

## Supporting Information

### Highly selective catalytic conversion of furfural to $\gamma$ -butyrolactone

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#### 1. Experimental

##### 1.1 Catalyst preparation

The supported metal catalysts were synthesized by incipient wetness impregnation using SiO<sub>2</sub> (Alfa Aesar, 147 m<sup>2</sup>/g) or TiO<sub>2</sub> (Xiya Reagent, 8 m<sup>2</sup>/g) as support. The monometallic catalysts were denoted as Mx/SiO<sub>2</sub> or Mx/TiO<sub>2</sub> (M = Pt, Pd, Rh, Ru, Ni, Co and Cu), where *x* was the loading in wt% of the supported metals. The precursor solutions were prepared by dissolving H<sub>2</sub>PtCl<sub>6</sub> (Alfa Aesar, 20.0%), PdCl<sub>2</sub> (Alfa Aesar, 59.5%), RhCl<sub>3</sub> (Alfa Aesar, 42.0%), RuCl<sub>3</sub> (Alfa Aesar, 48.0%), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Alfa Aesar, 98%), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Alfa Aesar, 98%) or Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O (Alfa Aesar, 98%) in an amount of distilled water just sufficient to fill the pores of the support. The precursor solution was added to the support dropwise and then treated with ultrasound for 1 h to facilitate metal dispersion. The catalysts were dried in air at 80 °C for 10 h and calcined at 450 °C for 3 h.

##### 1.2 Catalyst characterization

TEM images were taken with a JEM 2010 high-resolution transmission electron microscopy at 200 kV. More than 100 particles were collected to analyze the particle size distribution of the supported metal catalysts. The reduction and adsorption properties of the catalysts were measured on a Quantachrome ChemBET Pulsar TPR/TPD instrument equipped with a TCD. Temperature programmed reduction (H<sub>2</sub>-TPR) was used to test the reducibility of the catalysts. The sample was heated to 800 °C at a ramp of 10 °C/min with 5% H<sub>2</sub>/Ar mixture as reducing gas. The CO uptake

of the catalysts was determined by CO chemisorption, and each absorbed CO molecule was assumed to correspond to one active site. For each test, 200 mg of catalyst was placed in a sample tube and reduced in 10% H<sub>2</sub>/He at 450 °C for 1 h. After the reduction, the sample was purged with He at 450 °C for 30 min to remove absorbed H<sub>2</sub> on the catalyst surface and then cooled to room temperature. The titration was carried out by the pulse adsorption of 5% CO/He.

The dispersion of Cu 4.5/SiO<sub>2</sub> was determined by H<sub>2</sub>-N<sub>2</sub>O titration.<sup>1</sup> The catalyst (200 mg) was first pretreated at 200 °C for 2 h under Ar at a flow rate of 40 mL/min. Then a 10% H<sub>2</sub>/Ar mixture (40 mL/min) was shifted and the sample was heated to 300 °C for 1 h at a ramp of 10 °C/min. The amount of hydrogen consumption in this step was denoted as *X*. The reduced sample was purged with Ar at 300 °C for 1 h, and then it was cooled to 60 °C. Afterwards, a flow of 10% N<sub>2</sub>O/N<sub>2</sub> (40 mL/min) was used to oxidize the surface copper atoms to Cu<sub>2</sub>O at 60 °C for 1 h. Then the sample was flushed with Ar for 1 h to remove the oxidant. Finally, the oxidized sample was reduced in 10% H<sub>2</sub>/Ar at a flow rate of 40 mL/min, and the hydrogen consumption was denoted as *Y*. The dispersion of Cu was calculated as:

$$D = (2 \times Y/X) \times 100 \% \quad (1)$$

### 1.3 Oxidation of furfural

Isopropanol (SCR Beijing, > 99.5%), 1,2-dichloroethane (J&K Chemical, 99%),  $\gamma$ -butyrolactone (Xiya Reagent, 99%), hydrogen peroxide (Beijing Modern Oriental Fine Chemistry Co., Ltd., 30%), formic acid (SCR Beijing, 88%), Amberlyst-15 (Aladdin Industrial Corporation) and H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> (Alfa Aesar) were purchased. Methanol, tetrahydrofuran, benzene, toluene, ethyl acetate, tetrachloromethane, acetic acid, hydrochloric acid, phosphoric acid and sodium sulfate were all of analytical grade and purchased from Beijing Chemical Works. All the agents were used without further purification. The metal oxide ZrTiO<sub>4</sub> was prepared by calcining the Ti(OH)<sub>4</sub>-Zr(OH)<sub>4</sub> hydroxide derived from precipitation of the corresponding precursor solution at 923 K, according to the literature.<sup>2</sup> Furfural (SCR Beijing, 99%) was purified by vacuum distillation before use.

