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Article

Selective hydrogenolysis of biomass-derived furfuryl alcohol into 1,2- and 1,5-pentanediol over highly dispersed Cu-Al₂O₃ catalysts

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ABSTRACT

Cu nanoparticles supported on a variety of oxide supports, including SiO₂, TiO₂, ZrO₂, Al₂O₃, MgO and ZnO, were investigated for the hydrogenolysis of biomass-derived furfuryl alcohol to 1,2-pentanediol and 1,5-pentanediol. A Cu-Al₂O₃ catalyst with 10 wt% Cu loading prepared by a co-precipitation method exhibited the best performance in terms of producing pentanediols compared with the other materials. This catalyst generated an 85.8% conversion and a 70.3% combined selectivity for the target pentanediols at 413 K and 8 MPa H₂ over an 8-h reaction. The catalyst could also be recycled over repeated reaction trials without any significant decrease in productivity. Characterizations with X-ray diffraction, NH₃/CO₂-temperature programmed desorption, N₂ adsorption, transmission electron microscopy and N₂O chemisorption demonstrated that intimate and effective interactions between Cu particles and the acidic Al₂O₃ support in this material greatly enhanced its activity and selectivity. The promotion of the hydrogenolysis reaction was found to be especially sensitive to the Cu particle size, and the catalyst with Cu particles 1.9 to 2.4 nm in size showed the highest turnover frequency during the synthesis of pentanediols.

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1. Introduction

Due to concerns regarding declining petroleum resources and various environmental issues, the conversion of renewable biomass to chemicals and liquid fuels has been the subject of intense research over the past decade [1–3]. Furfural is an important platform molecule manufactured via acid hydrolysis of the lignocellulose found in various abundant agricultural raw materials, such as corncobs, oats, and wheat bran, at up to 10⁵ tons per year [4–6]. The catalytic transformation of furfural and its derivatives furfuryl alcohol (FFA) and tetrahydrofurfuryl

alcohol (THFA) to valuable chemicals and fuels by hydrogenation and hydrogenolysis has also received increasing attention in recent years [7–14]. As an example, the one-pot hydrogenolysis of furfural or its derivatives is an attractive method for the sustainable synthesis of useful glycols, such as 1,2-pentanediol (1,2-PeD) and 1,5-pentanediol (1,5-PeD) [8,10,15–24].

To date, the selective hydrogenolysis of furfural and its derivatives to 1,2-PeD and 1,5-PeD has been accomplished primarily using noble metal catalysts, including supported Ru [17], Rh [9,15,21,23], Pt [10,16,22] and Ir [24]. For example, Tomishige and co-workers [15,21,23,24] achieved 1,5-PeD

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yields up to 94% from the hydrogenolysis of THFA at 373 to 393 K and under 8 MPa H₂ using acidic, low-valent metal oxides (ReO_x, MoO_x or WO_x)-modified Rh or Ir catalysts. Xu et al. [16] attempted the direct conversion of furfural to 1,2-PeD and 1,5-PeD in an alcohol solvent using a Li-modified Pt/Co₂AlO₄ catalyst, obtaining high conversions (approximately 100%) and moderate yields of 1,2-PeD (16.2%) and 1,5-PeD (34.9%) at 413 K and 1.5 MPa H₂. More recently, 1,2-PeD (with a 73% yield) and 1,5-PeD (with a 78.2% yield) were separately attained over a hydrotalcite-supported Pt catalyst [10] and a Rh-added Ir-ReO_x/SiO₂ catalyst [20], respectively, from furfural hydrogenolysis. In addition, Zhang et al. [17] obtained a high yield of 1,2-PeD (42.1%) from the hydrogenolysis of FFA over a Ru/MnO_x catalyst under mild conditions consisting of 423 K and 1.5 MPa H₂, with no formation of 1,5-PeD. Although high yields of 1,2-PeD (40%) and 1,5-PeD (30%) have been reported from the hydrogenolysis of FFA over a copper chromite catalyst [25], the wide application of this system has been restricted due to the potential toxicity concerns associated with Cr and the harsh reaction conditions required (448 K, 10–15 MPa).

Clearly, the selective hydrogenolysis of furfural or its derivatives to PeDs over environmentally-friendly, Cr-free, non-precious catalytic systems under mild conditions remains challenging. Recently, we reported that highly dispersed Cu catalysts exhibit good activity and selectivity during the hydrogenolysis of C–O bonds in polyols [26–28] and cyclic carbonates [29]. Since then, we have demonstrated that non-precious Cu-Mg₃AlO_{4.5} catalysts with layered double oxide structures and weak basicity are exceptionally active and selective during the hydrogenolysis of biomass-derived FFA, achieving approximately 80% combined yields of 1,2-PeD and 1,5-PeD under mild conditions (413 K and 6 MPa H₂) [30]. Although basic supports are believed to be benefit for the transformation of furfural or FFA to specific PeDs, by partly suppressing the dehydration of FFA to 2-methylfuran [16] and/or stabilizing the hydrogenolysis intermediates of FFA [17], acidic supports [31] or additives [8,9] have also been applied to the hydrogenolysis of furfurals or their derivatives to diols. Herein, we report that acidic Al₂O₃-supported Cu bifunctional catalysts with high dispersion are also active and selective during the hydrogenolysis of FFA to 1,2-PeD and 1,5-PeD. The catalytic activity and selectivity of these Cu-Al₂O₃ catalysts were found to be affected by both their structure and surface properties. The reaction parameters, including temperature, H₂ pressure, catalyst amount and reaction time, were optimized to obtain high yields of PeDs. Based on the data obtained, this paper also proposes reaction pathways for formation of the main reaction products.

