

## Supporting Information

### **Sustainable synthesis of bio-based PTMEG and methane beyond the Reppe method**

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## Experimental Procedures

### Chemicals

All chemicals and reagents were obtained from commercial suppliers and used without further purification: Furfural (C<sub>5</sub>H<sub>4</sub>O<sub>2</sub>, Shanghai Aladdin Biochemical Technology Co., Ltd.), tetrahydrofurfuryl alcohol (C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>, Shanghai Aladdin Biochemical Technology Co., Ltd.), tetrahydrofuran (C<sub>4</sub>H<sub>8</sub>O, Shanghai Aladdin Biochemical Technology Co., Ltd.), nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Sinopharm Chemical Reagent Co., Ltd.), copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Sinopharm Chemical Reagent Co., Ltd.), cobalt nitrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Sinopharm Chemical Reagent Co., Ltd.), niron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Sinopharm Chemical Reagent Co., Ltd.), urea (CO(NH<sub>2</sub>)<sub>2</sub>, Sinopharm Chemical Reagent Co., Ltd.), palladium chloride (PdCl<sub>2</sub>, J&K, 59.5%), ruthenium chloride (RuCl<sub>3</sub>·3H<sub>2</sub>O, J&K, 59.5%), rhodium chloride (RhCl<sub>3</sub>·3H<sub>2</sub>O, J&K, 59.5%), platinum chloride (PtCl<sub>4</sub>, J&K, 58%), fumed silica (SiO<sub>2</sub>, Shanghai Maikun Chemical Co., Ltd.), activated carbon (C, Shanghai Aladdin Biochemical Technology Co., Ltd.), HZSM-5 (Nankai University, Si/Al ratio = 5), zirconia (ZrO<sub>2</sub>, Sinopharm Chemical Reagent Co., Ltd.), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>, Shanghai Maikun Chemical Co., Ltd.), ammonium hydroxide (NH<sub>3</sub>·H<sub>2</sub>O, Sinopharm Chemical Reagent Co., Ltd.), potassium chloride (KCl, Sinopharm Chemical Reagent Co., Ltd.), phosphotungstic acid (H<sub>6</sub>O<sub>80</sub>P<sub>2</sub>W<sub>24</sub>, Beijing Innochem Technology Co., Ltd.), phosphomolybdic acid (H<sub>3</sub>P(Mo<sub>3</sub>O<sub>10</sub>)<sub>4</sub>·xH<sub>2</sub>O, Shanghai Meriel Chemical Technology Co., Ltd.), glycol ((CH<sub>2</sub>OH)<sub>2</sub>, Shanghai Aladdin Biochemical Technology Co., Ltd.), epoxy chloropropane (C<sub>3</sub>H<sub>5</sub>ClO, Shanghai Aladdin Biochemical Technology Co., Ltd.), ethanol (CH<sub>3</sub>CH<sub>2</sub>OH, Sinopharm Chemical Reagent Co., Ltd.),

hydrogen (H<sub>2</sub>, Shanghai Pujiang Specialty Gas Co., Ltd.), nitrogen (N<sub>2</sub>, Shanghai Pujiang Specialty Gas Co., Ltd.).

## **Catalyst synthesis**

### **Synthesis of silica hollow spheres (SiO<sub>2</sub>) support**

Mesoporous silica hollow spheres were synthesized by the Stöber synthesis method. In a typical experiment, resorcinol (1.5 g) and formaldehyde (37 wt %, 2.1 mL) were added to the solution composed of aqueous ammonia solution (28 wt%, 30 mL), ethanol (700 mL) and deionized water (100 mL). The mixture was vigorously stirred at room temperature for 6 h, and then 6 mL of tetraethyl orthosilicate (TEOS) was added into the solution and stirred for 8 minutes before another addition of resorcinol (4 g) and formaldehyde (37 wt %, 5.6 mL). The mixture was stirred for another 2 h at room temperature, and then was collected by centrifugation, ethanol washing and drying overnight in 60 °C oven. After drying, the sample was fully ground and calcined in a tubular furnace at 550 °C for 5 h (heating rate: 2 °C·min<sup>-1</sup>, flowing rate: 150 mL·min<sup>-1</sup>).

### **Synthesis of Ni/SiO<sub>2</sub> and other supported metal catalysts with deposition-precipitation method**

In a typical experiment, the Ni/SiO<sub>2</sub> catalyst was synthesized by deposition precipitation method. Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (10.2 g) was firstly dissolved in the deionized water (250 mL), and one part of this solution (200 mL) was suspended with SiO<sub>2</sub> (2.0 g) with stirring and then heated to 70 °C. The rest solution (50 mL) was dissolved with urea (6.3 g), and then drop-wise added into the former SiO<sub>2</sub> suspension. Afterwards, the mixture was held at 90 °C with stirring for different times (4, 6, 8, 10, 12, 16, 18, 24 h). After cooled down, the solid was separated by vacuum filtration, and the sample was washed several times with deionized water until pH of the filtrate was 7. Finally, the samples were dried at 80 °C overnight. The ground sample was calcined at 450 °C for 4 h (flowing rate: 150 mL·min<sup>-1</sup>, heating rate: 2 °C·min<sup>-1</sup>) and reduced with H<sub>2</sub> at 450 °C for 4 h (flowing rate: 150 mL·min<sup>-1</sup>, heating rate: 2 °C·min<sup>-1</sup>).

Cu/SiO<sub>2</sub>, Fe/SiO<sub>2</sub>, Co/SiO<sub>2</sub>, Pt/SiO<sub>2</sub>, Ru/SiO<sub>2</sub>, Ni/ASA, Ni/Al<sub>2</sub>O<sub>3</sub>, Ni/HZSM-5, Ni/ZrO<sub>2</sub> were synthesized by the same method.

#### **Synthesis of Cu-K/SiO<sub>2</sub> catalyst with hydrothermal method**

Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (1.3413 g) was dissolved in deionized water (560 mL) with vigorous stirring. Then KCl (8.278 g) was added into the copper solution, followed by the addition of 10.192 g NH<sub>3</sub>·H<sub>2</sub>O. Finally, 0.7056 g SiO<sub>2</sub> was added into the above solution and stirred at ambient temperature for 30 min. Afterwards, the mixture was ultra-sonically treated for another 30 min, and then transferred into a Teflon-lined stainless steel autoclave for 3 h at 120 °C. After cooled down to room temperature, the solid was filtered and washed with deionized water until pH value decreased to 7. The precursor was dried at 60 °C overnight, calcined at 450 °C for 4 h (flowing rate: 150 mL·min<sup>-1</sup>, heating rate: 2 °C·min<sup>-1</sup>) and reduced with H<sub>2</sub> at 450 °C for 4 h (flowing rate: 150 mL·min<sup>-1</sup>, heating rate: 2 °C·min<sup>-1</sup>).

#### **Synthesis of Rh, Pd, Ru catalysts supported on activated carbon**

In a typical experiment, the corresponding catalysts were synthesized by impregnation method. Using Ru/C as an example, firstly a RuCl<sub>3</sub>·3H<sub>2</sub>O solution was prepared, and then was mixed with the activated carbon at continuous stirring at ambient temperature overnight. Afterwards, the sample was rotated to remove water and dried at 60 °C overnight. The ground sample was calcined at 350 °C for 4 h (flowing rate = 150 mL·min<sup>-1</sup>, heating rate: 2 °C·min<sup>-1</sup>) and reduced with hydrogen at 350 °C for 4 h (flowing rate = 150 mL·min<sup>-1</sup>, heating rate: 2 °C·min<sup>-1</sup>).

