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Selective hydrogenolysis of sorbitol to ethylene glycol and propylene glycol on ZrO_2-supported bimetallic Pd-Cu catalysts

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ABSTRACT

Sorbitol is one of the key building blocks in catalytic conversion of biomass, and its selective hydrogenolysis to ethylene glycol and propylene glycol provides a viable and sustainable route towards the synthesis of the two glycols. Herein, the hydrogenolysis of biomass-derived sorbitol was studied on Pd-modified Cu/monoclinic zirconia (Pd-Cu/ZrO_2) catalysts with a wide range of Cu/Pd atomic ratios in the presence of $La(OH)_3$. The bimetallic Pd-Cu/ZrO_2 catalysts showed superior activities and selectivities to the two target glycols, compared with the monometallic Cu/ZrO_2 and Pd/ZrO_2 catalysts under identical conditions. At nearly 100% sorbitol conversion, a combined selectivity of 61.7% to ethylene glycol, propylene glycol, and glycerol was obtained on Pd-Cu/ZrO_2 (Cu/Pd=5) at 493 K under 5.0 MPa H_2. Pd-Cu/ZrO_2 was also stable and recyclable, in contrast to Cu/ZrO_2, which suffered severe deactivation because of agglomeration of Cu particles during sorbitol hydrogenolysis. Clearly, the presence of Pd improved not only the activity and selectivity of the Cu catalyst, but also the hydrothermal stability. Characterization of these catalysts by X-ray diffraction, diffuse-reflectance infrared Fourier transform spectroscopy of CO adsorption, and H_2 temperature-programmed reduction suggests that the Cu particles deposited on the Pd surfaces with close contact and strong interaction between the two metals, most likely involving electron transfer from Pd to Cu. Such structural and electronic effects are proposed as the critical contributors to the significant promoting effect of Pd on the activity and stability of Pd-Cu catalysts in sorbitol hydrogenolysis. These findings provide useful information for design of new Cu-based catalysts with higher efficiency and stability for selective hydrogenolysis of polyols and other biomass-derived reactants under hydrothermal conditions.

1. Introduction

There is an increasing interest worldwide in utilizing renewable biomass for sustainable production of liquid fuels and chemicals [1–4]. As such, biomass-derived sorbitol and xylitol have been intensively studied as the key platform molecules, especially for synthesis of various value-added chemicals *via* different catalytic routes [5,6]. One such example is selective hydrogenolysis of sorbitol and xylitol to ethylene glycol and propylene glycol [7–18], the two important glycols that are currently manufactured from multistep reactions of petroleum-derived ethylene and propylene [19,20].

Selective hydrogenolysis of sorbitol and xylitol to ethylene glycol and propylene glycol has been explored on Ru-, Ni-, and

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Cu-based catalysts in the presence of base additives. Sun et al. [7] studied the xylitol hydrogenolysis on Ru/C with $Ca(OH)_2$ at 473 K under 4.0 MPa H_2, reaching ~61% combined selectivity to ethylene glycol and propylene glycol with near-complete conversion of xylitol. Using CaO as a promoter, Zhou et al. [8] reported 85.7% sorbitol conversion and 60.8% combined selectivity to ethylene glycol, propylene glycol, and glycerol on carbon nanofiber-supported Ru catalyst at 493 K under 8.0 MPa H_2. Alternatively, Ye et al. [9] obtained 55%–60% selectivity to ethylene glycol and propylene glycol with >90% sorbitol conversion on Ce-promoted Ni/Al_2O_3 catalysts with a small amount of $Ca(OH)_2$. Chen et al. [10] carried out sorbitol hydrogenolysis on a co-precipitated Ni-MgO catalyst, and observed 80.8% combined selectivity to ethylene glycol, propylene glycol, and glycerol at 67.8% sorbitol conversion at 473 K under 4.0 MPa H_2. Sun et al. [11] found that $Ni\text{-}CeO_2/C$ and Ni-CaO/C were efficient for xylitol hydrogenolysis, and achieved 69.5% combined selectivity to ethylene glycol, propylene glycol, and glycerol at nearly 100% xylitol conversion on Ni-CaO/C without additional bases. These studies show that the Ru- and Ni-based catalysts exhibit good activities and selectivities to the two target glycols from sorbitol and xylitol hydrogenolysis [7–12,15,17]. However, these materials also catalyze cleavage of C–C bonds to form undesirable by-products, especially methane [7,9], as also reported for glycerol hydrogenolysis [20,21].

Different from the aforementioned Ru and Ni catalysts, Cu is less active toward C–C bond cleavage in polyol hydrogenolysis [13,14,22,23]. This promising feature of Cu has been confirmed by Huang et al. [13,14], who recently studied xylitol hydrogenolysis on $Cu\text{-}SiO_2$ catalysts. They observed close to 100% conversion and 70.4% combined selectivity to ethylene glycol and propylene glycol at 473 K under 6.0 MPa H_2 in the presence of $Ca(OH)_2$. However, sintering of Cu particles and deactivation occurred during xylitol hydrogenolysis, even in the presence of $Ca(OH)_2$ [14], which can normally prevent the agglomeration and leaching of non-noble metal particles [8,11,24]. Moreover, Cu-based catalysts generally exhibit activities that are inferior to those of Ru and Ni catalysts. Therefore, it is of great importance to design Cu catalysts that show improved efficiency and high stability under the hydrothermal conditions of polyol hydrogenolysis.

