted slightly to lower temperature, similar to the reduction temperature of the reported monometallic Pd/SiO₂ catalyst [36]. However, the reduction peaks of CuO_x shifted to below 250 °C for the Cu₄₀Pd/SiO₂ and Cu₁₂Pd/SiO₂ catalysts, indicating the promoted reduction of CuO_x, which could be attributed to the

Fig. 1. TPR profiles of the Cu/SiO₂ (a), Cu₁₆₀Pd/SiO₂ (b), Cu₄₀Pd/SiO₂ (c), Cu₁₂Pd/SiO₂ (d), Cu₅Pd/SiO₂ (e), and Pd/SiO₂ (f) catalysts.

decreased Cu particle sizes or loadings. In addition, the formation of the Cu–Pd alloy also promoted the reduction of CuO_x. Similar to our previous findings, the reduction temperatures of CuO_x in these catalysts were lower than that of the monometallic Cu/SiO₂ catalyst, which could be attributed to the spillover of hydrogen from Pd, thus promoting the reduction of CuO_x [31]. Only one peak from 100 to 150 °C could be detected over the Cu₅Pd/SiO₂ catalyst, which may be attributed to the reduction of both CuO_x and PdO. All these results suggest the interaction between Cu and Pd, which may induce different reducibilities over all these samples.

The structures of the Cu–Pd/SiO₂ bimetallic catalysts with fixed Pd content and varied Cu loadings were analyzed using XRD. As observed in Fig. 2, the Cu₁₆₀Pd/SiO₂ catalyst with the highest Cu loading showed clear diffraction peaks at 43.3°, 50.4°, and 74.1°, which could be attributed to the crystal planes of Cu(111), (200), and (220), respectively [31]. According to the Scherrer equation, the corresponding particle size of the Cu₁₆₀Pd/SiO₂ catalyst was 40.7 nm. With decreased Cu loading, the intensity of the diffraction peaks sharply decreased (Fig. 2). For the Cu₄₀Pd/SiO₂ catalyst, only the diffraction peak of Cu (111) could be detected. Further decreasing the Cu loading resulted in much smaller bimetallic particle sizes, which could not be detected by XRD. No Pd diffraction peak was detected over any of the samples, mainly because the Pd content was too low to be detected by XRD. The detailed chemical environment

Table 1

Elemental analysis of the Cu–Pd/SiO₂ bimetallic catalysts.

Entry	Catalyst	Cu:Pd (atomic ratio)	Nominal loading		Actual loading ^a	
			Cu (wt%)	Pd (ppm)	Cu (wt%)	Pd (ppm)
1	Cu ₁₆₀ Pd/SiO ₂	160	5	523	4.96	494
2	Cu ₄₀ Pd/SiO ₂	40	1.25	523	1.31	583
3	Cu ₁₂ Pd/SiO ₂	12	0.38	523	0.38	552
4	Cu ₅ Pd/SiO ₂	5	0.16	523	0.16	648
5	Cu/SiO ₂	–	5	0	5.28	–
6	Pd/SiO ₂	0	0	523	–	448

^a Determined by ICP-AES.

Fig. 2. XRD patterns of the $\text{Cu}_{160}\text{Pd}/\text{SiO}_2$ (a), $\text{Cu}_{40}\text{Pd}/\text{SiO}_2$ (b), $\text{Cu}_{12}\text{Pd}/\text{SiO}_2$ (c), and $\text{Cu}_5\text{Pd}/\text{SiO}_2$ (d) catalysts after reduction at 250 °C.

of the Pd atoms will be discussed in the following section.

3.2. Isolation of Pd atoms

XAS is a powerful technique that can determine the chemical environment of a selected element, even though the loading of Pd was at the ppm level. To analyze the chemical environment of the Pd atoms in different catalysts, XAS analyses were performed over the Cu–Pd/ SiO_2 bimetallic catalysts with varied Cu loadings.