#### **Synthesis of the polymerization solid acid catalysts**

Phosphotungstic acid and phosphomolybdic acid were calcined at different temperatures (100, 120, 140, 170, 200, 230 °C) for 2 h (flowing rate = 100 mL·min<sup>-1</sup>, heating rate: 2 °C·min<sup>-1</sup>) before use.

Phosphotungstic acid and phosphomolybdic acid supported on SiO<sub>2</sub> were synthesized by impregnation method. Phosphotungstic acid (1.4060 g) or phosphomolybdic acid (1.7075 g) was mixed with SiO<sub>2</sub> at continuous stirring at ambient temperature overnight. Afterwards, the sample was rotated to remove water

and dried at 60 °C overnight. The ground sample was calcined at 230 °C for 3 h (flowing rate: 150 mL·min<sup>-1</sup>, heating rate: 2 °C·min<sup>-1</sup>). The loading amounts of phosphotungstic acid and phosphomolybdic acid on SiO<sub>2</sub> were both 35 %.

## **Activity tests**

### **Furfural hydrogenation to tetrahydrofurfuryl alcohol**

First, add 3.0 g furfural, 27 g ethanol, 0.2 g Cu-K/SiO<sub>2</sub> and Ni/SiO<sub>2</sub> into the autoclave (Shanghai Rock Signature Experimental Instrument Co., Ltd). Before inflating, first introduce the gas three times with N<sub>2</sub>, and then three times with H<sub>2</sub>, then 6 MPa H<sub>2</sub> was purged into the reactor at ambient temperature, and then heated up to 140 °C, and the reaction started at a stirring speed of 900 rpm. After reaction, the liquid product was analyzed by a Shimadzu QP-2010 Ultra GC-MS and GC instruments with the column of Rtx-5Sil MS (30 m × 0.25 m × 0.25 μm).

### **Hydrodeoxygenation of tetrahydrofurfuryl alcohol over nickel-based catalyst**

Reactions were carried out in a fixed bed reactor (Shanghai Rock Signature Experimental Instrument Co., Ltd). First, 2 g calcined catalyst (40–60 mesh) were diluted with 2 g quartz sand. Before reaction, the catalyst was reduced at 450 °C for 4 h under a pure H<sub>2</sub> atmosphere, and then adjusting the reaction conditions to 310 °C, H<sub>2</sub> flow 66.4 ml/min, 3 MPa H<sub>2</sub>, the feeding rate of THFA was 0.07 mL/min. The liquid product and gas product were collected once an hour. The composition of the product gases was analyzed using an gas chromatograph (Shimadzu GC 2014, Japan) equipped with a TDX-1 packed column and a thermal conductivity detector. The liquid product was analyzed by a Shimadzu QP-2010 Ultra GC-MS instrument with the column of Rtx-5Sil MS (30 m × 0.25 m × 0.25 μm).

### **Polymerization of tetrahydrofuran over phosphotungstic acid**

Before the polymerization reaction, adding a certain amount of shredded sodium, THF and benzophenone as chromogenic reagent into 50 mL three-mouth flask with nitrogen protection. After a period of condensation reflux at 67 °C, water and oxygen was removed from THF when the system became blue. Then THF was distilled out and preserved with nitrogen. Then a certain amount of phosphotungstic acid, redistilled

THF, and epichlorohydrin as accelerant were added into the round-bottomed flask with nitrogen as protective gas, and was then stirred strongly. It can be found that the viscosity of the polymerization system was increased with the polymerization reaction. After a period of reaction, water was added to the system to terminate the polymerization reaction, and the polymerization system became milky white. The reaction mixture liquid in the flask was transferred to the separating funnel and a certain amount of cyclohexane was added to extract the organic phase. Water was subsequently added to wash the organic phase until pH turned to be 7, and organic phase was then separated. Afterwards, the sample was rotated to remove water, and the organic layer was dried at 80 °C in vacuum drying chamber for 6 h.

### **Catalyst characterization**

Powder X-ray diffraction (XRD) patterns were measured on Rigaku Ultima IV X-ray diffractometer utilizing Cu K $\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) operated at 35 kV and 25 mA.

The metal contents were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP–AES) with a Thermo IRIS Intrepid II XSP emission spectrometer after dissolving the catalyst in a mixed HF and aqua regia solution.

The specific surface area and pore size distribution were performed by N<sub>2</sub> adsorption at 77 K on a Quantachrome Autosorb-3B instrument after activating the samples under vacuum at 573 K for 10h.

Scanning electron microscopy (SEM) images were performed with a Hitachi S-4800 microscope. Transmission electron microscopy (TEM) was detected on a Tecnai G2 f30 microscope at 300kV.

The temperature programmed reduction (H<sub>2</sub>-TPR) analysis of catalysts was performed by Micromeritics tp5080 apparatus using a 3% H<sub>2</sub>/He mixture (flowing rate: 30 mL·min<sup>-1</sup>) and at a heating rate of 10 °C·min<sup>-1</sup> with a thermal conductor detector (TCD).

In situ diffuse reflectance infrared Fourier transform spectra (DRIFTS) spectra were collected by a BRUKER TENSOR 27 spectrometer equipped with a MCT detector

and operated at a resolution of  $4 \text{ cm}^{-1}$ . Before the experiment, the samples in a powder form were reduced at  $450 \text{ }^\circ\text{C}$  for 1 h with  $\text{N}_2$  and aged at  $310 \text{ }^\circ\text{C}$  for 1 h with He. The background spectrum was recorded at  $310 \text{ }^\circ\text{C}$  and then THFA with  $\text{H}_2$  gas was introduced into the reaction cell at a total flow rate of  $25 \text{ mL}\cdot\text{min}^{-1}$  at  $310 \text{ }^\circ\text{C}$ . Then the spectra were collected every 5 min.

NMR spectra were recorded on a Bruker AM-400 spectrometer using tetramethylsilane as an internal standard in  $\text{CDCl}_3$ .

### **DFT calculation details**

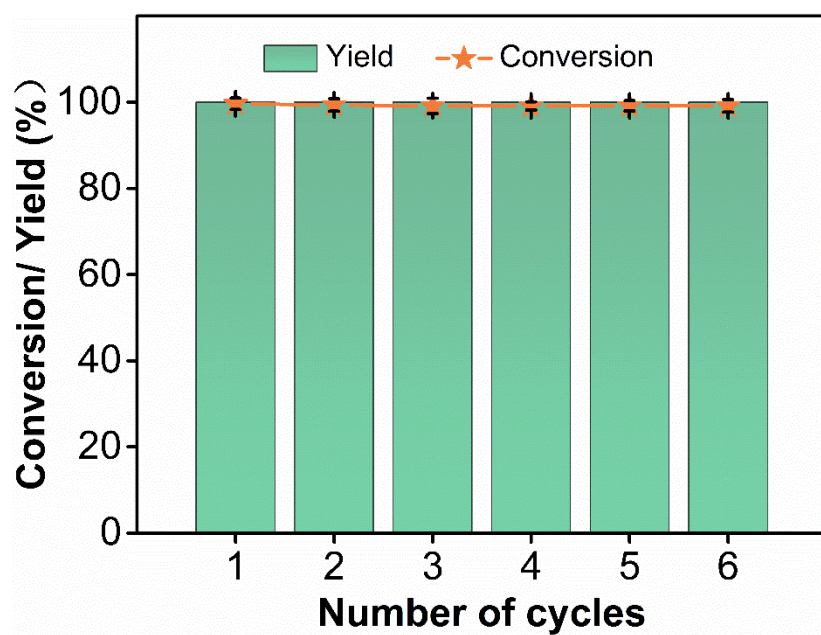
DFT calculations were performed using Vienna ab initio Simulation Package (VASP). The projector augmented wave (PAW) method combined with cutoff energy of 450 eV were adopted to describe the core and valence electrons. The exchange-correlation effects were described within the generalized gradient approximation with the use of Perdew-burke-Ernzhehof (PBE) functional. Ni(111) is modeled by 4-layer slabs separated by  $15 \text{ \AA}$  vacuum space, with the top two layers relaxed and bottom two layers fixed to simulate the Ni bulk.  $p(4\times 4)$  unit cells were chosen, which means a coverage of 1/16 monolayer for a single adsorbate on the surface. The Brillouin zone of the systems were sampled with a  $4 \times 4 \times 1$  Monkhorst-Pack grid. In this paper, adsorption energy  $E_{\text{ad}}$  of the adsorbed reactant and intermediates is defined as:

