Crystal-phase engineering of PdCu nanoalloys facilitates selective hydrodeoxygenation at room temperature

Shaopeng Li,1,5 Minghua Dong,1,2,6 Mi Peng,3,5 Qingqing Mei,1 Yanyan Wang,1,2 Junjuan Yang,1 Youdi Yang,1 Bingfeng Chen,1 Shulin Liu,1,2 Dequan Xiao,4 Huizhen Liu,1,2,* Ding Ma,3,* and Buxing Han1,2,*

*Correspondence: liuhz@iccas.ac.cn (H.L.); dma@pku.edu.cn (D.M.); hanbx@iccas.ac.cn (B.H.)
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Graphical abstract

Public summary
- Selectively cleaving of C–O bonds in lignocellulosic biomass is very difficult. The PdCu nanoalloys can catalyze the selective hydrodeoxygenation reaction of HMF to DMF
- The PdCu nanoalloys with specific crystallographic phases can improve the selectivity of hydrodeoxygenation reaction
- The body-centered cubic (BCC) PdCu nanoalloys exhibited outstanding performance with 93.6% yield of DMF at room temperature
- PdCu/AC-BCC could also catalyze other aromatic alcohols at room temperature
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Shaopeng Li, Minghua Dong, Mi Peng, Qingqing Mei, Yanyan Wang, Junjuan Yang, Youdi Yang, Bingfeng Chen, Shulin Liu, Dequan Xiao, Huizhen Liu, Ding Ma and Buxing Han

1 Beijing National Laboratory for Molecular Sciences, Key Laboratory of Colloid and Interface and Thermodynamics, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
2 School of Chemical Science, University of Chinese Academy of Sciences, Beijing 100049, China
3 Beijing National Laboratory for Molecular Engineering, College of Chemistry and Molecular Engineering and College of Engineering, BIC-ESAT, Peking University, Beijing 100871, China
4 Center for Integrative Materials Discovery, Department of Chemistry and Chemical Engineering, University of New Haven, West Haven, CT 06516, USA

*Correspondence: liuhz@iccas.ac.cn (H.L.); dma@pku.edu.cn (D.M.); hanbx@iccas.ac.cn (B.H.)

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Selective hydrodeoxygenation of biomass-derived aromatic alcohols to value-added chemical or fuel is of great importance for sustainable biomass upgrading, and hydrodeoxygenation of 5-hydroxymethylfurfural (HMF) to 2,5-dimethylfuran (DMF) is one of the most attractive reactions. Achieving the conversion of HMF to DMF using H2 at ambient temperature is challenging. In this work, we used PdCu nanoalloys to catalyze the selective hydrodeoxygenation reaction of HMF to DMF using H2 as the reducing agent. The reaction path and the product selectivity are governed by the crystallographic phase of the PdCu nanoalloys. It was discovered that body-centered cubic (BCC) PdCu nanoalloys supported on activated carbon (AC) exhibited outstanding performance with 93.6% yield of DMF at room temperature (PdCu/AC-BCC). A combination of experimental and density functional theory (DFT) studies showed that the tilted adsorption modes of furanic intermediates on PdCu-BCC nanoalloy surfaces accounted for the high selectivity of DMF, however, furan ring was activated on PdCu face-centered cubic (FCC) nanoalloy surfaces. Furthermore, PdCu/AC-BCC could also catalyze the hydrodeoxygenation of other aromatic alcohols at room temperature while maintaining the aromatic structures. This work opens the way for selective hydrodeoxygenation of the aromatic alcohols at room temperature with the aromatic ring intact.

INTRODUCTION

Production of commodity chemicals from renewable feedstocks has received significant attention as a promising way to diminish our dependence on fossil resources and construct sustainable chemical industries.

Transition-metal-catalyzed hydrodeoxygenation reaction of oxygenated organic compounds has attracted broad interest in recent years because of their important role in biomass feedstock transformation as well as in pharmaceuticals industry. However, selectively activating and cleaving C–O bonds in lignocellulosic biomass is very difficult. On the one hand, the commonly used noble metal catalysts often have strong hydrogenation ability to C=C bonds and aromatic rings, which are ubiquitous in biomass-derived compounds, resulting in undesirable product. On the other hand, in order to obtain high conversion and product selectivity, a high reaction temperature is often required.