3.2.1. Effect of Cu loading

In our previous work, with a Pd content of 494 ppm and Cu/Pd atomic ratio of 160/1 (corresponding to a $\text{CuPd}_{0.006}/\text{SiO}_2$ catalyst), the EXAFS data fitting result of Pd showed only Pd–Cu coordination in the catalyst, indicating the formation of a Cu-alloyed Pd SAC [31]. In this work, to determine the chemical environment of the Pd atoms in the Cu–Pd/ SiO_2 bimetallic catalysts with different Cu loadings, EXAFS characterization was first performed over the samples reduced at 250 °C. As ob-

Fig. 3. k^3 -weighted EXAFS spectra in k -space (a, c, e, g, i) and corresponding Fourier transform spectra in R -space (without phase correction) (b, d, f, h, j) of Pd foil (a, b) and $\text{Cu}_5\text{Pd}/\text{SiO}_2$ (c, d), $\text{Cu}_{12}\text{Pd}/\text{SiO}_2$ (e, f), $\text{Cu}_{40}\text{Pd}/\text{SiO}_2$ (g, h), and $\text{Cu}_{160}\text{Pd}/\text{SiO}_2$ (i, j) catalysts after reduction at 250 °C.

served in Fig. 3(a), (c), (e), (g), (i), compared with the Pd foil, the oscillation behaviors in the k -space of the Pd K-edge were disturbed by Cu neighbors in all the Cu–Pd/SiO₂ bimetallic catalysts. In agreement with our previous findings, because of the formation of Pd–Cu coordination, the distances between atoms in the first shell of the Pd atoms were obviously shorter than those of the Pd foil (Fig. 3(b), (d), (f), (h), (j)) [31]. The data fitting results of all the Cu–Pd/SiO₂ catalysts are summarized in Table 2. With decreased Cu loading, the Pd atoms could be isolated by Cu in the Cu₄₀Pd/SiO₂ catalyst, with only Pd–Cu coordination existing in this catalyst and a coordination number (CN) of 8.7. Nevertheless, for the Cu₁₂Pd/SiO₂ catalyst, both Pd–Cu and Pd–Pd coordination were observed, with CNs of 8.4 and 1.4, respectively. Further decreasing the Cu loading induced a decrease of the Pd–Cu CN to 5.0 and an increase of the Pd–Pd CN to 5.9 in the Cu₅Pd/SiO₂ catalyst. Consistent with the TPR results, with decreased Cu loading, the Pd in the bimetallic catalysts exhibited behavior similar to that of the monometallic Pd catalyst. These results indicate that Cu-alloyed Pd SACs can be synthesized with an optimized Cu/Pd atomic ratio using the simple wetness co-impregnation method by adjusting the Cu/Pd atomic ratio.

The normalized XANES spectra at the Pd K-edge of various Cu–Pd/SiO₂ bimetallic catalysts reduced at 250 °C are compared in Fig. 4. Compared with the Pd foil (with an adsorption energy at the Pd K-edge of 24350.0 eV), the Cu₁₆₀Pd/SiO₂, Cu₄₀Pd/SiO₂, Cu₁₂Pd/SiO₂, and Cu₅Pd/SiO₂ catalysts showed adsorption edges of the Pd K-edge at 24348.1, 24348.1, 24348.7, and 24347.4 eV, respectively. In agreement with our previous findings, these results indicated that the Pd atoms in these catalysts were negatively charged, which may be attributed to the electron transfer from Cu to Pd [31]. This result is reasonable, as the electronegativity of Cu is lower than that of Pd [31,38].

3.2.2. Effects of reduction temperature

To determine the effects of the reduction temperature on the formation of the Cu-alloyed Pd SACs, XAS experiments were performed over the Cu₁₂Pd/SiO₂ and Cu₁₆₀Pd/SiO₂ catalysts reduced at 400 °C. Based on the EXAFS results in Fig. 5, we know that for reduction at 250 °C, the oscillation behaviors of the Cu–Pd/SiO₂ bimetallic catalysts in k -space differed from that of the Pd foil because of the disturbance caused by the Cu neighbors (Fig. 5(a), (c), (e)). The formation of the Cu–Pd coordination

Fig. 4. Normalized XANES spectra at the Pd K-edge of the Pd foil and Cu₅Pd/SiO₂, Cu₁₂Pd/SiO₂, Cu₄₀Pd/SiO₂, and Cu₁₆₀Pd/SiO₂ catalysts after reduction at 250 °C.