In a typical experiment, a mixture of 10 mL of solvent, 1.5 mL of distilled water, 4.0 g of furfural, 4.0 g of sodium sulfate and an appropriate amount of acid catalyst was added in a three-necked flask equipped with a condenser. The flask was placed in an oil bath at 60 °C for 3 h, and

10 mL of hydrogen peroxide was added dropwise during the first hour while stirring. The reaction mixture was sampled and then analyzed by a gas chromatograph (GC 7900 II, Techcomp Instrument Company) equipped with a super-wax capillary column (30 m × 0.25 mm × 0.5 μm) and an FID detector. The water soluble products including maleic acid (MA) and succinic acid (SA) were analyzed on a Shimadzu 10 AT-VP HPLC equipped with a C18 column (150 mm × 4.6 mm) and a UV detector. The sample was diluted 500 times with distilled water and the injection volume was 20 μL. The mobile phase was methanol with distilled water (3/97, v/v) containing KH<sub>2</sub>PO<sub>4</sub> (0.02 mol/L), and the pH of the mobile phase was adjusted to 2.75 by H<sub>3</sub>PO<sub>4</sub>. The flow rate was fixed at 1.0 mL/min and the temperature of the column was kept at 30 °C.

The final yield of products was calculated as:

$$\text{Product yield (\%)} = (n_{\text{pro}}/n_{\text{furfural},0}) \times 100 \quad (2)$$

where  $n_{\text{pro}}$  refers to the mole quantity of the product in the reaction mixture, and  $n_{\text{furfural},0}$  refers to the initial mole quantity of furfural loaded into the reactor.

#### 1.4 Hydrogenation of 2(5H)-furanone

The hydrogenation of 2(5H)-furanone was carried out in a stainless steel autoclave (Weihai Chemical Machinery Co., Ltd., 300 mL). For each experiment, 6.0 g of purified 2(5H)-furanone, 100 mL of methanol as solvent, and 0.6 g of catalyst reduced in hydrogen at 450 °C for 3 h prior to the reaction, were added to the reactor. The reaction system was purged with 50 mL/min N<sub>2</sub> gas flow for 10 min and then purged with 50 mL/min H<sub>2</sub> gas flow for 10 min at room temperature. Afterwards, the reactor was heated to 80 °C under 0.5 MPa. At the reaction temperature, the pressure was increased to 3.5 MPa within 5 min. The time when the pressure reached 3.5 MPa was considered as the zero of reaction time. The pressure was controlled by a back-pressure valve. To eliminate the gas-liquid mass transfer resistance, the stirring speed was set at 800 r/min, and the H<sub>2</sub> flow rate was set at 180 mL/min. The products were sampled and analyzed by a gas chromatograph (GC 7900 II, Techcomp Instrument Company) equipped with a super-wax capillary column (30 m × 0.25 mm × 0.5 μm) and an FID detector.

The reaction order ( $p$ ) and reaction rate constant ( $k_r$ ) were determined by fitting the 2(5H)-furanone concentration data  $C_F$  as a function of the reaction time based on Eq. (3). When the reaction order was fixed at 1.0, Eq. (3) had a good agreement with the experimental data of all the

catalysts, with  $R^2 > 0.98$ .

$$\frac{dC_F}{dt} = k_r C_F^p \quad (3)$$

The selectivity to  $\gamma$ -butyrolactone (GBL) was calculated as:

$$S_{GBL}(\%) = n_{GBL}/(n_{furanone,0} - n_{furanone}) \times 100 \quad (4)$$

where  $n_{GBL}$  and  $n_{furanone}$  refer to the mole quantities of GBL and 2(5H)-furanone, respectively, and  $n_{furanone,0}$  refers to the initial mole quantity of 2(5H)-furanone loaded into the reactor.