For this purpose, a variety of oxides including Al_2O_3 [22], Ga_2O_3 [25], and B_2O_3 [23] have been employed to stabilize copper particles in glycerol hydrogenolysis. However, these catalysts still undergo deactivation over a prolonged reaction time. Recently, Kim et al. [26] found that addition of Pd enhances the activity of $CuCr_2O_4$ in glycerol hydrogenolysis *via* hydrogen spillover. Jin et al. [27] reported a graphene-supported Cu-Pd catalyst with excellent recyclability in glycerol conversion to lactic acid. These reports show the potential of the noble metals to increase the activity and stability of Cu catalysts.

In the present work, we studied Cu/monoclinic zirconia (Cu/ZrO_2) catalysts for sorbitol selective hydrogenolysis in the presence of $La(OH)_3$. The effect of noble metals including Pd, Pt, and Ru on the catalytic property of the Cu particles was examined, and $Pd\text{-}Cu/ZrO_2$ exhibited high activities and selectivities with enhanced reusability. The promoting effect of Pd on the Cu catalysts is discussed on the basis of the complementary characterization by X-ray diffraction (XRD), diffuse-reflectance infrared Fourier transform spectroscopy of CO adsorption (CO-DRIFT), and H_2 temperature-programmed reduction (H_2-TPR).

2. Experimental

2.1. Catalyst preparation

ZrO_2-supported Pd, Ru, and Pt catalysts were prepared by incipient wetness impregnation of monoclinic ZrO_2 (Alfa Aesar) with aqueous solutions of $[Pd(NH_3)_4](NO_3)_2$ (Sigma-Aldrich, St. Louis MO, United States), $RuCl_3\cdot nH_2O$ (GR, Sinopharm Chemical, Beijing, China), and $H_2PtCl_6\cdot nH_2O$ (GR, Sinopharm Chemical), respectively. The impregnated samples were dried at room temperature for 12 h and then at 393 K overnight. Afterward, the samples were calcined in flowing air at 673 K for 3 h. The loading of the supported noble metal was 1 wt%.

Cu/ZrO_2 and bimetallic $M\text{-}Cu/ZrO_2$ (M=Pd, Ru, or Pt) catalysts were prepared by an impregnation method, similar to that described above for ZrO_2-supported noble metals. The ZrO_2 support and the calcined M/ZrO_2 samples were impregnated

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Haichao Liu *(College of Chemistry and Molecular Engineering, Peking University)* ***received the Catalysis Award for Young Scientists*** *from The Catalysis Society of China* ***in 2012****. Professor Haichao Liu received his B.S. in 1990 and M.S. degree in 1993 from Sichuan University, and his Ph.D degree in 1996 from Research Institute of Petroleum Processing. From 1997 to 2003, he did postdoctoral research at The University of Tokyo and The University of California at Berkeley. At the end of 2003, he joined the faculty of Peking University, where he is now Changjiang Distinguished Professor of Chemistry. His research interests currently focus on molecular catalysis and sustainable energy chemistry with emphasis on design of new catalysts and control of reaction pathways for selective conversion of biomass and its derivatives to fuels and especially chemicals, etc. Some of his recent progresses include the novel approaches to catalytic deploymerization of cellulose to polyols, the controlled conversion of cellulose to propylene glycol and acetol, and the selective synthesis of important chemicals or intermediates exemplified by lactic acid and acetic anhydride respectively from aerobic oxidation of glycerol and ethanol. He has coauthored about 100 peer-reviewed papers and 30 patents.*

with aqueous solutions of $Cu(CH_3COO)_2{\cdot}H_2O$ (GR, Sinopharm Chemical). The impregnated samples were dried at ambient temperature until most of the water was evaporated and then at 393 K overnight. Afterward, the samples were calcined in flowing air at 623 K for 2 h, and then reduced in a 20% H_2/N_2 (Beijing Haipu) flow at 673 K for 2 h. The resulting Cu/ZrO_2 and $M\text{-}Cu/ZrO_2$ catalysts were denoted as xCu/ZrO_2 and 1M-xCu/ZrO_2, respectively, where x represents a Cu loading of x wt% in the catalyst and 1 M indicates 1 wt% noble metal in the catalyst. Pd-Cu/ZrO_2 catalysts with different Cu/Pd atomic ratios of 1.5, 3.0, 5.0, 8.0, and 10.0 were prepared by adjusting the amount of $Cu(CH_3COO)_2$ in the impregnation solutions while the Pd loading was kept constant at 1 wt%.

2.2. Catalyst characterization

XRD patterns of the catalysts were collected on a Rigaku D/MAX-2400 diffractometer with Cu K_α radiation (λ = 0.15406 nm) in the range of 20°–60° at a scanning rate of 2°/min. The operation voltage and current were 40 kV and 100 mA.

H_2-TPR experiments were conducted on a TP-5080 flow unit (Tianjin Xianquan). A catalyst portion of about 50 mg (25 mg for 1Pd-6Cu/ZrO_2) was placed in a quartz cell, and heated from 295 to 1073 K at 10 K/min in a 5% H_2/N_2 (Beijing Haipu, certified mixture) flow (30 mL/min). H_2 consumption was quantified by thermal conductivity detector signals, calibrated by reduction of CuO powder under identical conditions.