The selective hydrodeoxygenation of 5-hydroxymethylfurfural (HMF), which is considered an important biomass platform chemical, to 2,5-dimethylfuran (DMF) is one of the most attractive reactions in biomass transformation. DMF has been identified as a highly interesting candidate of liquid fuel with high energy densities (30 kJ/cm³) and research octane numbers (RON = 119), holding great potential to substitute for petroleum-based gasoline, and can also be converted to valuable benzene-based chemicals via Diele-Alder reactions. Various products, such as 2,5-bis(hydroxymethyl)furan (DHMF), 5-methylfurfural (5-MF), 5-methylfurfurylacol (5-MFA), 2,5-bis(hydroxymethyl)tetrahydrofuran (DTHF), 5-methyltetrahydrofuran-2-methanol (MTHFM), 2-hexanol (HOL), and 2,5-dimethyltetrahydrofuran (DMTHF), are produced in the catalytic HMF hydrodeoxygenation reaction as side products, as shown in Scheme S1. Indeed, different catalytic systems have been used for selective hydrodeoxygenation of HMF to DMF. Bimetallic catalytic systems play an important role in improving DMF selectivity by forming core-shell structure, electronic effect between two metals, and providing multiple sites. PtCo2 nanoparticles were used in transformation of HMF to DMF with 98% yield at 160°C, and it was modeled as an alloy core covered by a Co2O3 monolayer, in which the Co2O3 layer repelled furan rings to prevent further hydrogenation. Similar to PtCo2 core-shell structures, near-ambient-pressure X-ray photoelectron spectroscopy (NAP-XPS) suggested that NiCo2 nanocrystals involve a Cu-rich core and a 1:1 molar Ni: Cu shell, which exhibited a DMF yield of 98.7% at 180°C. One-hundred percent HMF conversion and 92.9% selectivity to DMF were obtained over Co-allyl Pt single-atom catalysts under 1.0 MPa H2 at 180°C, where Pt sites were responsible for H2 activation and PtCu1−x−yCo2x+y sites actively catalyzed C=O bonds. Cobalt and copper bimetallic catalyst on N-graphene-modified Al2O3 could efficiently catalyze the selective hydrodeoxygenation of HMF to DMF at 180°C, and the catalytic performance resulted from the synergistic effect between defects and active metal. Co@Cu/3CoAlOx sequentially catalyzed the C=O hydrogenation and C–OH hydrogenolysis to yield as high as 98.5% DMF at 180°C. It is generally accepted that crystallographic phases of nanoalloy catalysts could also affect the catalytic performance. However, synthesizing nanoalloys with specific crystallographic-phase catalysts to improve the selectivity of hydrodeoxygenation reaction of HMF has not yet been reported. More importantly, although satisfactory DMF yield has been obtained over the catalytic systems that have been reported, the harsh reaction conditions required usually cause serious issues and thus limit their practical applications. It is urgent to explore an efficient catalytic system to achieve the conversion of HMF to DMF under mild conditions, especially at room temperature. Cu–Pd/reduced graphene oxide could catalyze the selective hydrogenation of HMF to DMF using 2-propanol as the reducing agent. Hydrogen is an ideal reducing agent. However, when hydrogen was used as the hydrogenation agent, only Pd-based catalysts could catalyze the selective hydrodeoxygenation of HMF to DMF at temperatures lower than 100°C, but the addition of acid as promoter is necessary. For example, 96% yield of DMF was obtained over PdAu/C catalyst at 60°C in the presence of HCl. In this work, we synthesized PdCu nanoalloys and achieved the selective hydrogenation reaction of HMF to DMF at ambient temperature using H2 as the reducing agent. It was discovered that the synthesized body-centered cubic (BCC) PdCu nanoalloys supported on activated carbon (AC) (i.e. PdCu/AC-BCC) displayed outstanding performance for hydrodeoxygenation reaction, with a DMF yield of 93.6% at room temperature. The crystallographic phase of PdCu nanoalloys governed the selectivity of the hydrogenation of HMF. The hydrogenation of furan ring was dominating over face-centered cubic (FCC) PdCu nanoalloys supported on activated carbon (AC) (i.e., PdCu/AC-FCC) displayed low selectivity for hydrodeoxygenation reaction, with a DMF yield of 93.6% at room temperature.