$$E_{\text{ad}} = E_{\text{adsorbate/slab}} - E_{\text{slab}} - E_{\text{adsorbate}}$$

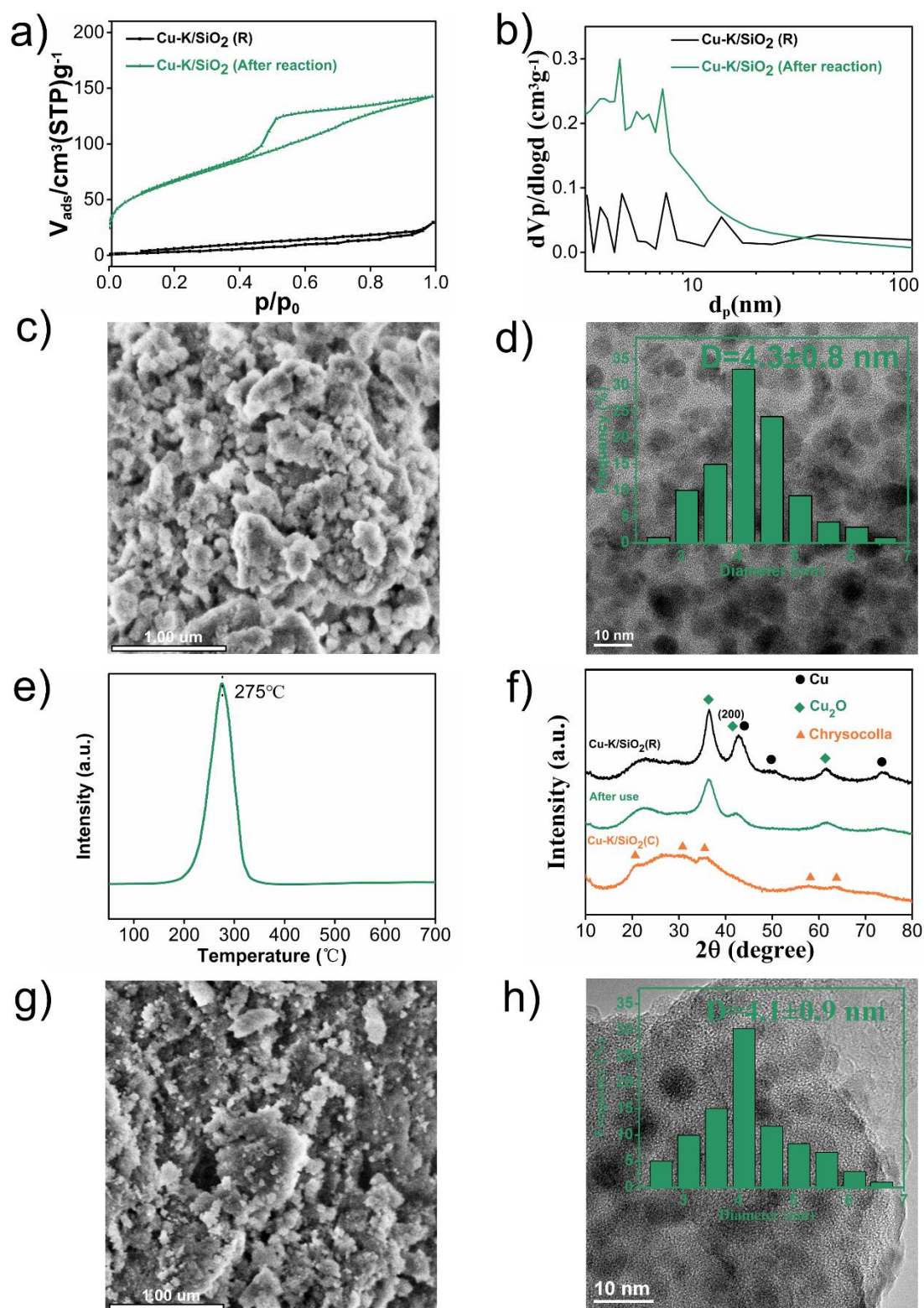
Where  $E_{\text{adsorbate/slab}}$  is the total energy of interacting system of both slab and adsorbate after surface optimization.  $E_{\text{slab}}$  is the energy of the 4-layer slab with  $15 \text{ \AA}$  vacuum space along z direction and  $E_{\text{adsorbate}}$  is the energy of adsorbate in vacuum.