2. Experimental

2.1. Materials

All reagents were analytical grade. An aqueous colloidal SiO₂ solution (25.0 wt%, ammonium stabilized type, pH in the range of 8.5 to 10.5, particle size from 10 to 20 nm) was purchased from the Qingdao Haiyang Chemical Co., China. Colloidal aque-

ous TiO₂ (15 wt%, particle size 15 nm) and ZrO₂ (40 wt%, particle size range 20 to 30 nm) solutions were obtained from the Xuancheng Jingrui New Material Co., China. PtCl₄ was purchased from the Beijing HWRK Chem. Co., Ltd., China and HZSM-5 zeolite (surface area 541 m²/g, Si/Al = 500) was purchased from the Nankai University Catalyst Plant, Tianjin, China. The copper chromite catalyst (CuCr₂O₄) was purchased from the Yingkou Tianyuan Chemical Industry Research Institute Co., Ltd., China. NH₃ (99.9%), 5% N₂O-95% N₂, 5% H₂-95% Ar, 20% H₂-80% N₂ and He (99.999%) were obtained from the Lanzhou Lanmei Cryogenic Products Co., Ltd., China.

2.2. Catalyst preparation

Catalysts consisting of 10 wt% Cu supported over SiO₂, TiO₂ or ZrO₂, were prepared by precipitation-gel (PG) method, using a previously reported process [27,28]. In a typical synthesis, an aqueous solution of NaOH (4 mol/L) was added dropwise to a Cu(NO₃)₂ solution (0.5 mol/L) with vigorous stirring at 303 K until the pH was above 11, to form a Cu(OH)₂ precipitate. The desired amount of a colloidal aqueous solution of SiO₂, TiO₂ or ZrO₂ was subsequently added dropwise to this Cu(OH)₂ precipitate to form a gel, and these gels were aged at 303 K for 4 h, with the exception of the Cu-SiO₂, which was aged at 373 K for 4 h. Following this, the gels were filtered and washed with distilled H₂O until the wash water showed a pH of approximately 7. Finally, the obtained solids were dried at 393 K overnight and calcined at 773 K for 4 h in air.

The catalysts with 10 wt% Cu supported over MgO or ZnO, as well as Cu-Al₂O₃ with Cu loadings from 2 to 30 wt%, were prepared by co-precipitation (CP) method. Briefly, a mixed solution of Cu(NO₃)₂ (0.1 mol/L) with Mg(NO₃)₂, Zn(NO₃)₂ or Al(NO₃)₃ and an aqueous solution of NaOH (4 mol/L) were concurrently added dropwise to a Na₂CO₃ solution (0.5 mol/L) while maintaining the pH at approximately 10. After aging at 303 K for 24 h, the obtained solids were filtered and washed with distilled H₂O until pH of approximately 7 was obtained. Finally, the samples were dried at 393 K overnight and calcined at 773 K for 4 h in air.

The Al₂O₃-supported 2 wt% Pt, 10 wt% Ni or 10 wt% Co catalysts were prepared in a similar manner from PtCl₄, Ni(NO₃)₂ or Co(NO₃)₂ precursors by the CP method, respectively. The calcined samples prepared by PG or CP methods are designated herein as ωMO-support, while the corresponding reduced catalysts are designated as ωM-support, where ω represents the nominal metal loading and M represents the active metal employed. For comparison, 10Cu/Al₂O₃-IM, 30Cu-Al₂O₃-W and 10Cu-Al₂O₃-W (with 1 wt% W loading), 10Cu-Al₂O₃-K (with 1 wt% K loading) and 10Cu/HZSM-5-IM reference catalysts were prepared by incipient wetness impregnation (IM) method. The Al₂O₃ support, or calcined 30CuO-Al₂O₃ or 10CuO-Al₂O₃ samples (prepared by the CP method described above), or the HZSM-5 support were impregnated with an aqueous solution containing the requisite amount of Cu(NO₃)₂, (NH₄)₁₀W₁₂O₄₁·H₂O or KNO₃, respectively, at room temperature, followed by drying at 393 K overnight and calcining at 773 K for 4 h in air. The pure Cu catalyst was prepared by precipi-

tating a $\text{Cu}(\text{NO}_3)_2$ aqueous solution (0.5 mol/L) with NaOH (4 mol/L), followed by treatment similar to that detailed above.

2.3. Catalyst characterization

X-ray powder diffraction (XRD) data were acquired using a PANalytical X'pert Pro Diffractometer with nickel filtered Cu K_α radiation at 40 kV and 30 mA. BET surface areas were obtained with a Micromeritics Tristar II 3020 instrument at liquid nitrogen temperature (77 K). Prior to these measurements, the samples were pretreated with N_2 at 573 K for 4 h. Transmission electron microscopy (TEM) investigations were carried out using a JEM2010 electron microscope at 200 kV. The TEM samples were prepared by ultrasonically dispersing each material in ethanol and then dropping the dispersions onto carbon-coated Cu grids.

NH_3 -temperature programmed desorption (TPD) and CO_2 -TPD were carried out with a DAX-7000 instrument (Huasi Technology Co., Ltd, China). Samples were pretreated at 473 K under a He flow at 40 mL/min for 1 h and then reduced at 623 K under 5% H_2 -95% Ar at 40 mL/min for 2 h. The reduced samples were subsequently exposed to an NH_3 flow (40 mL/min) at 373 K for 1 h and then heated linearly from 373 to 973 K at a rate of 10 K/min under a He flow (40 mL/min). The desorbed NH_3 was detected using a thermal conductivity detector (TCD), and the TCD signals were calibrated with specific volumes of NH_3 . CO_2 -TPD of the Cu catalysts was similar to the NH_3 -TPD procedure above but with the saturation adsorption of CO_2 at 313 K for 1 h.

The Cu dispersion was assessed by dissociative N_2O adsorption with H_2 -temperature programmed reduction (TPR) reverse titration [27,32]. After pretreatment in a He flow at 473 K for 1 h, the samples (containing approximately 10 mg Cu) were reduced in a 5% H_2 -95% Ar flow at 40 mL/min by heating from room temperature to 773 K at a rate of 5 K/min. This process represented a total TPR, with reduction of both bulk and surface Cu species. At the end of the first TPR, the samples were cooled to 323 K in the same reducing atmosphere and then exposed to 5% N_2O -95% N_2 (40 mL/min) at 323 K for 1 h. Subsequently, the resulting surface oxidized samples were subjected to a second TPR run from 323 to 623 K at a rate of 5 K/min (denoted as surface TPR). During the H_2 -TPR runs, the H_2 consumption was tracked using a thermal conductivity detector (TCD). Assuming a spherical shape for the Cu particles, 1.46×10^{19} Cu atoms per m^2 and a $\text{N}_2\text{O}/\text{Cu}_s$ molar ratio of 0.5 (where Cu_s denotes Cu atoms on the surface), the Cu dispersion (D_{Cu}), Cu^0 surface area (S_{Cu}) and average Cu particle size (d_{Cu}) values of the Cu catalysts were calculated using Equations (1), (2) and (3), respectively.