RESULTS

The PdCu/AC-BCC catalyst was synthesized by an impregnation-reduction-calcination method, the details of which are shown in the section "materials and methods." Figures 1A and S1 show the transmission electron microscopy (TEM) images of the as-prepared PdCu/AC-BCC. Uniform nanoparticles with average diameter of 4.8 nm were immobilized over the AC support. Figure 1B gives an aberration-corrected high-angle annular dark-field (HAADF) scanning...
TEM (AC-STEM) image taken from a typical PdCu nanoparticle. The alloy particles have a lattice spacing of 2.08 Å, which is in good agreement with the value of the (111) plane of PdCu/BCC nanocatalysts. The STEM line scan results show that the elements of Pd and Cu are homogeneously distributed throughout nanoparticle (Figure 1C), which is confirmed by the corresponding energy dispersive spectroscopy (EDS) elemental mapping images (Figure 1D). The Pd/Cu atomic ratio was about 1:1. Additional TEM images of PdCu/AC-BCC reveal the uniformity of PdCu nanocatalysts (Figure S2). For comparison, FCC-structured PdCu nanocatalysts (PdCu/AC-FCC) at an annealing temperature of 200 °C were prepared (using the same precursor and composition as that for PdCu/AC-BCC; see section “Materials and methods”). Figure S7 gives the HAADF-STEM image taken from a typical individual PdCu nanoparticle in the PdCu/AC-FCC, which demonstrates the formation of nanocatalysts with lattice spacing of 1.99 Å, and the result was consistent with the value of (100) plane of PdCu/FCC nanocatalysts. Furthermore, the PdCu nanocatalysts crystalline structure was also characterized by X-ray diffraction (XRD) and the results are shown in Figure S8. No obvious diffraction peaks of metallic PdCu were observed in the PdCu/AC-FCC and PdCu/AC-BCC catalysts, mainly because of ultra-small size and good dispersion of the nanocatalysts. To get more information about the crystal structure, the PdCu nanocatalysts without support were prepared and characterized by XRD (Figure S8). The XRD peaks of PdCu nanocatalysts without support annealed at 200 °C can be indexed as FCC structure. The PdCu/AC-BCC (110) and (100) peaks at 42.8° and 62° are clearly visible in Figure S8 for the PdCu nanocatalysts annealed at 400 °C, suggesting the formation of PdCu-BCC structure. Similarly, the results were obtained on the PdCu/AC 10 wt% without support annealed at 200 °C and the yield of DMF was only 6% at 30 °C (Table 1, entry 5). These results indicated PdCu/AC-BCC was an outstanding catalyst for hydrodeoxygenation of HMF. The reason for the excellent performance is discussed in the following sections. Interestingly, increasing the reaction temperature to 100 °C increased the reaction rate of PdCu/AC-BCC (71.2 h⁻¹, Table 1, entry 6), which is much higher than those in previous reports at similar reaction conditions (Table S1). At 160 °C, the yield of DMF could reach 97.2% (Table 1, entry 7), demonstrating that further hydrogenation to the furan ring was still inhibited at high temperature. Moreover, the hydrodeoxygenation of HMF to DMF could be carried out under atmospheric pressure and room temperature over PdCu/AC-BCC, and the yield of DMF reached 38.6% (Table 1, entry 8). These results verified that PdCu/AC-BCC is an excellent catalyst for selective hydrogenation of HMF at low temperature. The effect of H₂ pressure and initial HMF concentration were also checked and the results are shown in Table S4. The conversion and DMF yield increased as hydrogen pressure while decreasing as initial HMF concentration (Table S4, entries 1–5). The catalytic loading also affected the catalytic performance and, when the catalyst loading was 0.5 wt %, the HMF conversion and DMF yield were only 56% and 52%, respectively (Table S4, entries 6 and 7).