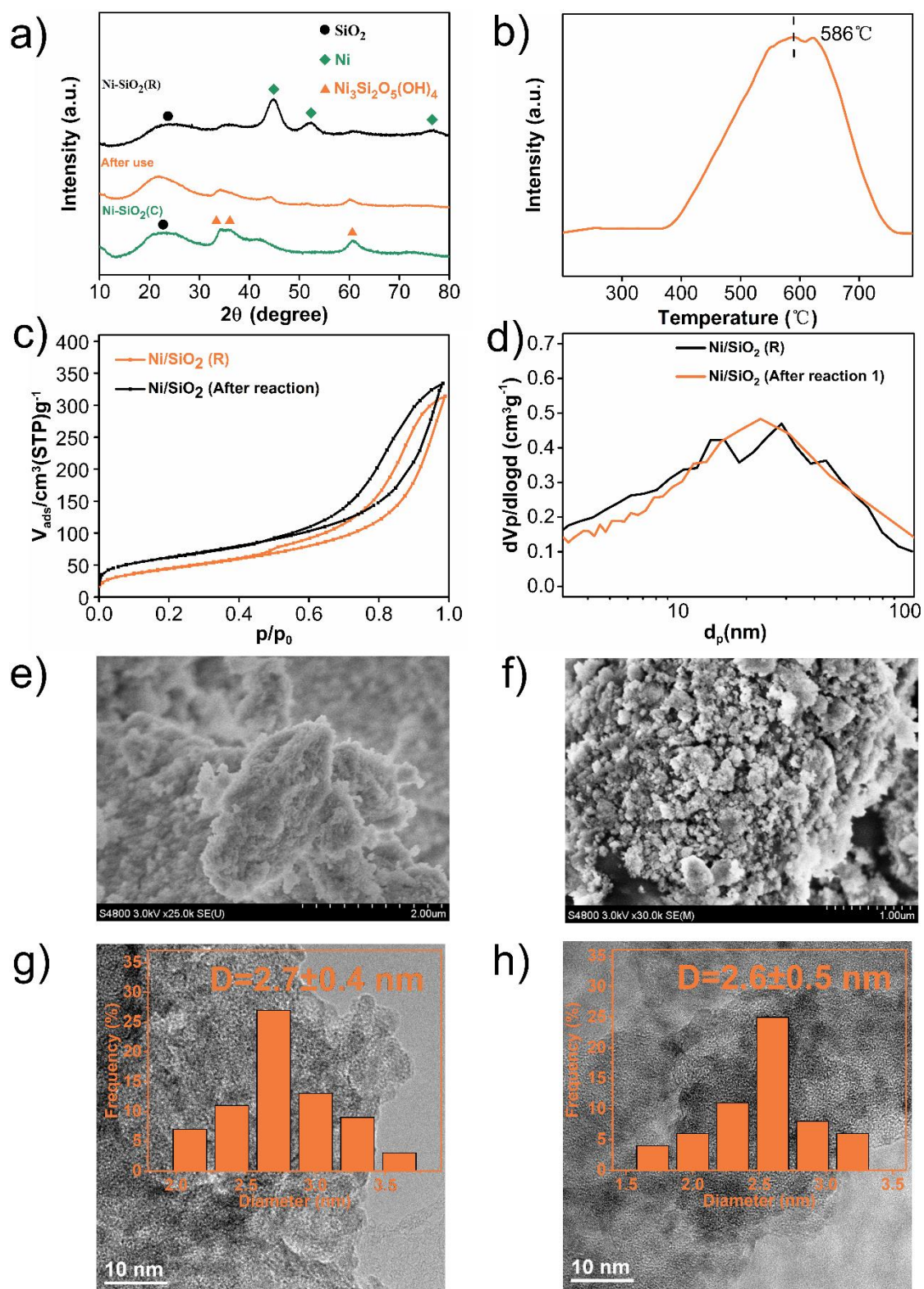
## Supplemental Figures and Tables



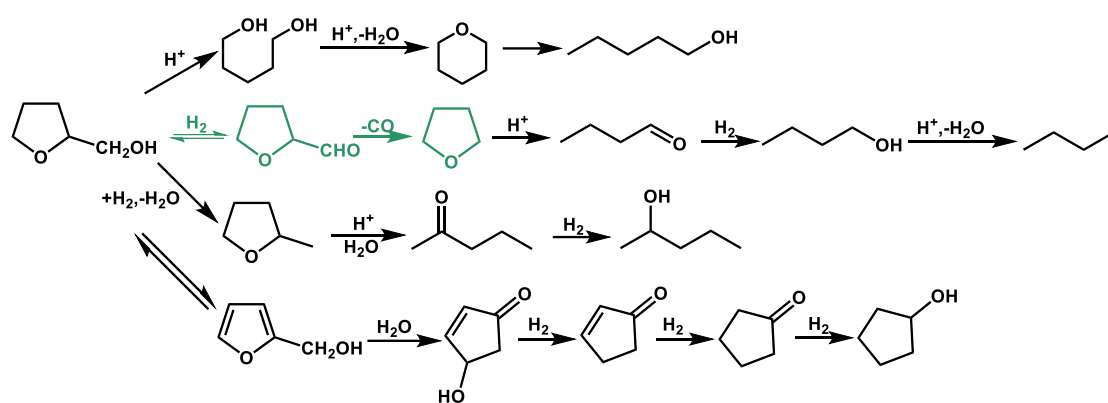
**Figure S1.** Six-run recycling tests on furfural hydrogenation over Ni/SiO<sub>2</sub> and Cu-K/SiO<sub>2</sub> catalyst. Reaction conditions: FA 1.5 g, ethanol 28.5 g, Ni/SiO<sub>2</sub> (DP16 h) 0.2 g, Cu-K/SiO<sub>2</sub> 0.2 g, 140 °C, 6 MPa H<sub>2</sub>, 3 h.



**Figure S2.** (a) N<sub>2</sub> adsorption and desorption isotherms of Cu-K/SiO<sub>2</sub> sample. (b) The pore size distribution of Cu-K/SiO<sub>2</sub> sample. (c-d) SEM and TEM images of the reduced Cu-K/SiO<sub>2</sub> catalyst. (e) H<sub>2</sub>-TPR profiles of air calcined Cu-K/SiO<sub>2</sub> sample. (f) XRD patterns of Cu-K/SiO<sub>2</sub> sample. (g-h) SEM and TEM images of the used Cu-K/SiO<sub>2</sub>.

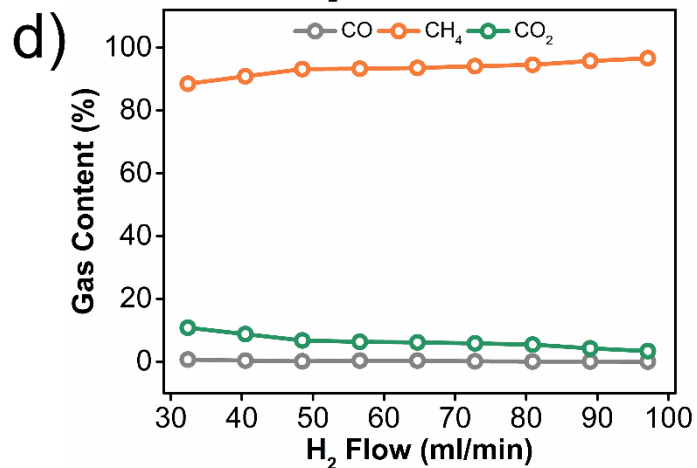
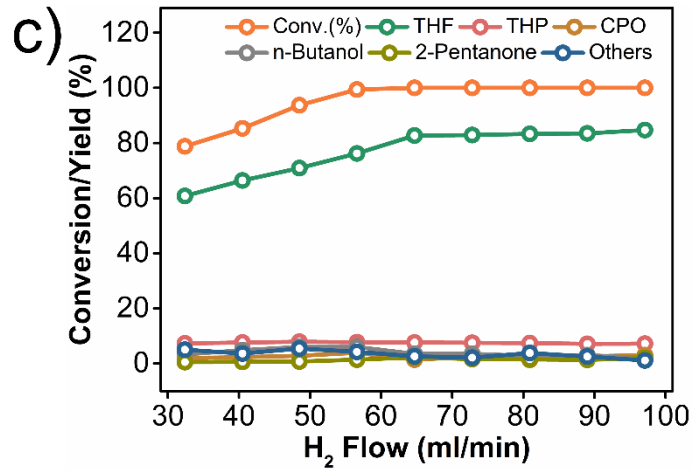
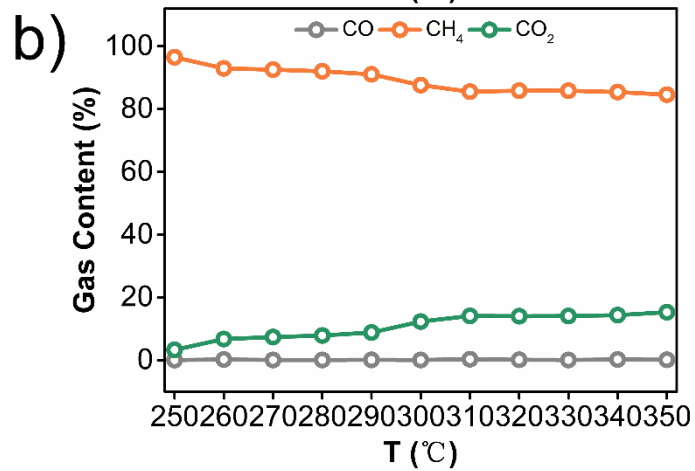
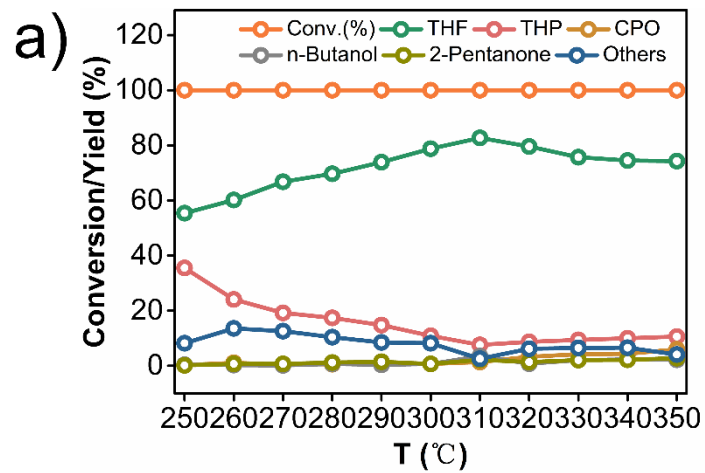