CO-DRIFTS experiments were carried out on a Bruker Tensor 27 spectrometer equipped with liquid nitrogen-cooled HgCdTe detector and a diffuse-reflectance reaction chamber with CaF_2 windows. The spectral resolution was 4 cm^{-1} and 100 scans were applied for each measurement. The pre-reduced catalyst was added to the chamber and treated in situ in a 5% H_2/N_2 flow at 673 K for 1 h in case of any surface oxidation. The sample was then flushed with N_2 for 30 min at 493 K before cooling to room temperature under N_2 flow. The background spectrum of the sample was recorded in N_2 at room temperature. Afterward, the sample was exposed to a 5% CO/He (Beijing Haipu, certified mixture) flow (20 mL/min) for 30 min. The chamber was then purged with N_2 for 20 min before the spectrum was recorded. All spectra were obtained by subtracting the background spectrum of each sample.

2.3. Sorbitol hydrogenolysis reaction

Sorbitol hydrogenolysis reactions were carried out in a stainless steel autoclave (100 mL) with vigorous stirring at 750 r/min to avoid the mass-transfer effect. Typically, 50 g of 10 wt% sorbitol (98%, Alfa Aesar) aqueous solution, the specified amount of Cu catalyst, and 0.2 g of $La(OH)_3$ (AR, Sinopharm Chemical) were loaded into the autoclave. The reaction was maintained at 493 K under 5.0 MPa H_2 for 4 h. The catalyst and liquid phase were separated by filtration after the reaction. The reactants and products in the liquid phase were analyzed by high-performance liquid chromatography (Shimadzu LC-20A) using Bio-Rad Aminex HPX-87H and HPX-87C columns connected to refractive index detectors. Gas products, mainly methane, were analyzed by gas chromatography (Shimadzu 2010, HJ-OV-101 column) with flame ionization detection. Activities in the sorbitol reaction were calculated by the molar sorbitol conversion per mole of metal loaded per hour (h^{-1}), and product selectivities were reported on a carbon basis.

3. Results and discussion

3.1. Activity and selectivity of bimetallic Pd-Cu catalysts in sorbitol hydrogenolysis

Table 1 shows the activities (normalized to total metal atoms) and selectivities for sorbitol hydrogenolysis on monometallic Cu/ZrO_2 and Pd/ZrO_2 and bimetallic Pd-Cu/ZrO_2, Pt-Cu/ZrO_2, and Ru-Cu/ZrO_2 catalysts in the presence of $La(OH)_3$ at 493 K under 5.0 MPa H_2. 1Pd-3Cu/ZrO_2 exhibited an activity of 20.3 h^{-1}, which was 2–3 times greater than those of monometallic 3Cu/ZrO_2 (6.5 h^{-1}) and 1Pd/ZrO_2 (8.7 h^{-1}) in the kinetic controlled regime. The lower activity of 1Pd/ZrO_2 is consistent with the finding in glycerol hydrogenolysis by Xia et al. [28] that monometallic $Pd_{0.04}/Mg_{5.56}Al_2O_{8.56}$ is less active than bimetallic $Pd_{0.04}Cu_{0.4}/Mg_{5.56}Al_2O_{8.56}$. 1Pd-3Cu/$ZrO_2$ was also more selective for the target glycols (ethylene glycol and propylene glycol) than the two monometallic catalysts. Including glycerol, the combined selectivity to the three polyol prod-

Table 1

Activity and product selectivity in sorbitol hydrogenolysis on monometallic Cu/ZrO_2 and Pd/ZrO_2 catalysts and various bimetallic Cu-based catalysts.

Catalyst	Activity (h^{-1})	Selectivity [a] (carbon basis, %)						
		Ethylene glycol	Propylene glycol	Glycerol	Lactic acid	C_4 polyols	C_5 polyols	C_6 polyols
1Pd-3Cu/ZrO_2	20.3	16.3	36.8	8.4	7.9	6.0	1.1	7.6
3Cu/ZrO_2	6.5	14.1	26.2(4.2) [b]	4.7	16.7	6.2	3.1	13.0
1Pd/ZrO_2	8.7 [c]	12.6	23.8	2.4	4.9	6.9	9.6	9.4
1Pt-3Cu/ZrO_2	10.7	16.3	35.7	3.3	7.8	5.8	1.7	8.1
1Ru-3Cu/ZrO_2	7.2	21.1	31.0	4.4	10.3	5.0	2.4	9.7
1Pd/ZrO_2 + 3Cu/ZrO_2	12.2 [d](6.9) [e]	14.2	34.9	7.0	9.0	6.6	1.6	10.4

Reaction conditions: 493 K, H_2 5.0 MPa, 10 wt% sorbitol aqueous solution 50 g, catalyst 0.2 g, $La(OH)_3$ 0.2 g, 4 h.

[a] C_4 polyols including 1,2-butanediol, erythritol, and threitol; C_5 polyols including arabitol and xylitol; C_6 polyols including mannitol and iditol.

[b] Data in parenthesis represents acetol selectivity.

[c] 1.0 g catalyst was used.

[d] Physical mixture of 0.2 g 1Pd/ZrO_2 and 0.2 g 3Cu/ZrO_2.