Very interestingly, the selectivity of DMF depended strongly on the crystallographic phase of PdCu nanocatalysts in the catalysts (Figure 3A and Table S2). The PdCu/AC-BCC catalystized the hydrodeoxygenation reaction selectively with 93.6% selectivity of DMF. However, the PdCu/AC-FCC promoted the hydrogenation of the furan ring with only 9.0% selectivity to DMF under the same reaction conditions. The effect of reaction time over the PdCu/AC-BCC is shown in Figure 3B. Clearly, for PdCu/AC-BCC, the conversion of HMF increased with the increase of reaction time, reaching a full conversion at around 16 h at 30 °C. The selectivity toward DMF of PdCu/AC-BCC increased with the increase of reaction time, reaching a full conversion at around 16 h at 30 °C. The selectivity toward DMF of PdCu/AC-BCC increased with the increase of reaction time, reaching a full conversion at around 16 h at 30 °C.
reaction time and reached 93.6% after 20 h, because DMF was formed via intermediates. At a reaction of 20 h, besides DMF and trace amounts of other products, only about 5% DHTHF was detected. Even after the reaction time was extended to 24 h, DMF was not hydrogenated to DMTMF, demonstrating that PdCu/AC-BCC was capable of selectively catalyzing the designated reaction rather than the deep hydrogenation of furan rings to undesired products. As shown in Table S7, the carbon balances of the reaction at different reaction times were all above 94%.

Different from that of PdCu/AC-BCC catalyst, the main product was DHMF with only 18% yield of the desired product DMF, although the conversion of HMF could reach 99.9% in 4 h over PdCu/AC-FCC (Figure S13). DHTHF became the dominant product with the prolonging reaction time, indicating that DHMF was converted to DHTHF. DMF, MTHFM, 5-MFA, and 5-MF were also detected. The yield of DHTHF decreased to 8% in 24 h and it was further hydrogenated to DMTMF. These results suggested that the reaction pathways over PdCu/AC-FCC include the hydrogenation of the furan ring and the hydrodeoxygenation reaction. Furthermore, the total yield of DHTHF and DMTMF was much higher than DMF. Throughout the reaction process, no single product could reach a selectivity higher than 50%, showing that PdCu/AC-FCC is not a highly selective catalyst for the hydrodeoxygenation of HMF. To verify the result for the high selectivity to DMF, control experiments using DMF as the substrate were conducted (Table S3). Notably, under the similar reaction conditions, while DMF was fully converted to DMTMF through the hydrogenation of furan ring over PdCu/AC-FCC, the hydrogenation of DMF was almost completely blocked over PdCu/AC-BCC, confirming that the lattice structure of PdCu is responsible for its selectivity. The support also affected the catalytic performance, and PdCu-BCC and PdCu-ACC are inactive for the reaction (Table S3).

Table 1. Hydrogenolysis of HMF to DMF over various catalysts

| Entry | Catalyst | Temperature (°C) | Time (h) | Conversion (%) | Yield (%) | Ratea (h⁻¹) |
|-------|----------|-----------------|---------|---------------|-----------|------------|
| 1     | –        | 30              | 20      | 0             | 0         | 0          |
| 2     | AC       | 30              | 20      | 0             | 0         | 0          |
| 3     | Pd/AC    | 30              | 20      | 15            | 6         | 1          |
| 4     | Cu/AC    | 30              | 20      | Trace         |           |            |
| 5     | PdCu/AC-BCC | 30             | 20      | >99           | 93.6      | 4.7        |
| 6a    | PdCu/AC-BCC | 100            | 2       | >99           | 94.3      | 71.2       |
| 7a    | PdCu/AC-BCC | 160            | 1       | >99           | 97.2      | 145.3      |
| 8a    | PdCu/AC-BCC | 30              | 20      | 45            | 38.6      | 1.6        |

Reaction conditions: HMF (38 mg); catalyst (30 mg); THF (2 mL); H₂ pressure (4 MPa).
aRate = moles of product × moles of metal⁻¹ × h⁻¹.