**Figure S3.** (a) XRD patterns of Ni/SiO<sub>2</sub> sample. (b) H<sub>2</sub>-TPR profiles of air calcined Ni/SiO<sub>2</sub> sample. (c) N<sub>2</sub> adsorption and desorption isotherms of Ni/SiO<sub>2</sub> sample. (d) The pore size distribution of Ni/SiO<sub>2</sub> sample. (e-h) SEM and TEM images of as-prepared samples: the reduced Ni/SiO<sub>2</sub> and the used NiSiO<sub>2</sub> catalysts.

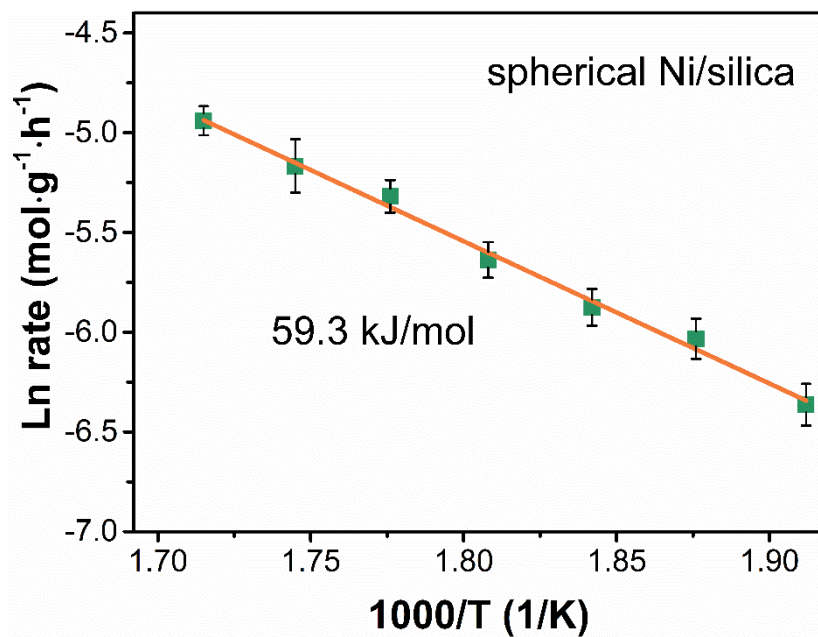


**Figure S4.** Possible reaction pathway for selective hydrodeoxygenation of THFA.

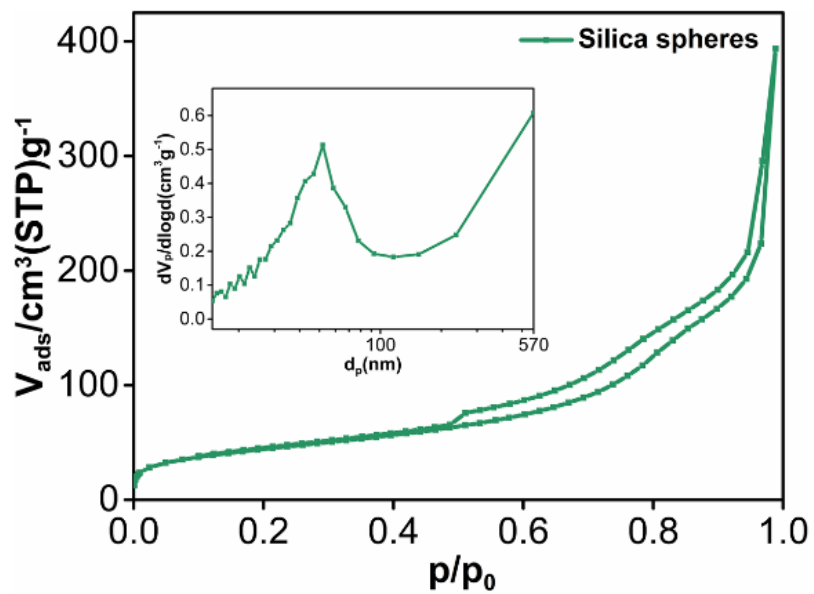




**Figure S5.** (a and b) Effect of temperatures on liquid and gas product distributions from selective hydrodeoxygenation of THFA. Reaction conditions: THFA 0.07 mL/min, 1 MPa, H<sub>2</sub> flow 66.4 mL/min, spherical Ni/silica 2.0 g. (c, d) The distribution of liquid and gas products with different H<sub>2</sub> flow speed on selective hydrodeoxygenation of THFA over spherical Ni/silica catalyst. Reaction conditions: THFA 0.07 mL/min, 310 °C, 1 MPa H<sub>2</sub>, spherical Ni/silica 2.0 g.

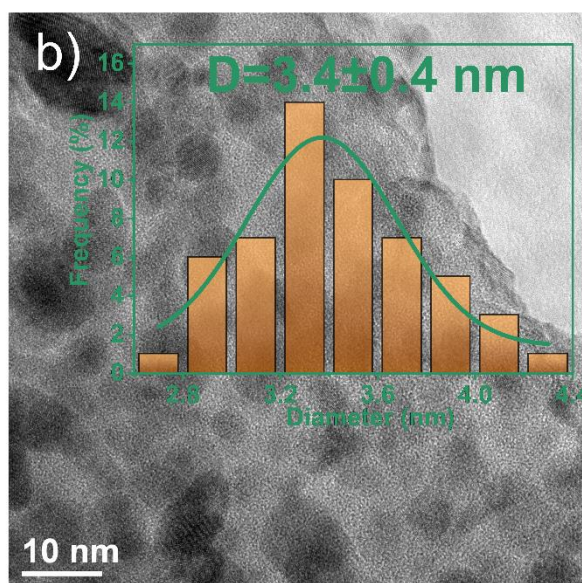
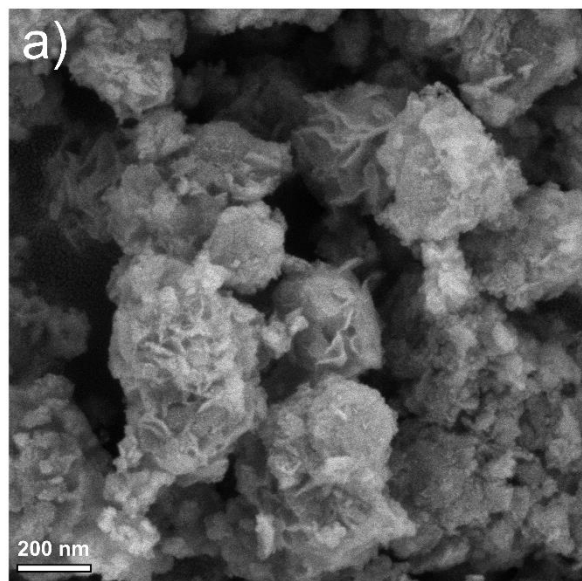