TOF (turnover frequency) for 2(5H)-furanone hydrogenation was defined as follows:

$$TOF = \Delta n_{furanone}/(\Delta t \times n_{active\ sites}) \text{ s}^{-1} \quad (5)$$

where  $\Delta n_{furanone}$  refers to moles of 2(5H)-furanone converted,  $\Delta t$  refers to the reaction time, and  $n_{active\ sites}$  refers to the moles of active sites.

The initial TOF for 2(5H)-furanone hydrogenation was calculated as:

$$TOF_{initial} = (k_r \times n_{furanone,0})/n_{active\ sites} \text{ s}^{-1} \quad (6)$$

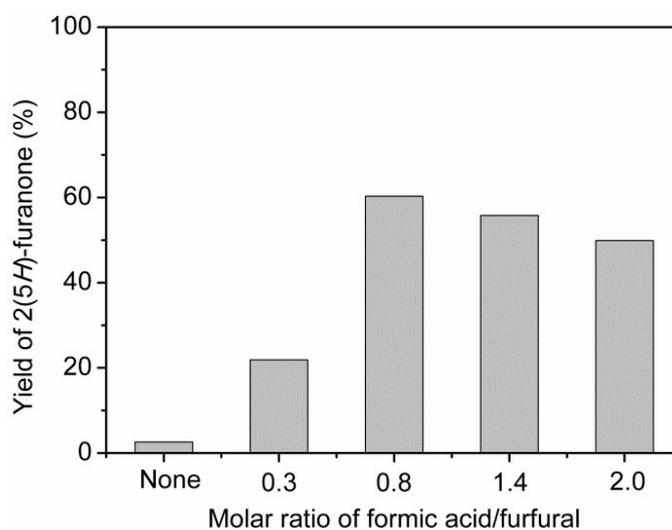
The moles of active sites were calculated based on the chemisorption results.