$$D_{\text{Cu}} (\%) = 2 \times \text{H}_2 \text{ consumption (surface TPR)} / \text{H}_2 \text{ consumption (total TPR)} \times 100\% \quad (1)$$

$$S_{\text{Cu}} (\text{m}^2/\text{g}) = (D_{\text{Cu}} \times N_{\text{av}}) / (M_{\text{Cu}} \times 1.46 \times 10^{19}) \approx 649 \times D_{\text{Cu}} \quad (2)$$

$$d_{\text{Cu}} (\text{nm}) = 6 / (S_{\text{Cu}} \times \rho_{\text{Cu}}) \approx 1.0 / D_{\text{Cu}} \quad (3)$$

Here N_{av} is Avogadro's constant ($6.02 \times 10^{23}/\text{mol}$), M_{Cu} is the relative atomic mass (63.5 g/mol) and ρ_{Cu} is the Cu density (8.92 g/mL).

2.4. Catalytic testing and product analysis

The FFA hydrogenolysis reactions were carried out in a stainless steel autoclave reactor (100 mL) at a stirring speed of 800 r/min. Prior to each reaction, the calcined catalyst sample was reduced at 623 K in 20% H_2 -80% N_2 at a flow of 40 mL/min for 3 h. In a typical trial, 40 g of 10 wt% FFA dissolved in ethanol was added into reactor together with a quantity of the reduced catalyst. After flushing with H_2 , the reactor was pressurized with H_2 to 6.0 MPa, and then heated to 413 K over the course of 0.5 h. The concentrations of the reactant and liquid products were analyzed by gas chromatography (Agilent 7890A GC) with a PONA capillary column (50 m $\times$ 0.20 mm $\times$ 0.50 μm). Products were also identified using an Agilent 7890A/5975C gas chromatograph-mass spectrometer (GC-MS) with an HP-5MS column. The liquid products identified in this manner consisted of 1,2-PeD, 1,5-PeD, 1,4-pentanediol, 2-methyl furan (2-MF), 2-methyl tetrahydrofuran (2-MTHF), 1-pentanol, 2-pentanol, *n*-pentane and tetrahydrofurfuryl alcohol (THFA). FFA conversions and product selectivities were calculated on the basis of the following equations.

$$\text{Conversion} (\%) = (\text{moles of FFA charged} - \text{moles of FFA left}) / \text{moles of FFA charged} \times 100\%$$

$$\text{Selectivity} (\%) = \text{moles of a product generated} / (\text{moles of FFA charged} - \text{moles of FFA left}) \times 100\%$$

3. Results and discussion

3.1. Structural characterization of Cu-Al₂O₃ catalysts

Fig. 1 presents the XRD patterns of calcined $\text{CuO-Al}_2\text{O}_3$ samples with different Cu loadings as well as both reduced and used 10Cu-Al₂O₃ catalysts. As can be seen from Fig. 1(a), mainly broad diffraction peaks assignable to $\gamma\text{-Al}_2\text{O}_3$ (JCPDS 10-0425) at approximately $2\theta = 37.5^\circ$, 45.8° and 66.7° were observed in all calcined $\text{CuO-Al}_2\text{O}_3$ samples. A diffuse diffraction peak at $2\theta = 35.5^\circ$ assignable to CuO (JCPDS 05-0661) is present in the 30CuO-Al₂O₃ pattern, but no CuO peaks are found in the patterns of the samples with Cu loadings below 30 wt%. This demonstrates the high dispersion of CuO in these samples, especially those with lower Cu loadings (2–20 wt%). After reduction at 623 K for 3 h in H_2 atmosphere, almost no diffraction peaks associated with Cu^0 and/or Cu_2O are observed in the pattern of the reduced 10Cu-Al₂O₃ catalyst (Fig. 1(b)(2)), showing the high dispersion and remarkable ability to resist sintering of these species in the reduced catalyst. The high stability of the catalyst is also reflected in the pattern of the used 10Cu-Al₂O₃ catalyst after five cycles, as only a very broad diffraction pattern assignable to Cu^0 is observed in its XRD profile (Fig. 1(b)(3)). The crystalline size of the Cu^0 species in the used 10Cu-Al₂O₃ catalyst was calculated to be approximately 3 nm by the Scherrer equation.

Fig. 2 presents representative TEM images of the calcined $\text{CuO-Al}_2\text{O}_3$ samples with Cu loadings of 2, 10 and 30 wt%, and the used 10Cu-Al₂O₃ after five cycles. A sponge-like mesoporous structure is observed in each of the samples, and it is difficult to discriminate between CuO nanoparticles and the Al_2O_3

Fig. 1. XRD patterns of (a) calcined CuO-Al₂O₃ samples with different Cu loadings and (b) calcined 10CuO-Al₂O₃ (1), reduced 10Cu-Al₂O₃ (2) and 10Cu-Al₂O₃ after five cycles (3).

supports even with Cu loadings up to 30 wt%, showing the uniform dispersion of CuO in these samples. In addition, only a few small Cu nanoparticles with sizes < 8 nm are occasionally observed in the image of the used 10Cu-Al₂O₃ after five cycles (Fig. 2(d)). These TEM results further support the XRD finding that the Cu-Al₂O₃ has both highly dispersed Cu species and remarkable resistance to sintering during FFA hydrogenolysis.