Also, no HMF conversion and DMF yield was obtained over PdCu/Al₂O₃ and PdCu/Al₆O₃. As shown in Figure S29, the average sizes of PdCu nanoparticles loaded on Al₂O₃ and TiO₂ all were above 10 nm, much larger than those in 1 wt % PdCu/Al₂O₃, which led to inactivity. Furthermore, the XRD in Figure S9 suggested that the PdCu-FCC phase still existed in the catalyst 10 wt % PdCu/Al₂O₃. The hydrogenation of furanic ring was dominant over 10 wt % PdCu/Al₂O₃ since the FCC-phase PdCu nanoparticles had higher hydrogenation activity than the BCC phase (Table S8).

The DFT calculations were performed to investigate the origin of crystalline-phase-controlled selectivity. According to the literature and AC-STEM results, (100) and (111) surfaces were built to represent the exposed facets of PdCu-FCC and BCC nanoparticles (Figures 4A, S15, and S16). The distance between metal atoms on the top layer in PdCu-BCC is longer than that in PdCu-FCC, which coincides with AC-STEM characterizations. It has been reported that the adsorption modes of HMF were highly sensitive to the microstructure of catalytic surfaces, and it further determined reactants’ transformation. Two kinds of adsorption configuration, η adsorptions and σ adsorptions, as noted in Figures 4B and 4C, were under discussion in our calculations. The interaction of HMF with PdCu surface involves the η-adsorption modes mainly via the oxygenated pendant functions (aldehyde and hydroxyl groups), while, in σ-adsorption mode, the furan ring lies flat on nanoalloy surfaces, as shown in Figure 4C. It is worth noting that dissociated adsorption modes were not taken into comparison. Besides the reactive HMF and the product DMF, the adsorptions of DMF and MFA as key intermediates during hydrodeoxygenation were explored and the most stable adsorption structures are presented in Figures S17–S20.

HMF adsorbed on BCC (111) and FCC (100) surfaces via σ-adsorption modes with ~1.00 eV and ~0.71 eV, respectively, both of which were stronger than corresponding η-adsorption modes in Figure S17. Although both furan ring and aldehyde group in HMF were activated in σ-adsorption mode, either on PdCu-BCC or -FCC, the aldehyde group was first hydrogenated to produce DHTMF in our experiment. This is also consistent with the results reported in the literature. A discussion of the reaction path of HMF hydrogenation and hydrodeoxygenation over PdCu-BCC below further demonstrates this in theory. When HMF adsorbed on the same PdCu-BCC surface, the η-configuration was favored, and the furan ring was not activated in η-adsorption of DHTMF. While on PdCu-FCC, HMF preferred to be adsorbed in σ-adsorption configuration, 0.43 eV stronger than its η-adsorption. The furan ring was activated in σ-adsorption on FCC (100), due to the formation of new metal-carbon bonds and the partial rehybridization of ring carbon atoms from sp² to sp³, which had been reported wildly. The present chemical interactions between furan rings and FCC (100) surfaces promoted the ring hydrogenations and explained the ring reactivity of PdCu-FCC. The adsorptions of MFA and DMF were also explored both on PdCu-FCC and -BCC, and the results were similar to that of DHTMF. MFA σ-adsorption with ring activation was favored on PdCu-FCC, yet on PdCu-BCC the ring activation was inhibited by η adsorption (Figure S19). DMF, precluding oxygenated pendant functions, adsorbed on PdCu-BCC (100) surface weakly (~0.33 eV adsorption energy), then the furan ring remained intact. The furan ring in DMF was activated and vulnerable to hydrogenation in σ-adsorption on FCC (100) with ~0.45 eV adsorption energy. Thus, different ring hydrogenation reactivity over PdCu-FCC and PdCu-BCC could be attributed to the different adsorption behaviors of furan rings on these surfaces with corresponding adsorption sites.