## 2. Tables and Figures

**Table S1.** Furfural oxidation with different acid catalysts <sup>a</sup>

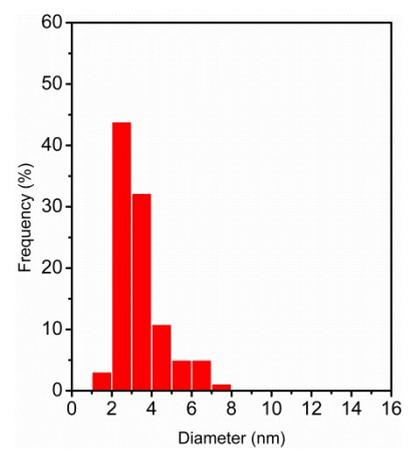
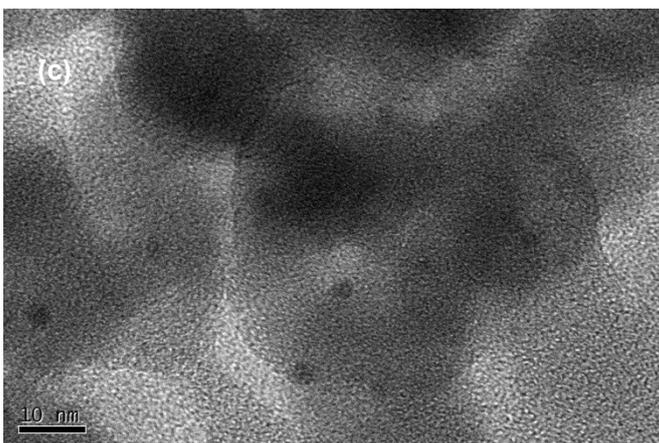
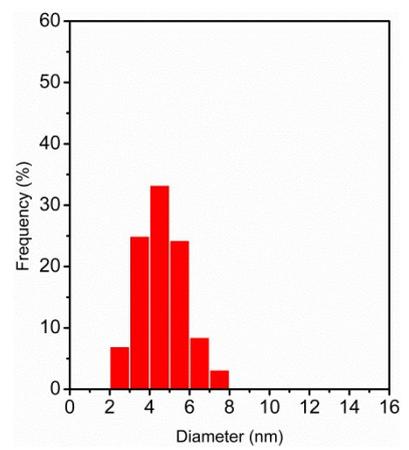
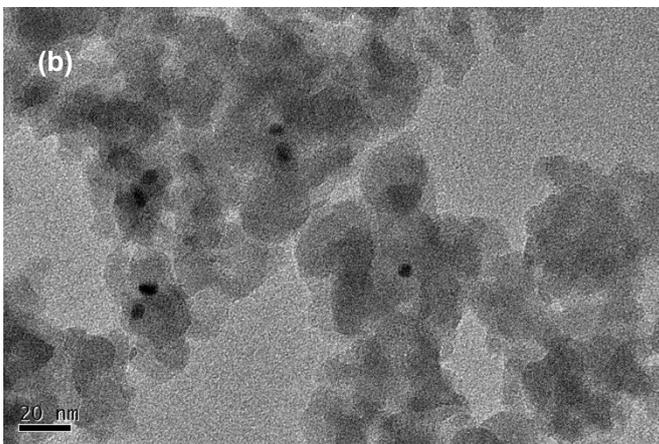
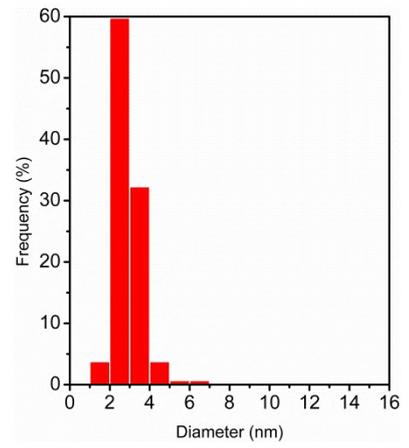
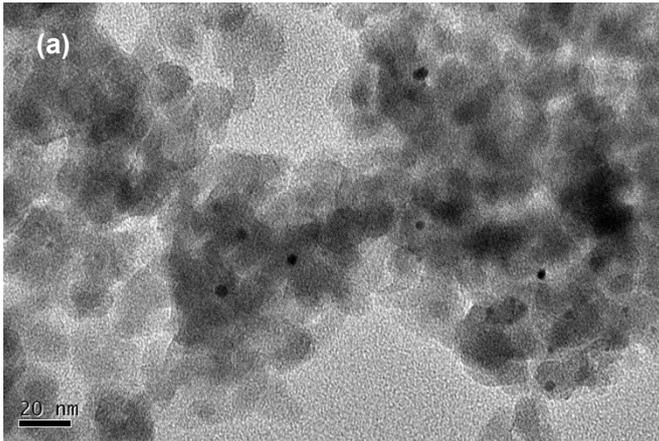
Entry	Catalyst <sup>b</sup>	Conversion (%)	Yield of 2(5 <i>H</i> )-furanone (%)
1	—	10.1	2.6
2	Formic acid	>99	60.3
3	Acetic acid	97.8	5.4
4	Hydrochloric acid	>99	6.7
5	Phosphoric acid	>99	6.6
6	H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	>99	9.1
7	Amberlyst-15	93.2	5.1
8	ZrTiO <sub>4</sub>	87.1	7.6