It has been reported that surface acidity plays an important role in determining the catalytic performance for THFA [9] and 5-hydroxymethylfurfural (HMF) [31] hydrogenolysis to diols. Thus, the acidic properties of Cu-Al₂O₃ catalysts with different Cu loadings were characterized by NH₃-TPD, with the results presented in Fig. 3(a). As can be seen, all the Cu-Al₂O₃ catalysts exhibited NH₃ desorption peaks at 373 to 523 K (weak acid sites) and 523 to 873 K (medium and strong acid sites). The NH₃ desorption peak areas gradually decreased with increasing Cu loading, indicating that the acidity of each Cu-Al₂O₃ catalyst declined at higher Cu loadings, in good agreement with previous reports [33]. We also determined the surface basicity of three representative Cu-Al₂O₃ catalysts with Cu loadings of 2, 10 and 30 wt%. Each of these catalysts generated a main CO₂ desorption peak centered at approximately 457 K, associated with weakly basic sites [34]. The basic site concentrations of

these catalysts, which decreased uniformly from 95.5 to 61.4 μmol/g with increasing Cu loading from 2 to 30 wt%, are two to three times lower than those of their acidic sites, demonstrating that these Cu-Al₂O₃ catalysts present mainly acidity properties. In additional experiments, WO₃ and K₂O were employed to tune the surface acidity-basicity of the Cu-Al₂O₃ catalysts [34]. Fig. 3 shows that the incorporation of 1 wt% W slightly increased the acidity of both the 10Cu-Al₂O₃ and 30Cu-Al₂O₃ catalysts, while doping with 1 wt% K increased the

Fig. 3. (a) NH₃-TPD and (b) CO₂-TPD patterns of Cu-Al₂O₃ catalysts with different Cu loadings prepared by CP method.

Fig. 2. TEM images of (a) 2CuO-Al₂O₃, (b) 10CuO-Al₂O₃, (c) 30CuO-Al₂O₃ and (d) 10Cu-Al₂O₃ after five cycles.

basicity of the 10Cu-Al₂O₃.

Table 1 summarizes the textural properties of calcined CuO-Al₂O₃ samples prepared by CP method with different Cu loadings, as well as the 10CuO/Al₂O₃-IM reference sample synthesized using a traditional impregnation method and pure CuO. The BET surface areas of the calcined CuO-Al₂O₃ samples declined monotonically from 297.4 to 197.1 m²/g with increasing Cu loadings from 2 to 30 wt%, likely due to the decrease in the amount of the Al₂O₃ support, which had a surface area as high as 285.4 m²/g. The BET surface areas of the reference 10CuO/Al₂O₃-IM and pure CuO were only 145.6 and 20.1 m²/g, much lower than those of the CuO-Al₂O₃ materials. The average pore diameters of the CuO-Al₂O₃ samples in the mesopore range were found to increase from 6.8 to 15.7 nm with increasing Cu loadings from 2 to 30 wt%. The Cu dispersions and Cu⁰ surface areas of the catalysts determined by N₂O chemisorption decreased gradually at higher Cu loading, and even the 30Cu-Al₂O₃ showed high dispersion and Cu⁰ surface area values of 32.8% and 234.3 m²/g, respectively. As a result of changes in dispersion, the Cu particle sizes in the catalysts increased gradually from 1.3 to 3.0 nm with increasing Cu loadings from 2 to 30 wt%. These small sizes are in line with the above XRD and TEM characterizations. In contrast, the reference 10CuO/Al₂O₃-IM and the pure CuO showed much lower dispersions of 6.0 and 2.8%, and rather large Cu particle sizes of 16.7 and 39.3 nm, respectively.

3.2. Catalytic testing for FFA hydrogenolysis over various catalysts

Table 2 summarizes the conversions and selectivities obtained during FFA hydrogenolysis over a wide variety of heterogeneous catalysts at 413 K and 6 MPa H₂. Among the Cu-base catalysts supported on traditional oxides (SiO₂, TiO₂, ZrO₂, MgO, ZnO and Al₂O₃), the 10Cu-Al₂O₃ (having a larger concentration of strongly acidic sites as in Fig. 3 and reference [29]) was more active and selective for the generation of 1,2-PeD and 1,5-PeD. This catalyst gave 48.6% and 22.7% selectivities for 1,2-PeD and 1,5-PeD at 60.4% FFA conversion, respectively (entries 1–6). In addition, 2-MF, 1-pentanol and THFA were determined to be the major byproducts from 10Cu-Al₂O₃, with selectivities of 10.0%, 9.9% and 3.7%, respectively. The FFA conversions of the Cu-Al₂O₃ catalysts with Cu

loadings from 2 to 30 wt% increased to a maximum of 61.9% in the case of the 20Cu-Al₂O₃, and then decreased to 49.5% with further increases in the Cu loading to 30 wt% (entries 6 and 10 to 13). The selectivities for 1,2-PeD and 1,5-PeD over these catalysts also increased with the Cu loading, reaching maximum values of 48.6% and 22.7% over the 10Cu-Al₂O₃, respectively. In contrast, almost no 1,2-PeD and 1,5-PeD were obtained over the 10Ni-Al₂O₃ and 10Co-Al₂O₃ catalysts; THFA was found to be the dominant product (selectivity > 83%) with the former catalyst being much more active (entries 15 and 16). Previous studies showed that supported Pt catalysts (with approximately 2 wt% Pt loading) were both active and selective during the hydrogenolysis of FA and FFA [10,16]. Under our experimental conditions, however, the 2Pt-Al₂O₃ catalyst exhibited inferior selectivity for 1,2-PeD and 1,5-PeD compared with the Cu-Al₂O₃ catalysts (entry 17). In addition, the conversions and combined selectivities for pentanediols over the Cu-Al₂O₃ catalysts with Cu loadings ≥ 5 wt% were noticeably greater than those obtained using a commercial CuCr₂O₄ catalyst (entry 21). Clearly, the above findings show the distinguished performances of the Cu-Al₂O₃ catalysts prepared by CP method with regard to generating pentanediols, especially in the case of the catalyst with 10 wt% Cu loading. Moreover, because the Al₂O₃ support itself is almost inactive in FFA hydrogenolysis (not shown in Table 2), while pure Cu exhibits rather weak activity and selectivity (entry 20), the remarkable increase in both FFA conversion and selectivities obtained with the 10Cu-Al₂O₃ (entry 6) and 10Cu/Al₂O₃-IM catalysts (entry 18) demonstrates that the intimate and effective interaction of Cu and the acidic Al₂O₃ support is beneficial to the transformation of FFA to the target PeDs.