The reaction pathway of HMF hydrogenation and hydrodeoxygenation over PdCu-BCC was also confirmed with DFT computations (Figures S5, S22, and S23). The H₂ dissociation barrier was calculated as about 0.2 eV (Figure S21), consistent with previous calculations. Due to the low H₂ dissociation barrier, in the following steps the hydrogen atoms were assumed to adsorb on the surface directly. Hydrogenation of the carbonyl group first takes place on the C atom,
leading to an alkoxide intermediate IM1. Next, a second hydrogen atom was added to IM1 and yielded DHMF. The overall barrier of C=O hydrogenation was 0.47 eV, then the overall barriers of hydrodeoxygenation and ring hydrogenation were calculated as 0.56 eV and 0.80 eV, indicating that the first step of HMF conversion on PdCu-BCC was hydrogenation of the carbonyl group (Figures S22 and S23). Three transition states (TS3–TS5) were confirmed during the subsequent hydrodeoxygenation of DHMF to MFA. The C–O bond scission took place over a Cu–Pd site, and the formed intermediate IM2 and OH adsorbed on sublayer Pd and top Cu, where an exothermic 0.52 eV reaction energy and a 0.46 eV barrier was calculated. One H2O molecule was later produced from co-adsorbed OH and H, with an exothermic 0.52 eV reaction energy and a 0.46 eV barrier. After the H2O desorption, MFA was formed through the combination of IM2 and another surface H species, which exhibited an exothermic 0.62 eV reaction energy and a 0.48 eV barrier. A similar hydrodeoxygenation pathway from MFA to DMF was calculated with an overall reaction barrier 0.89 eV and exothermic energy 1.62 eV.

The loose arrangement of surface atoms with PdCu-BCC repelled furan rings of hydrogenation intermediates, while ring adsorptions were favored by close-packing PdCu-FCC surfaces. Our work opened a new insight into the selective hydrodeoxygenation of biomass-derived furanics catalyzed by bimetallic nanoparticles. We also investigated the hydrodeoxygenation of other aromatic alcohols, and the results are presented in Table S6. PdCu/AC-BCC could catalyze the hydrodeoxygenation of a series of substrates under mild conditions with high conversions and excellent selectivities to the desired products with the aromatic rings intact.

The recyclability of PdCu/AC-BCC catalyst was evaluated at 100°C and the activity of the catalyst slightly decreased after recycling four times (Figure S14). As shown in Figure S3, the average diameter of PdCu/AC-BCC after reaction was 5.0 nm, which is similar to the fresh PdCu/AC-BCC catalyst, thus no significant sintering was observed. Also, EDS mapping shows no segregation of Pd or Cu after reactions (Figure S4). The crystallographic phase was characterized by high-resolution TEM (HRTEM), and the d-spacing of PdCu nanoalloys after reaction was 2.14 Å, corresponding to PdCu-BCC (111) facets, which means that the BCC phase of PdCu was not changed after reaction. Maybe the decrease in catalyst activity is attributed to the inevitable loss of catalyst in the recovery process, since only 16 mg of PdCu/AC-BCC (80% of the original amount) was recovered.

Figure 4. Furanics adsorption behaviors on PdCu surfaces (A) Exposed surfaces of PdCu-FCC/BCC considered in DFT calculations. The distances between neighbor top metal atoms are marked. (B) Adsorption energies of HMF, DHMF, MFA, and DMF on PdCu-BCC, respectively. (C) Optimized geometries for adsorption configuration of HMF and DHMF on PdCu-BCC. Dark blue, Pd; light blue, sublayer Pd; orange, Cu; pink, sublayer Cu; silver, H; gray, C; red, O.
DISCUSSION

In summary, we reported that the introduction of Cu into Pd could tune the electronic structure of Pd through the electron transfer from Cu to Pd. This electronic structure feature greatly promoted the catalytic activity of PdCu nanoalloys for the hydrodeoxygenation of HMF at room temperature. The crystallographic structure feature greatly promoted the catalytic activity of PdCu nanoalloys for hydrodeoxygenation of HMF. On PdCu/AC-BCC, a 93.6% yield toward the desired DMF product could be reached even at room temperature. The lower energy barrier of hydrodeoxygenation of C–OH and C=O than that of furan hydrogenation over PdCu/AC-BCC resulted in the high selectivity of DMF. However, PdCu/AC-FCC preferred to promote the hydrogenation of furan ring with low DMF selectivity. We believe that the PdCu/AC-BCC catalyst has great potential for applications due to its obvious advantages, such as extremely high activity and selectivity, and being easy to prepare. In addition, the findings of this work are useful for designing other efficient catalysts for selective hydrogenation of compounds with two or more unsaturated bonds.