[e] Data in parenthesis represents a theoretical activity of the mixture estimated from the weighted average activity based on its two individual components tested separately.

ucts was 61.5% on 1Pd-3Cu/ZrO_2, which was much higher than those on 3Cu/ZrO_2 and 1Pd/ZrO_2, being 45.0% and 38.8%, respectively. Other products included lactic acid, sorbitol epimers (mannitol and iditol) as well as insignificant C_5 and C_4 polyols (arabitol, xylitol, 1,2-butanediol, erythritol, and threitol). Notably, no methane was detected in the gas phase of these reactions. Using 3Cu/ZrO_2, acetol (4.2%) was also detected together with a high selectivity to lactic acid (16.7%), reflecting the inferior hydrogenation activity of Cu particles [13,14]. The selectivity to lactic acid decreased significantly to 7.9%, and no acetol was observed on 1Pd-3Cu/ZrO_2. Such change in the selectivities shows that the addition of Pd improved the hydrogenation activity of the Cu catalyst, most likely because of its excellent H_2 activation ability. Consequently, the formation of propylene glycol was favored from the glyceraldehyde-derived intermediate, which would otherwise undergo metal-catalyzed partial hydrogenation to acetol or base-catalyzed benzilic acid rearrangement to lactic acid [7].

For comparison, the effects of Ru and Pt on the Cu catalyst were also examined under identical conditions (Table 1). However, the activity only increased slightly from 6.5 h^{-1} on 3Cu/ZrO_2 to 7.2 h^{-1} on 1Ru-3Cu/ZrO_2 and 10.7 h^{-1} on 1Pt-3Cu/ZrO_2, which are much lower than that observed for 1Pd-3Cu/ZrO_2. The combined selectivity to ethylene glycol, propylene glycol, and glycerol was 56.5% and 55.3%, respectively, on 1Ru-3Cu/ZrO_2 and 1Pt-3Cu/ZrO_2, which were also lower than that on 1Pd-3Cu/ZrO_2. Clearly, Pd is superior to Ru and Pt for promoting the activity and selectivity of the Cu catalyst in sorbitol hydrogenolysis. Although the reason for the different effects of the three noble metals needs to be clarified, it may be related to their different interactions with Cu. The interaction of Pd with Cu is confirmed by the results with a physical mixture of 1Pd/ZrO_2 and 3Cu/ZrO_2 (Table 1). The activity of this physical mixture was 12.2 h^{-1}, which is much lower than that on 1Pd-3Cu/ZrO_2 (20.3 h^{-1}), implying that the promoting effect of Pd is not just a result of the coexistence of Cu and Pd, but requires interaction of the two metals.

Notably, the promoting effect of Pd was observed over a wide range of Cu/Pd atomic ratios of 1.5, 3.0, 5.0, 8.0, and 10.0 on Pd-Cu/ZrO_2. As shown in Table 2, compared at ~30% sorbitol conversion in the kinetic controlled regime, the activities (normalized to total metal atoms) varied slightly between 17.8 and 20.3 h^{-1}, irrespective of the Cu/Pd ratios, at 493 K under 5.0 MPa H_2. Similarly, with Cu/Pd ratio increasing from 1.5 to 5.0, the combined selectivities to ethylene glycol, propylene glycol, and glycerol remained essentially constant (around 61.5%–62.8%) and was still as high as 57.3% at the high Cu/Pd ratio of 10.0. Moreover, these Pd-Cu/ZrO_2 catalysts retained such high selectivities at high sorbitol conversions. For example, a 61.7% combined selectivity to ethylene glycol, propylene glycol, and glycerol was achieved at ~100% conversion on 1Pd-3Cu/ZrO_2 at 493 K under 5.0 MPa H_2.

For the Cu-based catalysts, the ease with which the Cu particles aggregate under hydrothermal conditions to deactivate the catalyst is a significant problem. Thus, the recyclability of the Pd-Cu/ZrO_2catalysts was examined. Fig. 1(a) shows representative results for 1Pd-3Cu/ZrO_2 in the kinetic controlled regime of sorbitol hydrogenolysis at 493 K under 5.0 MPa H_2. During the recycling experiments, the used catalyst was collected by simple filtration and washed thoroughly with deionized water. No significant decline in the sorbitol conversion (maintained at ~34%) was observed after five successive cycles. The selectivities to ethylene glycol, propylene glycol, and lactic acid decreased slightly from 16.3%, 36.8%, and 7.9% in the first run, to 14.5%, 35.4%, and 3.8% in the second run, respectively. Concurrently, the selectivity to glycerol increased slightly from 8.4% to 12.6%. Then the selectivities remained essentially unchanged in the following cycles. These results demonstrate that 1Pd-3Cu/ZrO_2 is stable and reusable under the reaction conditions employed in this work. For comparison, the reusability of 3Cu/ZrO_2 was also tested under identical conditions. As shown in Fig. 1(b), the selectivities to ethylene glycol, propylene glycol, glycerol and lactic acid remained essentially unaltered on Cu/ZrO_2 for the five successive cycles. However, the sorbitol conversions decreased sharply from 28.7% in the first run to 20.4% in the second run, and continuously to 16.5% in the fifth run, showing the instability of the monometallic Cu/ZrO_2 catalyst under hydrothermal conditions, even in the presence of $La(OH)_3$ base. Taken together, these results demonstrate that the introduction of Pd into Cu/ZrO_2 improves not only the activity and selectivity of the Cu particles, but also their stability, most likely as a result of the strong interaction of Pd with Cu and the consequent effect on the structural and electronic properties of the Cu particles.