dination resulted in a short distance of the first Pd neighbors (Fig. 5(b), (d), (f)). The results in Table 3 also demonstrate that both Pd–Cu and Pd–Pd coordination were detected in the Cu₁₂Pd/SiO₂ catalyst with CNs of 10.4 and 0.9, respectively. Only Pd–Cu coordination was detected in the Cu₁₆₀Pd/SiO₂ catalyst, indicating the complete isolation of the Pd atoms by Cu in this catalyst, with a CN of 10.2. The coordination environments of the Cu₁₆₀Pd/SiO₂ and Cu₁₂Pd/SiO₂ reduced at 400 °C were similar to those reduced at 250 °C (Table 2), indicating that increasing the reduction temperature hardly affects the coordination environment of the Pd atoms. This finding differs from that for our Ag–Pd/SiO₂ system, for which an increased reduction temperature induced restructuring of Pd and Ag, thereby resulting in better isolation of Pd atoms [30]. The XANES results in Fig. 6 also indicate that the Pd atoms in all these catalysts were slightly negatively charged, with adsorption energies at the Pd K-edge of 24347.7 and 24348.7 eV for the CuPd₁₂/SiO₂ and Cu₁₆₀Pd/SiO₂ catalysts, respectively.

3.3. Catalytic performance

Selective hydrogenation of acetylene in an ethylene-rich stream was performed over the as-prepared Cu–Pd/SiO₂ bimetallic catalysts, and the effects of the Cu loading and pretreatment temperature were evaluated. First, the catalytic performances of the Cu–Pd/SiO₂ bimetallic catalysts with different Cu loadings were analyzed. As observed in Fig. 7(a), after reduction at

Table 2

EXAFS fitting results at Pd K-edge for the Pd foil and Cu₅Pd/SiO₂, Cu₁₂Pd/SiO₂, Cu₄₀Pd/SiO₂, and Cu₁₆₀Pd/SiO₂ catalysts reduced at 250 °C.

Sample	Shell	CN ^a	$R(\text{\AA})$ ^b	$\sigma^2 \times 10^3 (\text{\AA}^2)$ ^c	$\Delta E_0 (\text{eV})$ ^d	R-factor (%)	$\Delta k (\text{\AA}^{-1})$	$\Delta R (\text{\AA})$
Pd foil	Pd–Pd	12	2.74	4.8	2.1	0.19	3.0–11.1	1.3–3.4
Cu ₅ Pd/SiO ₂	Pd–Cu	5.0	2.61	7.2	2.6	0.68	3.0–11.1	1.3–3.4
	Pd–Pd	5.9	2.69	7.2	2.6			
Cu ₁₂ Pd/SiO ₂	Pd–Cu	8.4	2.58	5.5	0.6	0.39	3.2–11.7	1.4–3.2
	Pd–Pd	1.4	2.64	5.5	0.6			
Cu ₄₀ Pd/SiO ₂	Pd–Cu	8.7	2.55	5.3	–1.8	0.98	3.0–11.1	1.3–3.4
Cu ₁₆₀ Pd/SiO ₂	Pd–Cu	11.6	2.58	6.2	2.1	0.31	3.0–13.1	1.3–3.1

^a CN for the absorber-backscatterer pair; ^b Average absorber-backscatterer distance; ^c Debye-Waller factor; ^d Inner potential correction. The accuracies of these parameters were estimated as CN, $\pm 20\%$; R , $\pm 1\%$; σ^2 , $\pm 20\%$; ΔE_0 , $\pm 20\%$. Δk and ΔR are the data fitting ranges used in k -space and R -space, respectively.

Fig. 5. k^3 -weighted EXAFS spectra in k -space (a, c, e) and corresponding Fourier transform spectra in R -space (without phase correction) (b, d, f) of the Pd foil (a, b) and $\text{Cu}_{12}\text{Pd}/\text{SiO}_2$ (c, d) and $\text{Cu}_{160}\text{Pd}/\text{SiO}_2$ (e, f) catalysts reduced at 400 °C.

Table 3

EXAFS fitting results at Pd K-edge for the Pd foil and $\text{Cu}_{12}\text{Pd}/\text{SiO}_2$ and $\text{Cu}_{160}\text{Pd}/\text{SiO}_2$ catalysts after reduction at 400 °C.