**Figure S6.** The Arrhenius curve of THFA conversion with spherical Ni/silica catalyst at selected temperatures (523-583 K). Reaction conditions: THFA 0.07 mL/min, 1 MPa H<sub>2</sub>, H<sub>2</sub> flow 66.4 ml/min, spherical Ni/silica 2.0 g.

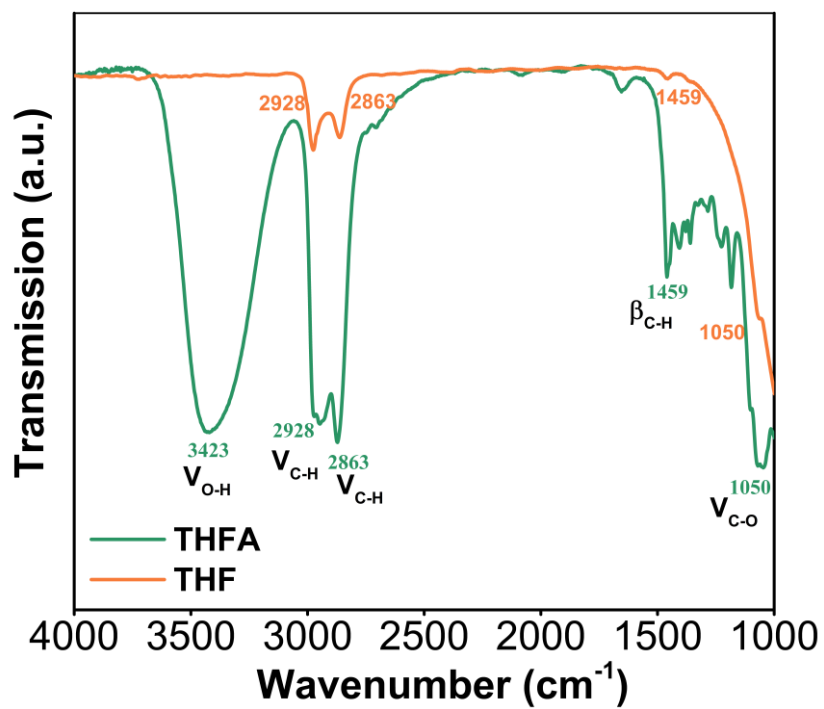


**Figure S7.**  $\text{N}_2$  adsorption and desorption isotherms and the pore size distribution of spherical silica sample.

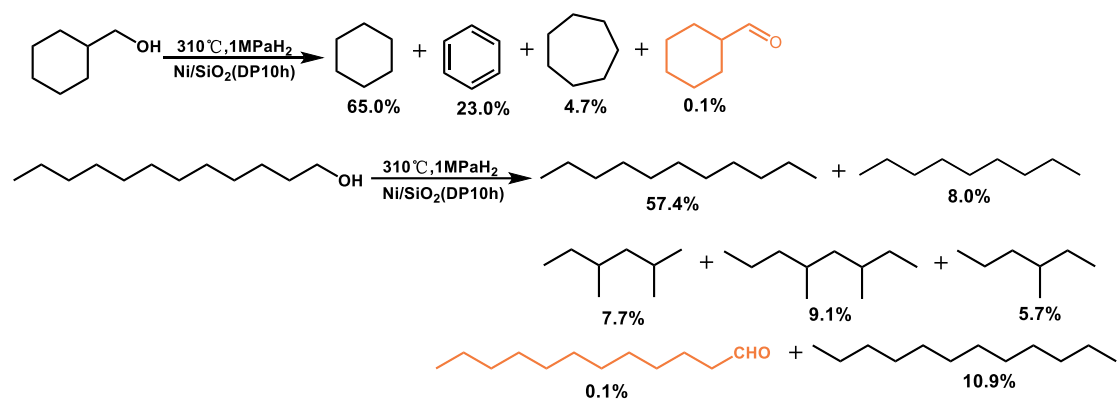




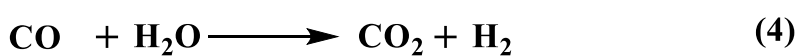
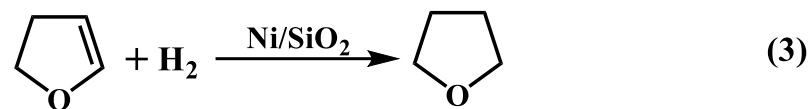
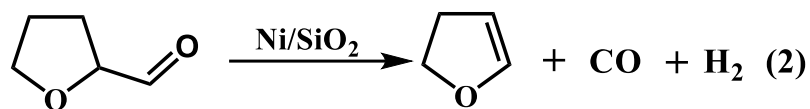
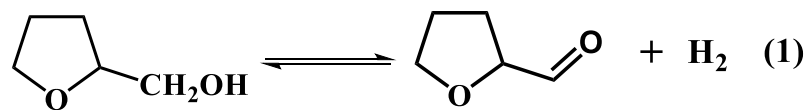
**Figure S8.** (a) SEM and (b) TEM images of the used spherical Ni/silica catalysts.