Table 2
Activity and product selectivity in sorbitol hydrogenolysis on bimetallic Pd-Cu/ZrO_2 catalysts with different Cu/Pd ratios.

Catalyst	Cu/Pd ratio	Activity (h^{-1})	Selectivity [a] (carbon basis, %)						
			Ethylene glycol	Propylene glycol	Glycerol	Lactic acid	C_4 polyols	C_5 polyols	C_6 polyols
1Pd-0.9Cu/ZrO_2	3/2	17.8	16.1	38.3	7.4	4.2	6.3	1.3	6.0
1Pd-1.8Cu/ZrO_2	3/1	20.3	15.9	37.8	9.1	4.9	6.8	1.0	6.5
1Pd-3.0Cu/ZrO_2	5/1	20.3	16.3	36.8	8.4	7.9	6.0	1.1	7.6
1Pd-4.8Cu/ZrO_2	8/1	20.0	15.5	36.2	8.0	8.0	6.3	0.8	7.9
1Pd-6.0Cu/ZrO_2	10/1	18.6	14.7	33.4	9.2	10.0	6.7	1.3	10.0
1Pd-3.0Cu/ZrO_2	5/1	—[b]	15.9	37.0	8.8	3.6	6.4	0.3	2.0

Reaction conditions: 493 K, H_2 5.0 MPa, 10 wt% sorbitol aqueous solution 50 g, $La(OH)_3$ 0.2 g, 4 h, ca. 30% sorbitol conversion obtained by varying catalyst amount.

[a] C_4 polyols including 1,2-butanediol, erythritol, and threitol; C_5 polyols including arabitol and xylitol; C_6 polyols including mannitol and iditol.

[b] At ~100% sorbitol conversion.

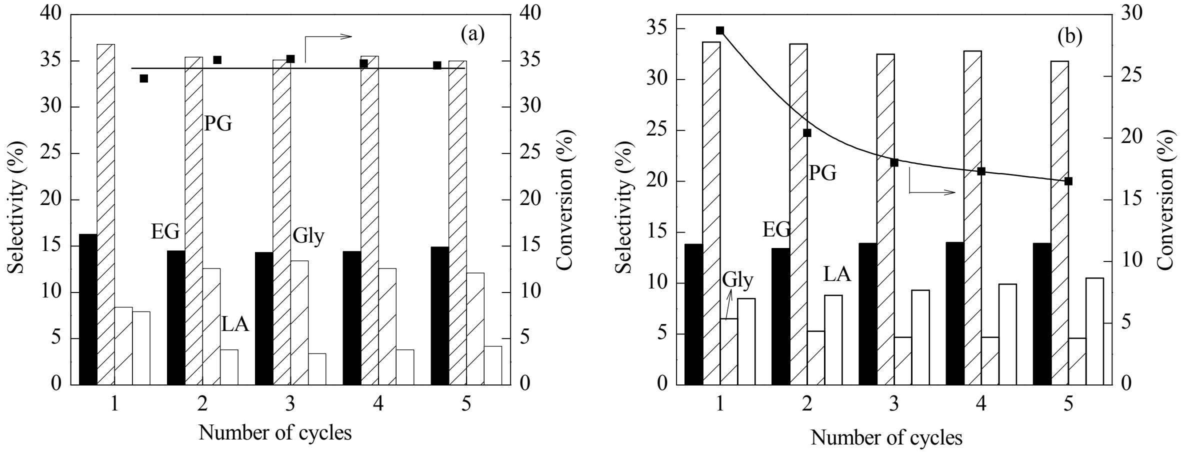

Fig. 1. Sorbitol conversions and selectivities to ethylene glycol (EG), propylene glycol (PG), glycerol (Gly), and lactic acid (LA) in five successive reaction cycles of sorbitol hydrogenolysis on 1Pd-3Cu/ZrO_2 catalyst (a) and 3Cu/ZrO_2 catalyst (b). Reaction conditions: 493 K, 5.0 MPa H_2, 10 wt% sorbitol aqueous solution 50 g, 1Pd-3Cu/ZrO_2 0.2 g or 3Cu/ZrO_2 0.6 g, $La(OH)_3$ 0.2 g in the first run and $La(OH)_3$ 0.1 g in runs 2–5, 4 h.

3.2. Interaction between Cu and Pd in Pd-Cu/ZrO2 catalysts

Figure 2 shows the XRD patterns of 1Pd/ZrO_2, Cu/ZrO_2, and Pd-Cu/ZrO_2 catalysts after reduction in H_2 at 673 K in the 2θ range of 35°–50°. The characteristic diffraction peaks of the ZrO_2 support were present for all the samples. No peaks corresponding to Pd were detected for the 1Pd/ZrO_2 and Pd-Cu/ZrO_2 catalysts, suggesting that the Pd particles were highly dispersed on ZrO_2 with such a low Pd loading of 1 wt% used in this work. Similarly, no characteristic peaks of metallic Cu were observed on fresh 3Cu/ZrO_2 and Pd-Cu/ZrO_2 catalysts, even with a high Cu/Pd atomic ratio of 10.0, implying high dispersion of Cu on ZrO_2 for these fresh monometallic and bimetallic catalysts. For catalysts with higher Cu content, a weak diffraction signal for Cu (2θ = 43.4°) was detected for monometallic 6Cu/ZrO_2 catalyst, but not for 1Pd-6Cu/ZrO_2. This result suggests that the addition of Pd can improve the dispersion of Cu particles on ZrO_2, especially for Cu catalysts with high Cu loadings.