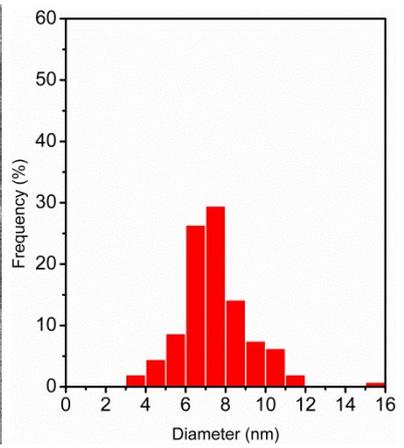
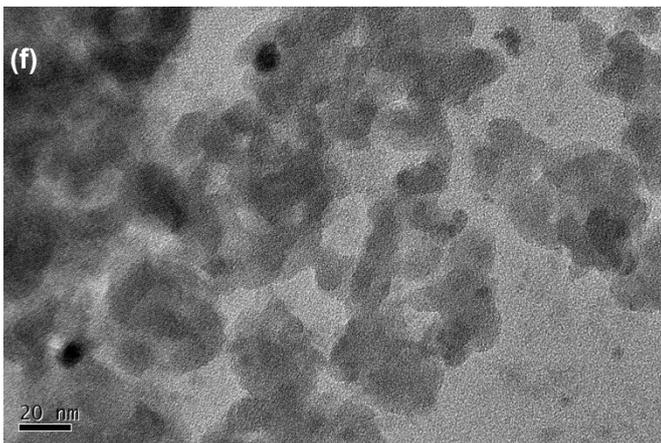
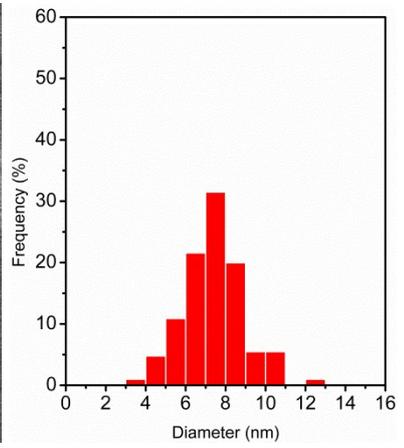
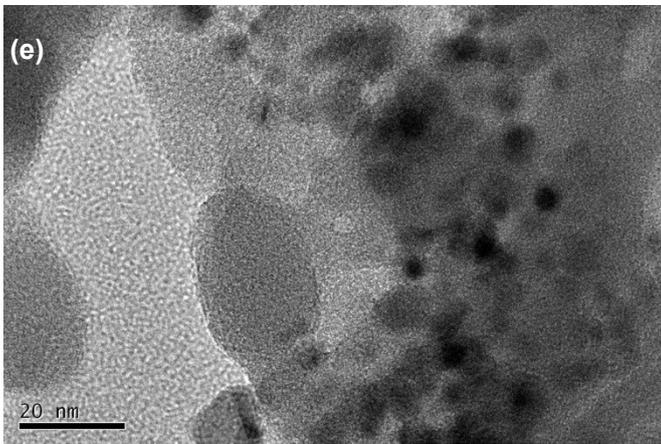
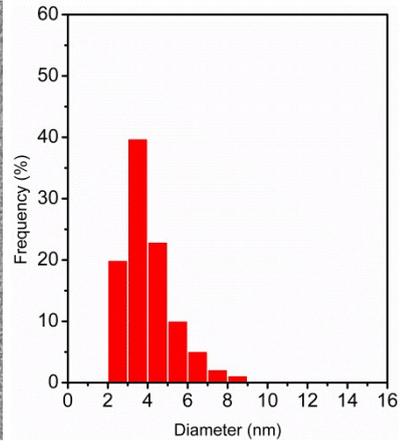
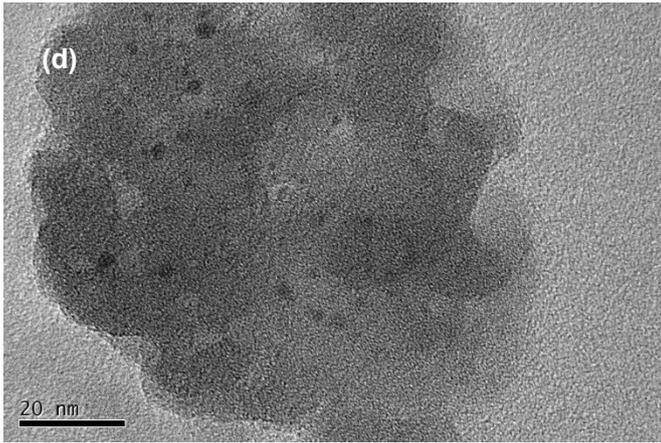
<sup>a</sup> Reaction conditions: 1,2-dichloroethane (10 mL), furfural (4.0 g), sodium sulfate (4.0 g), H<sub>2</sub>O<sub>2</sub> (30%, 10 mL), distilled water (1.5 mL), 3 h (homogeneous catalysts) or 10 h (heterogeneous catalysts), 333 K. <sup>b</sup> H<sub>3</sub>PO<sub>4</sub> (85%, 0.5 mL), HCl (36%, 0.5 mL), acetic acid (95%, 0.15 mL), formic acid (88%, 1.5 mL), solid acids (0.4 g).