The above characterizations (Table 1 and Fig. 3) show that the Cu particle sizes of the Cu-Al₂O₃ catalysts and their surface acidic concentrations varied in different manners. That is, the Cu particle sizes increased nearly linearly with increasing Cu loadings, while the surface acidic amounts declined monotonically (Fig. 4(a)). Plotting the TOF values, defined as the moles of 1,2-PeD and 1,5-PeD generated per Cu site per time, against the Cu particle size of the Cu-Al₂O₃ catalysts showed that the TOF increased rapidly with increasing Cu size and reached a maximum between 1.9 and 2.4 nm, then declined with further increases in the Cu size (Fig. 4(b)). This trend indicates that FFA hydrogenolysis over these Cu catalysts is likely a struc-

Table 1

Textural properties of calcined CuO-Al₂O₃ samples with different Cu loadings, a reference 10CuO/Al₂O₃-IM sample and pure CuO.

Sample	Cu content ^a (wt%)	Surface area ^b (m ² /g)	Average pore diameter ^b (nm)	Dispersion ^c (%)	Cu surface area ^d (m ² /g)	Particle size ^e (nm)
2CuO-Al ₂ O ₃	1.9	297.4	6.8	84.4	548.0	1.3
5CuO-Al ₂ O ₃	4.8	254.9	8.3	69.7	452.3	1.6
10CuO-Al ₂ O ₃	9.6	229.3	10.4	57.6	374.0	1.9
20CuO-Al ₂ O ₃	19.6	210.8	13.3	45.4	294.9	2.4
30CuO-Al ₂ O ₃	27.6	197.1	15.7	32.8	234.3	3.0
10CuO/Al ₂ O ₃ -IM	10.0	145.6	15.6	6.0	39.0	16.7
Pure CuO	100	20.1	19.2	2.8	18.2	39.3
Al ₂ O ₃	—	285.4	7.4	—	—	—

^a Cu content determined by ICP analysis. ^b BET method. ^c Cu dispersion obtained from dissociative N₂O adsorption. ^d Cu⁰ surface area obtained from dissociative N₂O adsorption. ^e Mean Cu particle size calculated from dissociative N₂O adsorption.

Table 2

Conversion and selectivity during FFA hydrogenolysis over various catalysts.

Entry	Catalyst	Conversion (%)	Selectivity (%)					
			1,2-PeD	1,5-PeD	2-MF	1-Pentanol	THFA	Others ^a
1	10Cu-SiO ₂	29.1	33.2	18.0	7.7	11.3	8.9	20.2
2	10Cu-TiO ₂	14.3	14.4	7.9	13.2	8.4	8.2	47.4
3	10Cu-ZrO ₂	45.7	39.8	11.5	16.3	10.6	4.8	16.7
4	10Cu-MgO	54.3	39.9	27.4	5.5	12.2	3.0	11.9
5	10Cu-ZnO	8.6	10.8	5.9	1.8	4.3	5.6	71.6
6	10Cu-Al ₂ O ₃	60.4	48.6	22.7	10.0	9.9	3.7	4.9
7 ^b	10Cu-Al ₂ O ₃	85.8	48.1	22.2	9.3	13.2	2.7	3.6
8	10Cu-Al ₂ O ₃ -W	52.4	43.7	30.9	7.3	10.7	3.0	4.4
9	10Cu-Al ₂ O ₃ -K	42.5	36.1	22.3	4.0	6.7	3.5	27.4
10 ^c	2Cu-Al ₂ O ₃	20.1	23.8	8.5	27.6	10.6	6.4	23.1
11	5Cu-Al ₂ O ₃	42.1	37.0	14.0	18.3	11.6	4.2	14.8
12	20Cu-Al ₂ O ₃	61.9	41.2	16.2	18.4	14.5	4.5	4.9
13	30Cu-Al ₂ O ₃	49.5	36.2	15.7	15.8	15.2	3.3	13.8
14	30Cu-Al ₂ O ₃ -W	52.6	36.9	20.4	16.3	11.8	3.7	10.9
15	10Ni-Al ₂ O ₃	>99	1.0	1.3	0.8	—	91.7	4.9
16	10Co-Al ₂ O ₃	7.7	—	—	9.7	—	83.7	6.6
17 ^c	2Pt-Al ₂ O ₃	45.8	13.6	7.0	7.3	—	69.2	2.0
18	10Cu/Al ₂ O ₃ -IM	37.9	29.6	4.4	21.1	9.6	7.7	27.4
19	10Cu/HZSM-5-IM	>99	9.9	0.8	1.6	0.7	0.3	86.7
20	Pure Cu	7.9	2.1	1.4	3.1	0.2	6.4	85.8
21	CuCr ₂ O ₄	24.4	34.1	15.6	10.0	12.1	3.6	24.5

Reaction conditions: 0.20 g active metal, 40 g 10 wt% FFA in ethanol, 413 K, 6 MPa H₂, 8 h. PeD = Pentanediol, 2-MF = 2-Methyl furan, THFA = Tetrahydrofurfuryl alcohol. ^a These include *n*-pentane, 1,4-PeD, 2-methyl tetrahydrofuran, 2-pentanol and some undetermined products (for 10Cu/HZSM-5-IM, the main byproduct is ethyl levulinate). ^b 0.40 g Cu, 40 g 10 wt% FFA in ethanol, 413 K, 8 MPa H₂, 8 h. ^c 0.05 g active metal, 40 g 2.5 wt% FFA in ethanol, 413 K, 6 MPa H₂, 8 h.

ture-sensitive reaction [35], which is in agreement with the results of our previous study on the hydrogenolysis of FFA over Cu-Mg₃AlO_{4.5} bifunctional catalysts [30]. The lower TOFs of the catalysts with Cu sizes below 1.9 nm likely resulted from the stronger adsorption for the reactants and products on the smaller Cu particles, resulting in a decrease in the quantity of vacant Cu sites, analogous to the behavior reported for Ru catalyst during glycerol hydrogenolysis [36]. The decrease in TOF with further increases in Cu size above 2.4 nm might be caused by steric hindrance to the approach of the C=C in the aromatic furan ring to the surfaces of larger Cu particles [37], retarding the activation and further transformation of the FFA molecules. Variations in the Cu particle size would also be expected to affect the electronic structure and the Cu-Al interfacial sites of

the Cu-Al₂O₃ catalysts, which could also change the catalytic reactivity [38,39].