To examine the stability of the Cu/ZrO_2 and Pd-Cu/ZrO_2 catalysts, especially their Cu particles, $La(OH)_3$ base was replaced with MgO-Al_2O_3 (Mg/Al atomic ratio=3/1) in sorbitol hydrogenolysis. This allowed a clear spectral window to observe the peak of Cu at around 2θ = 43.4°, which would otherwise be obscured by the intense peaks (2θ = 43.0°, 43.9°) of lanthanum carbonate hydroxide ($LaCO_3OH$), formed by reaction of $La(OH)_3$ with the CO_2 formed in polyol hydrogenolysis [7,14]. As presented in Fig. 3, a sharp peak appeared at 2θ = 43.4° for the used 3Cu/ZrO_2 catalyst, showing agglomeration of the Cu particles during sorbitol hydrogenolysis under the hydrothermal conditions applied in this work. The Cu particle size was estimated to be 30 nm by the Scherrer equation. This phenomenon is in line with previous findings [22,23]. Such a dramatic increase in the size of Cu particles after the reaction can explain the sharp decrease in the activity of 3Cu/ZrO_2 during the recycling experiments (Fig. 1(b)). For the representative 1Pd-3Cu/ZrO_2 catalyst, however, no characteristic Cu peak was detected after the hydrogenolysis reaction. Such stability of the Cu particles suggests a strong interaction between Pd and Cu, which efficiently prevents the agglomeration of Cu particles under the hydrothermal conditions, and consequently leads to

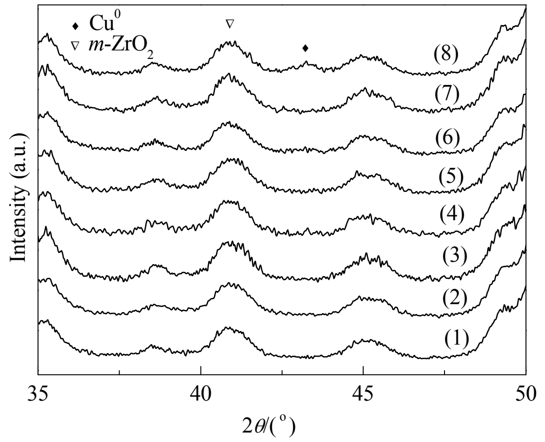

Fig. 2. XRD patterns of freshly reduced samples. (1) 1Pd/ZrO_2; (2) 1Pd-0.9Cu/ZrO_2; (3) 1Pd-1.8Cu/ZrO_2; (4) 1Pd-3Cu/ZrO_2; (5) 1Pd-4.8Cu/ZrO_2; (6) 1Pd-6Cu/ZrO_2; (7) 3Cu/ZrO_2; (8) 6Cu/ZrO_2.

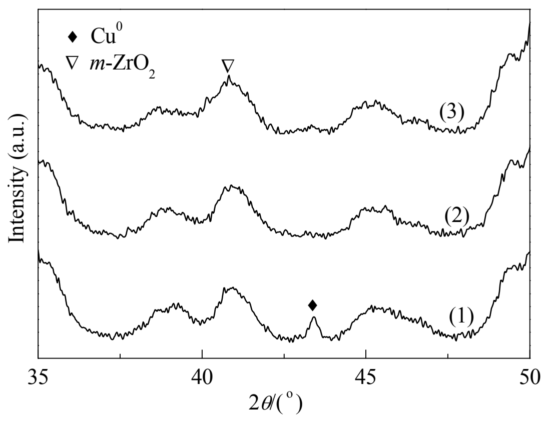

Fig. 3. XRD patterns of 3Cu/ZrO_2 (1), 1Pd-3Cu/ZrO_2 (2), a physical mixture of 1Pd/ZrO_2 and 3Cu/ZrO_2 (3) after sorbitol hydrogenolysis reaction at 493 K under 5.0 MPa H_2.

the observed stable sorbitol conversions on 1Pd-3Cu/ZrO_2 during the five successive cycles (Fig. 1(a)).