Sample	Shell	CN ^a	$R(\text{Å})$ ^b	$\sigma^2 \times 10^3 (\text{Å}^2)$ ^c	ΔE_0 (eV) ^d	R-factor (%)	$\Delta k (\text{Å}^{-1})$	$\Delta R (\text{Å})$
Pd foil	Pd-Pd	12	2.74	4.8	2.1	0.19	3.0–11.1	1.3–3.4
$\text{Cu}_{12}\text{Pd}/\text{SiO}_2$	Pd-Cu	10.4	2.58	6.1	2.6	0.59	3.0–11.1	1.3–3.4
	Pd-Pd	0.9	2.71	6.1	2.6			
$\text{Cu}_{160}\text{Pd}/\text{SiO}_2$	Pd-Cu	10.2	2.58	6.1	2.4	0.47	3.0–13.1	1.3–3.1

^aCN for the absorber-backscatterer pair; ^bAverage absorber-backscatterer distance; ^cDebye-Waller factor; ^dInner potential correction. The accuracies of these parameters were estimated as CN, $\pm 20\%$; R , $\pm 1\%$; σ^2 , $\pm 20\%$; ΔE_0 , $\pm 20\%$. Δk and ΔR are the data fitting ranges used in k -space and R -space, respectively.

250 °C, the Cu–Pd/SiO₂ bimetallic catalyst with a Cu/Pd atomic ratio of 5/1 exhibited high acetylene conversion at low temperatures. The conversion reached 100% at 80 °C, and the corresponding selectivity to ethylene was approximately ~300% (the selectivity greatly decreased with increasing reaction temperature) (Fig. 7(b)). This finding is consistent with most of the previous results, which indicate that a large amount of ethylene in the feedstock is hydrogenated to ethane [39,40]. With increased Cu loading, the temperature needed to achieve complete acetylene conversion also increased (Fig. 7(a)). However, the corresponding ethylene selectivity also clearly increased (Fig. 7(b)). The $\text{Cu}_{12}\text{Pd}/\text{SiO}_2$ catalyst displayed > 60% ethylene selectivity at 100% acetylene conversion. The $\text{Cu}_{40}\text{Pd}/\text{SiO}_2$ and $\text{Cu}_{160}\text{Pd}/\text{SiO}_2$ catalysts displayed similar ethylene selectivity at 160 °C, all of which were improved by > 650% compared with that of the $\text{Cu}_5\text{Pd}/\text{SiO}_2$ catalyst, indicating that the isolation of Pd atoms significantly contributed to the enhanced ethylene selectivity. Upon increasing the reaction temperature to 240 °C, the acetylene conversion remained at 100%; however, the ethylene selectivity showed some differences, which may be attributed to the different positions of Pd atoms on Cu nanoparticles. This behavior was also reported by Zhu *et al.* [41,42] who showed that Pd atoms on different sites of the particles may contribute differently to the catalytic performance.

After the catalysts were reduced at 400 °C, we evaluated the catalytic performance of the $\text{Cu}_{12}\text{Pd}/\text{SiO}_2$ and $\text{Cu}_{160}\text{Pd}/\text{SiO}_2$ catalysts for the semi-hydrogenation of acetylene in an eth-

ylene-rich stream and compared the results with those of the catalysts reduced at 250 °C. As observed in Fig. 8, after the reduction pretreatment at 400 °C, the acetylene conversion and ethylene selectivity showed similar behaviors as those of the catalysts reduced at 250 °C. These results indicate that the catalytic performance of the Cu–Pd/SiO₂ bimetallic system is not as sensitive to the reduction temperature as the Ag–Pd system [30]. This finding can be attributed to the insensitive restructuring of Cu and Pd atoms against varied reduction temperatures and is consistent with the EXAFS fitting results, which indicated that with increased reduction temperature, the

Fig. 6. Normalized XANES spectra at Pd K-edge of the Pd foil and $\text{Cu}_{12}\text{Pd}/\text{SiO}_2$ and $\text{Cu}_{160}\text{Pd}/\text{SiO}_2$ catalysts after reduction at 400 °C.

Fig. 7. Acetylene conversion (a) and ethylene selectivity (b) with increased reaction temperature over the Cu₁₆₀Pd/SiO₂, Cu₄₀Pd/SiO₂, Cu₁₂Pd/SiO₂, and Cu₃Pd/SiO₂ catalysts after reduction at 250 °C.

Fig. 8. Acetylene conversion (a) and ethylene selectivity (b) with increased reaction temperature over the Cu₁₂Pd/SiO₂ and Cu₁₆₀Pd/SiO₂ catalysts after reduction at 250 and 400 °C.

chemical environment of the Pd atoms was hardly disturbed in the Cu₁₂Pd/SiO₂ and Cu₁₆₀Pd/SiO₂ catalysts (Table 2 and Table 3).