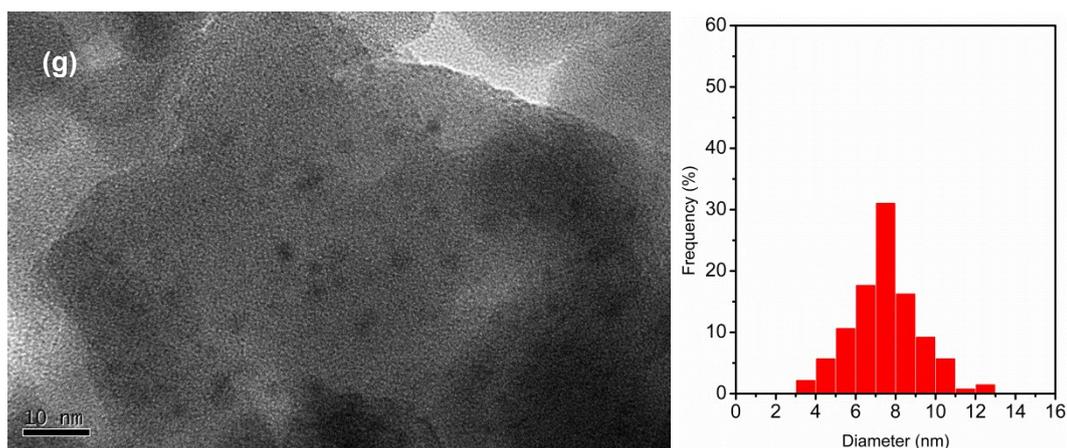


**Fig S1.** Yield of 2(5*H*)-furanone with different molar ratios of formic acid/furfural.

Reaction conditions: furfural (4.0 g), sodium sulfate (4.0 g), 1,2-dichloroethane (10 mL), H<sub>2</sub>O<sub>2</sub> (30%, 10 mL), 333 K, 3 h.





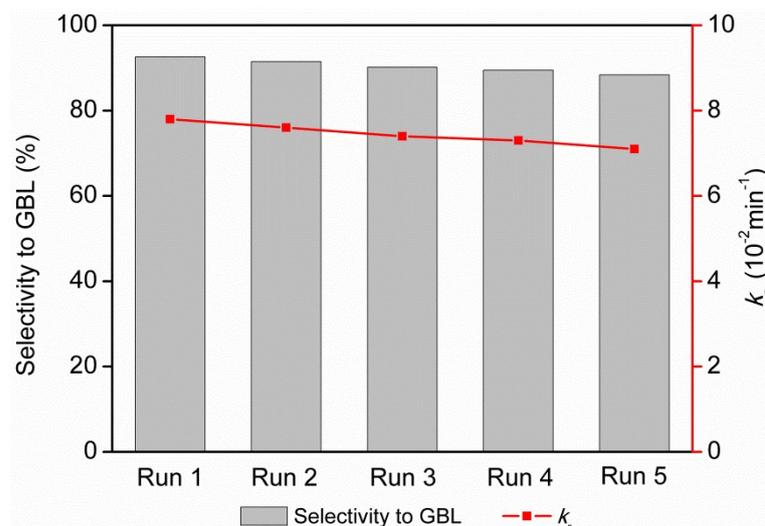


**Fig S2.** TEM images and particle size distributions of (a) Pt0.5/SiO<sub>2</sub>, (b) Pd0.5/SiO<sub>2</sub>, (c) Rh0.5/SiO<sub>2</sub>, (d) Ru0.5/SiO<sub>2</sub>, (e) Ni4.5/SiO<sub>2</sub>, (f) Co4.5/SiO<sub>2</sub> and (g) Cu4.5/SiO<sub>2</sub>.