Figure 4 shows the DRIFT spectra of adsorbed CO on the monometallic Pd and Cu catalysts and the bimetallic Pd-Cu catalysts after treatment in H_2 at 673 K. For the monometallic 1Pd/ZrO_2 catalyst, a band at 2079 cm^{-1} was assigned to the linear adsorption of CO on the Pd surfaces. Other spectral features at 1800–2000 cm^{-1}, the broad band at around 1958 cm^{-1}, and a shoulder at 1855 cm^{-1} were attributed respectively to bridging and multi-bonded CO species on Pd [29]. These bands were dramatically attenuated for 1Pd-1.8Cu/ZrO_2, and only an extremely weak band of linearly adsorbed CO on the Pd sites was observed for 1Pd-6Cu/ZrO_2 with a high Cu/Pd ratio of 10.0. Such phenomena, especially the decrease in the intensities of the bridging and multi-bonded CO bands on the Pd sites with increasing Cu/Pd ratios, are consistent with previous findings for bimetallic Pd-Cu catalysts [29,30], and are likely the result of dilution or coverage of the Pd ensembles with the Cu sites. Concurrent with such change, a new intense band appeared at around 2106 cm^{-1} for the bimetallic catalysts, resembling the single peak observed for monometallic 3Cu/ZrO_2 catalyst in terms of both intensity and shape. A band in the range of 2100–2110 cm^{-1} has been previously assigned to the linear adsorption of CO on metallic Cu^0 sites on Cu/ZrO_2 catalysts [31]. Therefore, this intense band can be also tentatively assigned to linearly adsorbed CO species on the metallic Cu^0 sites of Pd-Cu/ZrO_2. Based on these results, we envisaged that Cu was deposited on the Pd particles for the Pd-Cu/ZrO_2 catalysts, and most of the Pd surfaces were covered with Cu at the high Cu/Pd ratios, such as 1Pd-6Cu/ZrO_2. Taken together with the observed stability of the Pd-Cu catalysts and their superior activity in sorbitol hydrogenolysis, such close contact between Cu and Pd particles should lead to strong interaction between them for these Pd-Cu catalysts, as indeed evidenced from their H_2-TPR results (see below).

Figure 5 shows the H_2-TPR profiles for monometallic Pd/ZrO_2 and Cu/ZrO_2 and bimetallic Pd-Cu/ZrO_2 after treatment in air at 623 K. For 1Pd/ZrO_2, the main peak centered at around 374 K was assigned to the reduction of PdO, which closely interacts with the ZrO_2 support [32]. The peak at ~563 K corresponds to the reduction of ZrO_2 [33]. Such improved reduction of ZrO_2 may be caused by the promoting effect of PdO on the mobility of the lattice oxygen on the ZrO_2 surface, or because of hydrogen spillover from Pd to ZrO_2, as generally found on other ZrO_2-supported noble metal catalysts [33,34]. For 3Cu/ZrO_2, two major reduction peaks were observed at around 423 and 435 K. The first peak was assigned to the highly dispersed CuO phase, which closely interacts with ZrO_2, whereas the second peak was ascribed to the reduction of CuO, which has weaker interaction with ZrO_2 [35]. Compared with 1Pd/ZrO_2 and 3Cu/ZrO_2, only a broader single peak appeared at 384 K for 1Pd-3Cu/ZrO_2, which increased from 376 to 415 K as the Cu loading increased from 1.8 to 6.0 wt% (i.e., the Cu/Pd atomic ratio from 3.0 to 10.0). Apparently, the presence of Pd enhanced the reducibility of the Cu species, which is indicative of the close contact and strong interaction between Cu and Pd in the Pd-Cu catalysts.

The reduction features of the Pd-Cu catalysts could be also associated with the effect of H_2 spillover, which is derived from the dissociation of H_2 to H atoms on Pd, and their subsequent spillover to the Cu surfaces [29,36,37]. To examine such an effect, the H_2-TPR profile for the 1:1 (wt/wt) physical mixture of 1Pd/ZrO_2 and 3Cu/ZrO_2 was collected. As shown in Fig. 5, this sample presents two peaks at 378 and 432 K, corresponding to the reduction of PdO and CuO species, respectively. The presence of Pd indeed improved the reducibility of the Cu species as a result of the H_2 spillover. However, the reduction feature is different from those for bimetallic Pd-Cu catalysts, which further confirms the strong interaction between Pd and Cu in Pd-Cu/ZrO_2 catalysts. Such a difference can account for the observed difference in their activities. As shown in Table 1, the physical mixture of 1Pd/ZrO_2 (0.2g) and 3Cu/ZrO_2 (0.2g) had an activity of 12.2 h^{-1}, obviously higher than the weighted average activity (6.9 h^{-1}), which is derived from the activities for the two individual components (0.2 g 1Pd/ZrO_2 and 0.2 g 3Cu/ZrO_2) tested separately. Such enhanced activity of the physical mixture might be a result of Cu particle growth being inhibited by the addition of 1Pd/ZrO_2 *via* hydrogen spillover

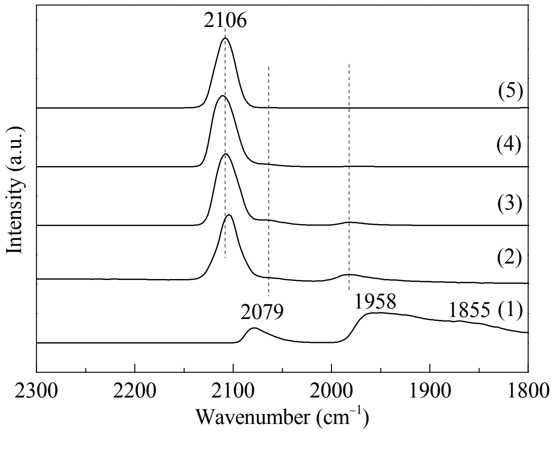

Fig. 4. DRIFT spectra of CO adsorption on 1Pd/ZrO_2 (1), 1Pd-1.8Cu/ZrO_2 (2), 1Pd-3Cu/ZrO_2 (3), 1Pd-6Cu/ZrO_2 (4) and 3Cu/ZrO_2 (5).