Apart from the above Cu size effect, the decreased acidity of the catalysts with increasing Cu contents (Fig. 4(a)) might also to some extent reduce the activities and PeD selectivities of the catalysts with Cu loadings above 20 wt% (Cu size > 2.4 nm). This possibility is supported by the simultaneous increases in the surface acidic concentration (Fig. 3(a)) and catalytic performance (FFA conversion and PeDs selectivity) of the 1 wt% W-loaded 30Cu-Al₂O₃-W (Table 2, entry 14) as compared with the 30Cu-Al₂O₃ (Table 2, entry 13). The incorporation of W also favors the PeDs selectivity of 10Cu-Al₂O₃ (Table 2, entry 8), albeit with a slight decrease in FFA conversion, likely due to the partial coverage of the active Cu sites by WO_x particles. None-

Fig. 4. (a) Cu particle sizes and acidic group concentrations of Cu-Al₂O₃ catalysts as functions of Cu loading and (b) TOF as a function of Cu particle sizes during FFA hydrogenolysis over Cu-Al₂O₃ catalysts. Reaction conditions: 40 g 10 wt% FFA in ethanol, 413 K, 6 MPa H₂, approximately 20% FFA conversion.

theless, due to the more prevalent acid catalyzed side-reactions (as compared with metal catalyzed C–O bond hydrogenolysis), such as the hydrolysis of FFA to levulinic acid [40], supports with rather higher acidity (such as the HZSM-5, Table 2, entry 19) were also not appropriate for FFA hydrogenolysis. Thus, it is clear that optimal acidity favors the hydrogenolysis of FFA to PeDs, not higher acidity. It should also be noted that, although basic supports enhance the transformation of FA/FFA to PeDs, as discussed above, the surface acidity of the Cu-Al₂O₃ is believed to have played a more important role in FFA hydrogenation in the present work. This is because of the much lower concentrations of basic sites in these catalysts (Fig. 3). This finding is also supported by the decrease in both FFA conversion and PeDs selectivity in the case of the 10Cu-Al₂O₃ treated with K₂O and having increased basicity (Table 2, entry 9) as compared with the untreated 10Cu-Al₂O₃.

The efficient 10Cu-Al₂O₃ catalyst could also be readily recycled over repeated runs without significant loss in either the FFA conversion or the PeDs selectivities (Fig. 5). After each run, the catalyst was easily recovered by centrifugation and recharged into the autoclave together with fresh reactant for the next run. The FFA conversions gradually decreased from 60.4% to 47.8% over five cycles, while the selectivities for 1,2-PeD and 1,5-PeD underwent only moderate declines, from 48.6% and 22.7% to 41.8% and 18.2%, respectively. Additionally, almost no leaching of Cu ($< 0.5 \times 10^{-6}$) could be detected by inductively couple plasma-atomic emission spectroscopy (ICP-AES), demonstrating the high durability of the catalyst. The slight decrease in activity and selectivity of the catalyst are thought to have resulted from the gradual aggregation of Cu particles during repeated runs, as was evident from the XRD (Fig. 1(b)) and TEM (Fig. 2(d)) characterizations of the used catalyst after five cycles.

3.3. Effects of reaction parameters on FFA hydrogenolysis to 1,2-PeD and 1,5-PeD

Fig. 6 shows the activity and selectivities of the 10Cu-Al₂O₃ catalyst during FFA hydrogenolysis at different reaction temperatures at approximately 20% FFA conversion and 6 MPa H₂.

Fig. 5. Reusability of the 10Cu-Al₂O₃ catalyst during FFA hydrogenolysis. Reaction conditions: 0.20 g Cu, 40 g 10 wt% FFA in ethanol, 413 K, 6.0 MPa H₂, 8 h.

The TOF values increased from 1.25 h⁻¹ at 403 K to a maximum of 2.35 h⁻¹ at 423 K, and then declined to 2.15 h⁻¹ with further increase in the temperature up to 433 K. The selectivities for 1,2-PeD and 1,5-PeD rose sharply, from 36.5% and 18.0% at 403 K to maximums of 48.9% and 21.9% at 413 K, and then dropped steadily to 20.0% and 6.1% at 433 K, respectively. These findings demonstrate that 413 K is the optimal temperature for the production of PeDs with the highest selectivity and high reactivity. The selectivities for 2-MF and 1-pentanol also increased almost linearly with increasing temperature. As 2-MF is a dehydration product of FFA through -CH₂OH group hydrogenolysis [41–43], the increase in the selectivity for this product with temperature suggests that high temperatures favor the direct dehydration of FFA. The greater selectivity for 1-pentanol with increasing temperature is attributed to additional hydrogenolysis of the PeD products [9,19]. The selectivity for THFA, the total hydrogenation product of FFA, remained almost constant (5.0% to 6.0%) over the temperature range of 403 to 433 K. The hydrogenolysis of THFA under more severe conditions (433 K and 8 MPa H₂) over 10Cu-Al₂O₃ showed no PeD products, suggesting that THFA is relatively stable under hydrogenolysis conditions, which is in line with the results of previous studies [17].

Fig. 7 plots the effect of H₂ pressure on the activity and selectivity during FFA hydrogenolysis over the 10Cu-Al₂O₃ catalyst. The TOF is seen to have steadily risen from 0.16 to 3.41 h⁻¹ with increasing H₂ pressure from 1 to 8 MPa. The selectivities for 1,2-PeD and 1,5-PeD also increased monotonically from 19.7% and 7.0% at 1 MPa H₂ to 50.2% and 22.5% at 8 MPa H₂, respectively. On the contrary, the selectivity for 2-MF decreased rapidly, from 31.6% to 7.4%, as the H₂ pressure rising to 8 MPa. These changes in the selectivities for PeDs and 2-MF indicate that the formations of these compounds are competitive reactions and that high pressure favors the hydrogenolysis of the C–O bond in the furan ring while suppressing the dehydration of the -OH group in the hydroxymethyl moiety. The slight decrease in the 1-pentanol selectivity (from 13.0% to 7.6%) and 2-pentanol selectivity (from 0.4% to < 0.1%, not shown) suggests that the further hydrogenolysis of the PeD products was also to some extent being suppressed by in-

Fig. 6. Effect of reaction temperature on FFA hydrogenolysis over the 10Cu-Al₂O₃ catalyst. Reaction conditions: 0.03–0.18 g Cu, 40 g 10 wt% FFA in ethanol, 6 MPa H₂, 4 h, approximately 20% conversion.