**Table S2.** Properties of SiO<sub>2</sub> supported Group VIII metals

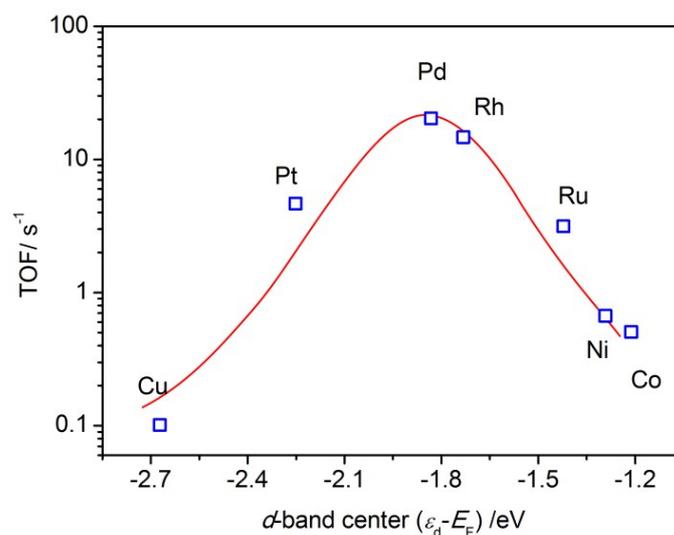
Entry	Catalyst	CO-uptake (10 <sup>-6</sup> mol/g)	Metal dispersion <sup>a</sup> ( <i>D</i> <sub>1</sub> , %)	Diameter <sup>b</sup> (nm)	Metal dispersion <sup>b, c</sup> ( <i>D</i> <sub>2</sub> , %)
1	Ni4.5/SiO <sub>2</sub>	18.9	2.5	7.4	9.2
2	Co4.5/SiO <sub>2</sub>	22.5	2.9	7.3	9.0
3	Cu4.5/SiO <sub>2</sub>	—	1.8	7.2	9.6
4	Pt0.5/SiO <sub>2</sub>	3.7	14.5	2.9	25.7
5	Pd0.5/SiO <sub>2</sub>	2.2	4.7	4.6	16.4
6	Rh0.5/SiO <sub>2</sub>	3.0	6.1	3.3	21.8
7	Ru0.5/SiO <sub>2</sub>	2.1	4.3	4.8	15.6

<sup>a</sup> The metal dispersion *D*<sub>1</sub> was determined by chemisorption. <sup>b</sup> The average diameter of metal particles and the metal dispersion *D*<sub>2</sub> were determined by TEM. <sup>c</sup> For the same supported metal catalyst, the metal dispersion determined by TEM (*D*<sub>2</sub>) was higher than that determined by chemisorption (*D*<sub>1</sub>). However, the trend of metal dispersion among different supported metal catalysts revealed by TEM was similar to that revealed by chemisorption.



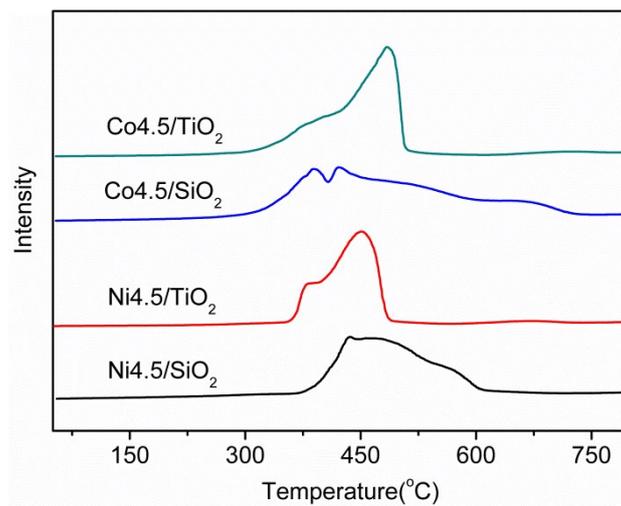
**Fig S3.** Reuse of the Pd<sub>0.5</sub>/SiO<sub>2</sub> catalyst in 2(5*H*)-furanone hydrogenation.

Reaction conditions: 2(5*H*)-furanone (6.0 g), catalyst (0.6 g), methanol as solvent (100 mL), 353 K, 3.5 MPa, 180 mL/min H<sub>2</sub> gas flow, 800 r/min stirring. The catalyst was washed with methanol and filtrated after each run.



**Fig S4.** Correlation of initial TOF for 2(5*H*)-furanone hydrogenation with  $d$ -band center relative to Fermi level, with the number of active sites determined by TEM.

Reaction conditions: 2(5*H*)-furanone (6.0 g), catalyst (0.6 g), methanol as solvent (100 mL), 353 K, 3.5 MPa, 180 mL/min H<sub>2</sub> gas flow, 800 r/min stirring.



**Fig S5.** H<sub>2</sub>-TPR profiles of Ni<sub>4.5</sub>/SiO<sub>2</sub>, Ni<sub>4.5</sub>/TiO<sub>2</sub>, Co<sub>4.5</sub>/SiO<sub>2</sub> and Co<sub>4.5</sub>/TiO<sub>2</sub>.

## References

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- 2 B. M. Reddy and A. Khan, *Catal. Rev.*, 2007, **47**, 257.