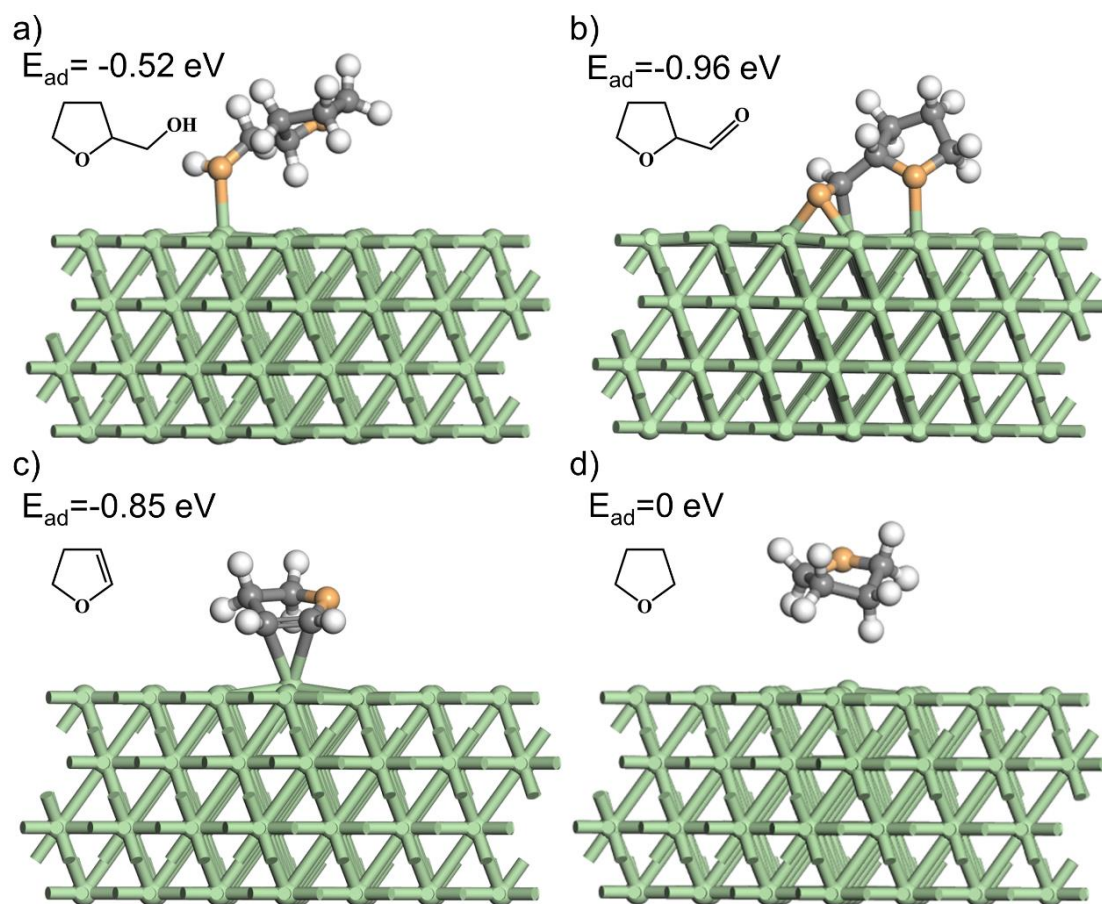
**Figure S9.** FTIR spectra of THF and THFA.



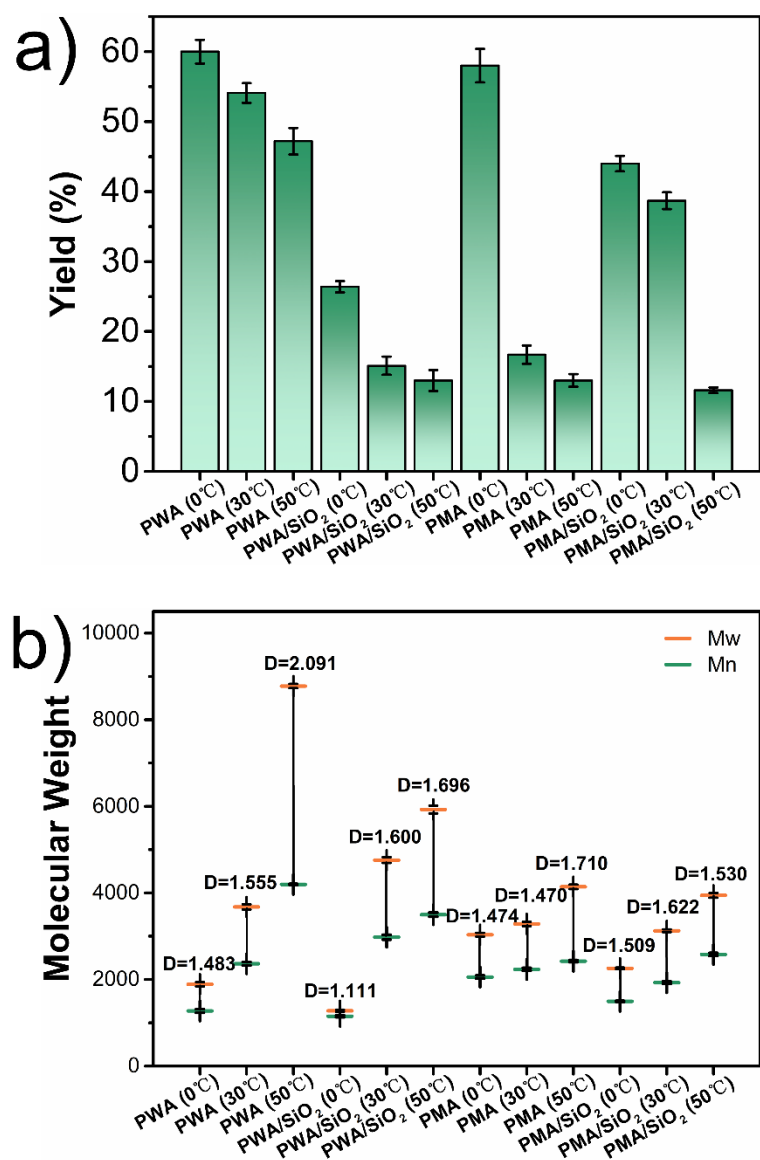
**Figure S10.** The results for selective hydrodeoxygenation of cyclohexanemethanol and dodecanol over spherical Ni/silica catalyst.



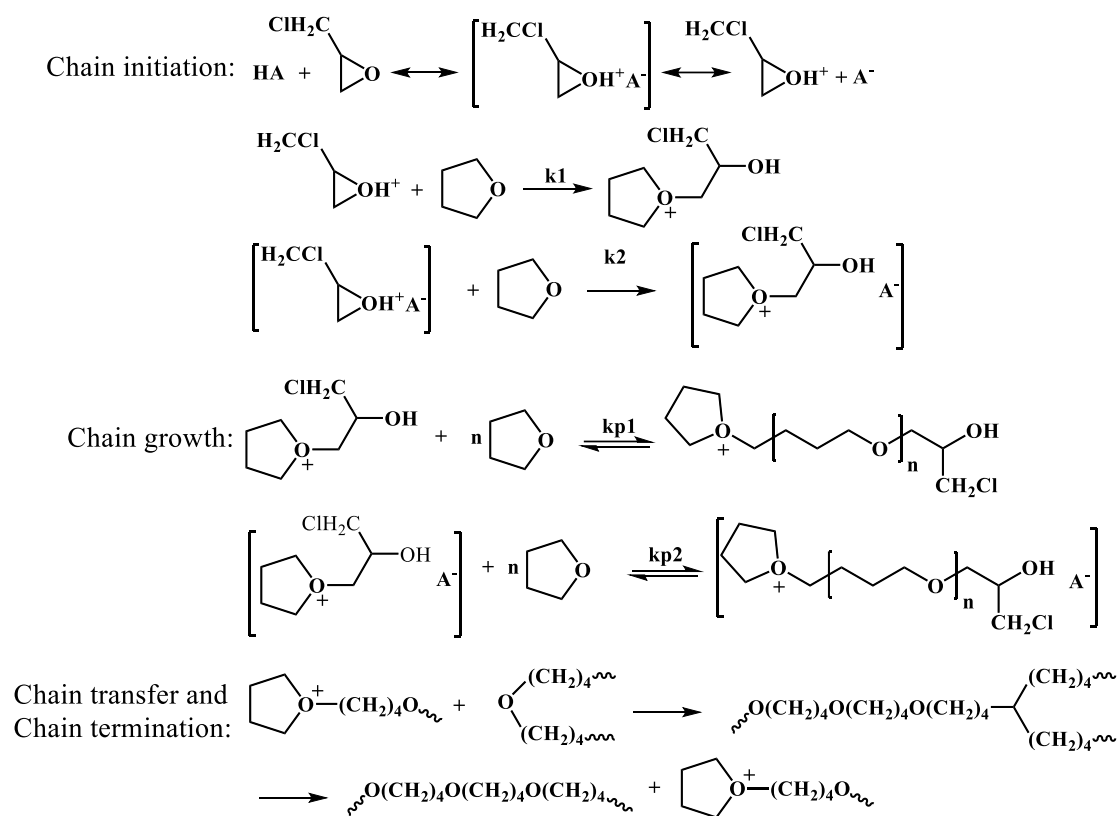
**Figure S11.** The equations for gaseous reactions during the hydrodeoxygenation of THFA.