Fig. 7. Effects of H₂ pressure on FFA hydrogenolysis over the 10Cu-Al₂O₃ catalyst. Reaction conditions: 0.06–0.25 g Cu, 40 g 10 wt% FFA in ethanol, 413 K, 4 h, approximately 20% conversion.

creasing H₂ pressure.

Fig. 8 summarizes the effects of the active Cu amount on the conversion and PeDs selectivity during FFA hydrogenolysis. The FFA conversion increased almost linearly, from 45.3% to 82.6%, as the active Cu amount was raised from 0.10 to 0.40 g. In contrast, the combined selectivity for 1,2-PeD and 1,5-PeD over the 10Cu-Al₂O₃ catalyst was nearly constant at approximately 70%, while the value for the material with 0.20 g active Cu was a bit higher (71.3%). These data reveal that a high catalyst amount favors the generation of PeDs from FFA hydrogenolysis, which is consistent with previously reported results [10]. Based on the above findings, 1,2-PeD (48.1% selectivity) and 1,5-PeD (22.2% selectivity) with a combined yield up to approximately 60% at 85.8% FFA conversion were attained when using the 10Cu-Al₂O₃ with a higher catalyst amount at 413 K, 8 MPa H₂ and 8-h reaction time (Table 2, entry 7).

The effect of reaction time was investigated when using 10Cu-Al₂O₃ to elucidate the reaction pathways of FFA hydrogenolysis (Fig. 9). The conversion of FFA increased drastically, to 60.4%, in the first 8 h, and then rose gradually to 87.6% as the reaction time was extended to 24 h. Both 1,2-PeD and

Fig. 8. Effect of the active Cu amount in the 10Cu-Al₂O₃ catalyst during FFA hydrogenolysis. Reaction conditions: 40 g 10 wt% FFA in ethanol, 413 K, 6.0 MPa H₂, 8 h.

Fig. 9. Effect of reaction time during FFA hydrogenolysis over the 10Cu-Al₂O₃ catalyst. Reaction conditions: 0.20 g Cu, 40 g 10 wt% FFA in ethanol, 413 K, 6 MPa H₂.

1,5-PeD were the major products, and their selectivities increased to maximums of 48.6% and 22.7% after 8 h, respectively. The 1,2-PeD selectivity subsequently underwent a gradual decrease to 43.8% with increasing time, while the 1,5-PeD selectivity essentially plateaued. From these results, it is evident that 1,2-PeD is more prone to excessive hydrogenolysis compared to 1,5-PeD, in agreement with previous reports [9]. The continual decrease in 2-MF selectivities can be attributed to further hydrogenation to 2-MTHF (for which the selectivity increased from 0.2% to 3.3%, not shown) and further C–O hydrogenolysis to 1-pentanol and 2-pentanol [16].

Based on the above analytical results and the existing literature [17,44,45], we propose the reaction pathways for FFA hydrogenolysis over a Cu-Al₂O₃ bifunctional catalyst shown in Scheme 1. Initially, the FFA is adsorbed on the Lewis acid sites of the Al₂O₃ support via the –OH group [45], analogous to the adsorption of FFA on the basic sites of hydrotalcite [10,30]. Subsequently, the C²=C³ or C⁴=C⁵ bond in the furan ring of FFA is partially hydrogenated to form semi-hydrogenated species [17,44], most likely via hydrogenation of the C² or C⁵ atoms. This induces the ring opening reaction by decreasing the barrier to C–O cleavage [17,37,44]. Finally, the ring-opened species are rapidly hydrogenated to the target products 1,2-PeD or 1,5-PeD. Because of the steric hindrance of the –CH₂OH group, it is more likely that the active H species on the Cu particles will partially hydrogenate the C⁴=C⁵ bond to form the key intermediate that generates 1,2-PeD, as opposed to partially hydrogenating the C²=C³ to eventually produce 1,5-PeD. Therefore, a much higher selectivity for 1,2-PeD is predicted over the Cu catalysts, which is consistent with previous studies regarding the hydrogenolysis of FFA over Ru/MnO_x [17,44] and Cu-Mg₃AlO_{4.5} catalysts [30]. It should be noted that the Lewis acid sites of the Al₂O₃ support could also assist in the dehydration of the –OH group of FFA to give 2-MF, which is a major competitive reaction during the production of PeDs from FFA. In addition, these Lewis acid sites could also induce secondary reactions of the PeDs products to 1-pentanol or 2-pentanol by dehydration. Due to the weak affinity of Cu for C=C bonds [8,37], the complete hydrogenation of FFA to THFA and of 2-MF

Scheme 1. The proposed reaction paths for FFA hydrogenolysis over a Cu-Al₂O₃ bifunctional catalyst.

to 2-MTHF are not favored over the Cu-Al₂O₃ catalysts, leading to low selectivities for THFA and 2-MTHF (both < 8%) in most cases. Further work is currently underway to more clearly elucidate the reaction pathways and mechanism associated with PeD generation from FFA over Cu-based bifunctional catalysts.

4. Conclusions

Cu-Al₂O₃ bifunctional catalysts with Cu loadings from 2 to 30 wt% were prepared by co-precipitation and tested in the hydrogenolysis of biomass-derived FFA to 1,2-PeD and 1,5-PeD. At 413 K and 8 MPa H₂, the best catalyst, having 10 wt% Cu content, generated 85.8% conversion and 70.3% combined selectivity for 1,2- and 1,5-PeDs. The cooperative function of highly dispersed Cu particles and an acidic Al₂O₃ support evidently played an important role in obtaining high PeDs yields. In addition, the combination of active Cu particle sizes and surface acidity is also very important to attaining high PeD yields. Even though the present catalytic performances of these catalysts requires further improvement, the important findings of this work demonstrate the potential applications of inexpensive Cu-based, Cr-free catalysts to the efficient hydrogenolysis of biomass-derived furan compounds with multifunctional groups to valuable diol products.