4. Conclusions

Cu-alloyed Pd SACs with varied Cu loadings were synthesized using an incipient wetness co-impregnation method. Decreased Cu loading resulted in smaller Cu–Pd bimetallic particle sizes. The formation of the Cu–Pd bimetallic catalyst induced facile reduction of the catalysts. The optimized Cu and Pd loadings can be used for the synthesis of Cu-alloyed Pd SACs, which will contribute to enhanced catalytic performance as well as efficient use of both metals. Upon increasing the reduction temperature from 250 to 400 °C, the chemical environment of Pd was hardly changed, as demonstrated by XAS analysis. Thus, the catalytic performances of the Cu–Pd/SiO₂ catalysts were not as sensitive to the reduction pretreatment as those of Pd–Ag/SiO₂ catalysts. This study will inspire the design of other alloyed SACs to achieve excellent catalytic performance for selective hydrogenation reactions.

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Graphical Abstract

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

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Cu-alloyed Pd single-atom catalysts were formed for Cu/Pd atomic ratios $\geq 40/1$ and displayed excellent catalytic performance for the semi-hydrogenation of acetylene in excess ethylene.

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Cu分隔开的Pd单原子用于乙炔选择加氢: Cu担载量的影响

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摘要: 大量乙烯中少量乙炔的去除是化工生产中的重要过程之一, 理想途径是将其选择加氢生成乙烯。负载型Pd催化剂因具有很高的乙炔转化率而被广泛用于该过程, 但乙炔选择性很低, 同时会使原料气中的乙烯被加氢, 造成原料气的浪费。采用其它元素对Pd纳米粒子表面修饰, 覆盖部分活性位, 可以在一定程度上提高乙炔选择性, 但是会大大降低Pd的利用率。因此, 制备兼具高活性和高选择性且经济实用的催化剂, 仍是这一过程亟待解决的主要问题之一。我们的前期工作中, 将Pd与IB族金属(Au, Ag, Cu)分别结合制备得到了一系列含Pd的合金单原子催化剂(SAC), 发现它们在大量乙烯存在条件下的乙炔选择加氢反应中表现出优异的催化性能。其中, Pd的用量仅为ppm级别, 大大提高了Pd的利用率。作为IB族最为廉价的金属, Pd与Cu形成的合金SAC在提高Pd原子利用率的同时, 能够进一步降低催化剂的经济成本。然而, 当形成合金SAC时, Cu/Pd原子比例的极限值仍然不确定。

本文通过固定Pd的担载量, 采用简单的等体积共浸渍的方法, 制备了一系列不同Cu/Pd原子比例的氧化硅负载的双金属催化剂。首先, 我们采用程序升温还原(TPR)和X射线衍射(XRD)对催化剂的还原能力和双金属纳米粒子的尺寸进行了考察。进一步, 采用X射线吸收光谱(XAS, 包括EXAFS和XANES)对双金属催化剂中Pd的配位环境进行了分析。最后, 结合它们在大量乙烯存在条件下的乙炔选择加氢反应中的催化性能, 对形成合金SAC时Cu/Pd原子比例进行了讨论。

TPR结果显示, Cu与Pd结合时会促进双金属纳米粒子的还原。XRD结果表明, 随着Cu含量的降低, 双金属纳米粒子的尺寸明显减小。XANES结果证实, 当Pd与Cu结合时, Pd会带有部分负电荷, 这也与Pd的电负性大于Cu相一致。通过对EXAFS拟合结果进行分析, 我们发现当Cu/Pd的原子比例 $\geq 40/1$ 时, Pd原子可以被Cu原子完全分隔开, 形成含Pd的合金SAC, 使其在大量乙烯存在条件下的乙炔选择加氢反应中表现出优异的催化性能。通过对还原温度的考察, 我们发现还原温度由250 °C升高到400 °C时, 对同一催化剂的催化性能影响不大; EXAFS拟合结果显示, 对比分别经过250和400 °C还原后的催化剂, Pd的配位环境变化不明显, 这可能是导致催化性能相似的主要原因。

关键词: 铜; 钯; 单原子催化剂; X射线吸收光谱; 乙炔加氢; 大量乙烯

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