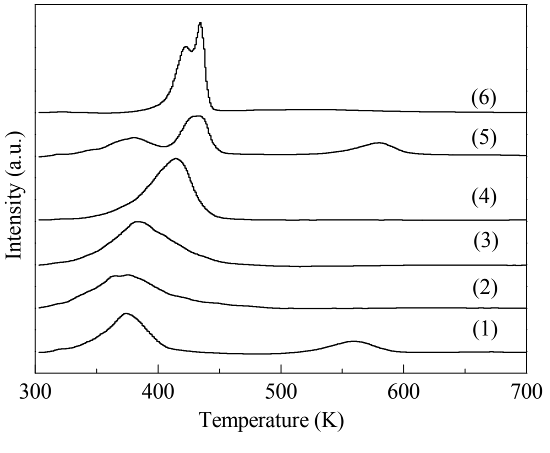

Fig. 5. H_2-TPR profiles of 1Pd/ZrO_2 (1), 1Pd-1.8Cu/ZrO_2 (2), 1Pd-3Cu/ZrO_2 (3), 1Pd-6Cu/ZrO_2 (4), the 1:1 (wt/wt) physical mixture of 1Pd/ZrO_2 and 3Cu/ZrO_2 (5) and 3Cu/ZrO_2(6).

during sorbitol hydrogenolysis. This physical mixture also possessed higher stability, as confirmed by its XRD pattern, which showed no agglomeration of the Cu particles after sorbitol hydrogenolysis (Fig. 3). The combined selectivity of the physical mixture to ethylene glycol, propylene glycol, and glycerol was 56.1%, which is higher than that for 1Pd/ZrO_2 (38.8%) and 3Cu/ZrO_2 (45.0%). Furthermore, compared with 3Cu/ZrO_2, the physical mixture showed a lower selectivity to lactic acid (16.7% vs 9.0%) and no detectable formation of acetol. These results show the physical mixture of 1Pd/ZrO_2 and 3Cu/ZrO_2 possessed higher hydrogenation activity than its two individual components as a result of hydrogen spillover. This is in accordance with the finding for hydrogenation of nitrate using a physical mixture of Pd/C and Cu/C catalysts [38]. However, as discussed in Section 3.1, the physical mixture is much less efficient than the 1Pd-3Cu/ZrO_2 catalyst in terms of activity and selectivity in sorbitol hydrogenolysis with the same amount of Pd and Cu.

Clearly, these results reveal that the observed superior activity, selectivity, and stability of the bimetallic Pd-Cu catalysts are caused by close contact between Pd and Cu particles and their strong interaction, which involves electron transfer from Pd to Cu [30,36]. This electronic effect consequently facilitates sorbitol dehydrogenation, which is the rate-determining step in the hydrogenolysis reaction, and subsequent hydrogenation steps toward the formation of the target glycols on the Cu surface [7].

4. Conclusions

Bimetallic Pd-Cu/ZrO_2 catalysts show significantly higher activities and selectivities than monometallic Pd/ZrO_2 and Cu/ZrO_2 catalysts in sorbitol hydrogenolysis to ethylene glycol and propylene glycol in the presence of $La(OH)_3$. A combined selectivity of 61.7% to ethylene glycol, propylene glycol, and glycerol at ~100% sorbitol conversion was obtained at 493 K under 5.0 MPa H_2 on 1Pd-3Cu/ZrO_2 (Cu/Pd=5). The presence of Pd in Pd-Cu/ZrO_2 catalysts prevents agglomeration of Cu particles and leads to high catalyst stability and recyclability in sorbitol hydrogenolysis under hydrothermal conditions. Such a remarkable promoting effect of Pd on the activity and stability of the Pd-Cu catalysts is considered to be directly related to the close contact and strong interaction between the two metals, most likely involving electron transfer from Pd to Cu. These findings may be beneficial to the design of new Cu-based catalysts with high efficiency and hydrothermal stability for different reactions of polyols and other biomass-derived feedstocks.

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Graphical Abstract

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Selective hydrogenolysis of sorbitol to ethylene glycol and propylene glycol on ZrO_2-supported bimetallic Pd-Cu catalysts

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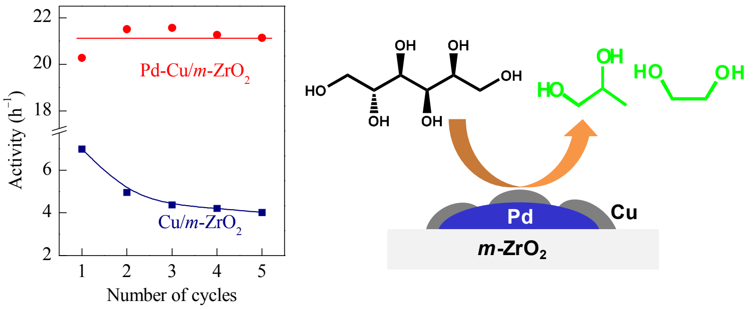
The presence of Pd largely improves the activity and stability of Cu/ZrO_2 catalyst in selective sorbitol hydrogenolysis to ethylene glycol and propylene glycol as a result of strong interaction between Pd and Cu.



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