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Graphical Abstract

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Selective hydrogenolysis of biomass-derived furfuryl alcohol into 1,2- and 1,5-pentanediol over highly dispersed Cu-Al₂O₃ catalystsHailong Liu, Zhiwei Huang*, Haixiao Kang, Chungu Xia, Jing Chen*
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The size and cooperative effects of highly dispersed Cu nanoparticles and an acidic Al₂O₃ support are significant factors affecting the selective hydrogenolysis of furfuryl alcohol to 1,2- and 1,5-pentanediols over Cu-Al₂O₃ catalysts.

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高分散 Cu-Al₂O₃ 催化剂选择氢解生物质基糠醇制备 1,2-和 1,5-戊二醇刘海龙^{a,b}, 黄志威^{a,*}, 康海笑^a, 夏春谷^a, 陈 静^{a,#}^a中国科学院兰州化学物理研究所苏州研究院, 羰基合成与选择氧化国家重点实验室, 甘肃兰州730000^b中国科学院大学, 北京100049

摘要: 生物质是唯一可再生的有机碳资源, 开发清洁高效稳定的催化剂体系, 将富氧的生物质及其平台化合物高选择性的 C–O 键氢解转化为可供石化行业利用的高附加值产品成为当前的研究热点. 糠醛可由农林副产物如玉米芯, 甘蔗渣和秸秆等中富含的半纤维素经酸水解而得. 采用便宜的糠醛及其衍生物糠醇和四氢糠醇为原料, 通过温和条件下一步选择氢解合成高附加值的 1,2-和/或 1,5-戊二醇的研究受到了越来越多的关注, 但目前的研究主要集中在 Ru, Rh, Pt 和 Ir 等贵金属催化剂, 对无铬非贵金属催化剂的研究甚少; 此外, 目前文献报道催化剂的活性和选择性还有待提高. 开发清洁高效的非贵金属催化剂在温和条件下选择氢解糠醇或糠醛是目前面临的一项难题. 我们的最新研究发现采用以水滑石为前驱体制备的弱碱性 Cu-Mg₃AlO_{4.5} 双功能催化剂在糠醇选择氢解反应中表现出优异的催化性能, 在 413 K 和 6 MPa 的温和条件下可取得约 80% 的戊二醇总收率. 虽然碱性载体有利于稳定糠醇氢解中间体并抑制羟基脱水从而提高戊二醇选择性, 但也有文献报道酸性载体或助剂同样对呋喃衍生物的选择氢解制二元醇有促进作用. 为了研究固体酸负载的双功能催化剂在糠醇氢解中的催化性能, 我们采用共沉淀法制备了酸性 Al₂O₃ 载体分散的不同 Cu 含量 (2–30 wt%) 的纳米双功能催化剂, 并对比考察了其他不同载体 (SiO₂, TiO₂, ZrO₂, MgO 和 ZnO) 负载的催化剂, Al₂O₃ 负载的 Ni, Co 和 Pt 催化剂及商业 Cu-Cr 催化剂的糠醇氢解性能. 研究发现, 在金属负载量相同时, Cu-Al₂O₃ 催化剂表现出最优异的糠醇氢解性能, 而 Cu-Al₂O₃ 催化剂的转化率随 Cu 铜含量的升高先增高后降低, 在 20 wt% 时达最高, 而戊二醇的总选择性在 10 wt% 时达最高.

为了揭示 Cu-Al₂O₃ 催化剂在糠醇氢解反应中的构效关系, 采用 X 射线衍射 (XRD), 透射电镜 (TEM), N₂ 物理吸附, N₂O 化学吸附和 NH₃/CO₂ 程序升温脱附 (NH₃/CO₂-TPD) 等多种物理化学手段对催化剂的结构和表面性质进行了表征. XRD, TEM 和 N₂O 化学吸附的表征结果说明, 共沉淀法制备的 Cu-Al₂O₃ 催化剂中 Cu 颗粒高分散于 Al₂O₃ 载体上, 且两者结合紧密. NH₃/CO₂-TPD 表征发现, Cu-Al₂O₃ 催化剂中酸性位占主导地位, 随铜含量的升高表面酸量递减. 由于不同 Cu 含量的 Cu-Al₂O₃ 催化剂中 Cu 颗粒尺寸, 酸碱量和 Cu 与载体之间相互作用的差异, 在催化糠醇选择氢解中表现出不同

的催化性能.

通过关联催化剂中 Cu 颗粒尺寸与戊二醇生成 TOF 发现, 该反应为结构敏感性反应, 催化剂的 TOF 受 Cu 颗粒尺寸控制, Cu 颗粒尺寸在 1.9–2.4 nm 范围内时取得最高的催化活性. 催化剂的表面酸碱性也是影响 Cu-Al₂O₃ 催化性能的另一重要原因, 适当增加 Cu-Al₂O₃ 催化剂的表面酸性可以提高糠醇氢解活性和戊二醇选择性, 但是采用强酸性载体时, 反应副产物急剧增加而降低戊二醇选择性, 增加催化剂的碱性同样对催化活性和选择性不利. 通过比较不同制备方法合成的 Cu-Al₂O₃ 催化剂的糠醇氢解性能发现, 催化剂中高分散的 Cu 与酸性 Al₂O₃ 载体之间的高效紧密接触是取得高戊二醇收率的关键, 同时催化剂中 Cu 不同的电子状态, 可能也会影响催化性能. 在考察催化剂的循环使用过程中发现, 催化剂的结构稳定, 使用多次后催化剂结构未发生明显变化, 性能未发生明显下降.

此外, 我们还考察了反应温度, 氢气分压, 催化剂量和反应时间等动力学条件对 Cu-Al₂O₃ 催化剂性能的影响, 发现催化剂活性和产物的选择性均受反应条件明显影响, 在优化条件 (413 K, 8.0 MPa H₂) 下, 采用共沉淀法制备的 10Cu-Al₂O₃ 催化剂可以取得约 70% 戊二醇的选择性和 60% 的总收率. 结合对实验结果的分析及相关文献报道, 我们还推测了 Cu-Al₂O₃ 双功能催化剂上糠醇氢解的反应路径.

关键词: 糠醇; 1,2-戊二醇; 1,5-戊二醇; 选择氢解; 铜铝催化剂

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