MATERIALS AND METHODS

Materials

CuCl2·2H2O (>99.0%), PdCl2 (>99.0%), sodium borohydride, and ethyl alcohol were purchased from Sinopharm Chemical Reagent. The AC was purchased from Fujian Xinsen Chemical Industry. Tetrahydrofuran, 5-hydroxymethylfurfural, 2,5-dimethylfuran, 2,5-bis(hydroxymethyl)furan, 5-methylfurfural, 5-methylfurfurylcarboxyl, 5-methyltetrahydrofuran-2-methanol, 2-hexanol, 2,5-dimethyltetrahydrofuran, and n-decane were purchased from J&K. H2 (99.0%) and Ar (99.99%) were supplied by Beijing Analytical Instrument Company. Ultrapure water (resistivity > 18 MΩ·cm) was used during the experimental process.

Methods

The PdCu/AC catalysts were synthesized via the co-reduction method and were then annealed at a controlled temperature. In a typical experiment, 0.2 g of AC was dispersed in 50 mL of ultrapure water with sonication for 3 h to get a well-dispersed AC suspension.

Then, 5.0 mL of aqueous solution containing CuCl2 and H2PdCl4 (with molar ratio of Cu2+:Pd2+ = 1:1) was mixed with AC suspension in an ice water bath. Then fresh aqueous solution containing NaBH4 was added drop-wise with continuous magnetic stirring under ultrapure water three times (3 × 30 mL) and ethanol twice (2 × 30 mL) and dried in a vacuum oven at 60°C for 12 h. The ground powder was calcined in a tube furnace (Anhui Kemi Machinery Technology; model TFV-1200-50-I-220) for 4 h (reducing gas contains 10 vol % hydrogen and 90 vol % argon) to obtain PdCu/AC. The PdCu/AC-FCC and PdCu/AC-BCC were obtained at annealing temperatures of 200°C and 400°C, respectively. The synthesis conditions for Pd/AC and Cu/AC were similar to those of PdCu/AC-BCC except for the changing ratio of Pd2+/Cu2+. PdCu/TiO2 and PdCu/Al2O3 were synthesis with the same method as PdCu/AC-BCC.

Characterization

The TEM and EDS images of the catalysts were obtained using a JEOL-2100F and JEM-200F electron microscope operated at 200 kV. JEM ARM300F equipped with an EDX detector (JEOL) and an energy filter (GATAN) operated at 300 kV was used for aberration-corrected HAADF-STEM images. The XPS measurements were carried out on an ESCALAB 220Xi spectrometer at a pressure of ~3 × 10−9 mbar (1 mbar = 100 Pa) using Al Kα as the excitation source (hv = 1,486.6 eV) and operated at 15 kV and 20 mA. The binding energies were calibrated with the C1s level of adventitious carbon at 284.8 eV as the internal standard reference. The XPS samples were prepared without exposure to the air. The XRD experiment was performed on Rigaku D/ max 2500 with nickel filtered Cu Kα (λ = 0.154 nm) operated at 40 kV and 20 mA. The contents of different elements in the PdCu/AC catalysts were analyzed by ICP-AES.

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Figure 5. Reaction pathway from HMF to DMF on PdCu-BCC (111) The structures of transition states are shown in insets, in which the key atomic distances are labeled in angstroms. Dark blue, Pd; orange, Cu; silver, H; gray, C; red, O.
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AUTHOR CONTRIBUTIONS

B.H., H.L., and D.M. conceived the idea and designed research. M.D. performed the DFT calculations. S.L. synthesized the catalysts and conducted the reaction tests. M.P. performed the XPS experiments. Q.M., Y.W., J.Y., Y.Y., B.C., and S.L. performed certain experiments, and discussed and analyzed data. S.L., M.D., D.X., D.M., and H.L. wrote the paper. All authors discussed the results and commented on the paper.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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SUPPLEMENTAL INFORMATION

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