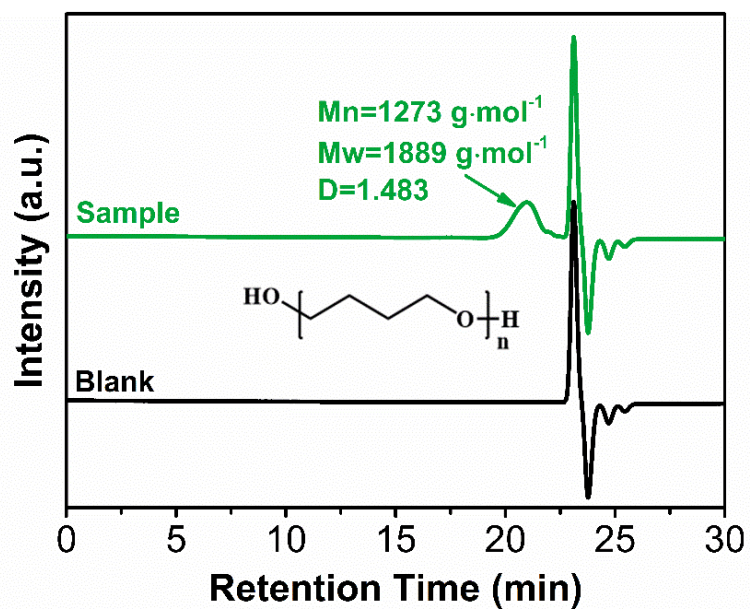
**Figure S12.** Configurations and corresponding adsorption energies of (a) tetrahydrofurfuryl alcohol, (b) tetrahydrofurfural, (c) 2,3-dihydrofuran, (d) tetrahydrofuran.



**Figure S13.** (a) Yield of polymerization of THF over PMA, PMA/SiO<sub>2</sub> and PWA, PWA/SiO<sub>2</sub> with different reaction temperatures. Reaction conditions: 0-2°C, THF 20 mL, ECH 3.13 mL, EG 0.25 mL, catalyst 0.23 g, 4 h. (b) Distribution of molecular weight and dispersity of PTMEG as synthesized by PMA, PMA/SiO<sub>2</sub> and PWA, PWA/SiO<sub>2</sub>.

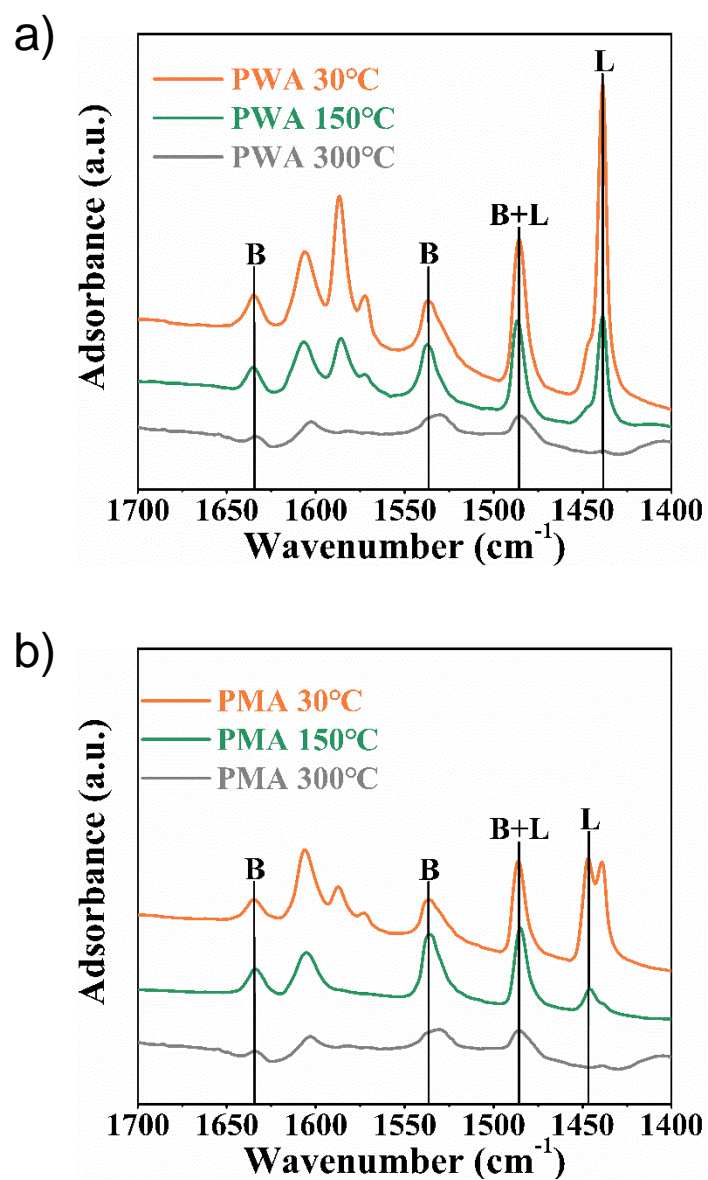


**Figure S14.** Possible mechanism for polymerization of THF to PTMEG.

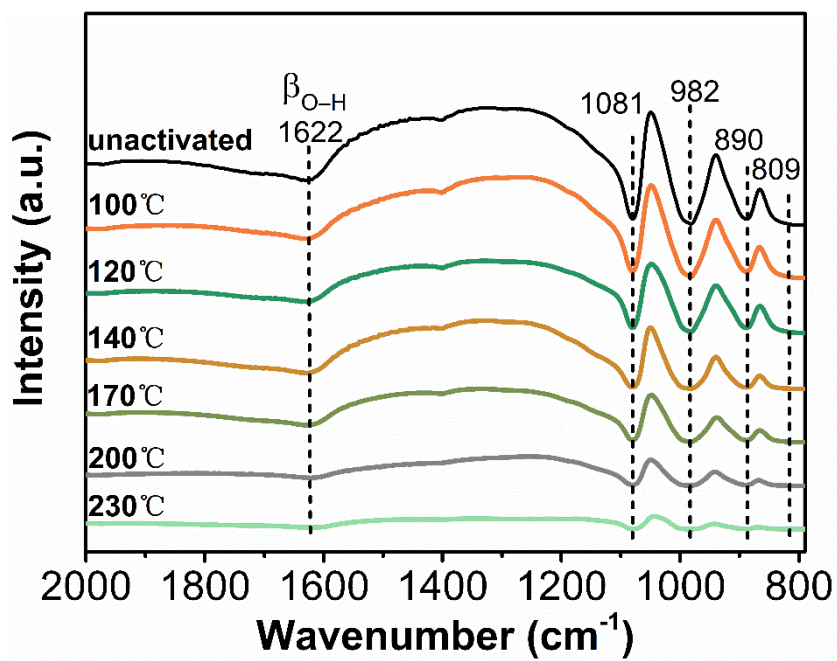


**Figure S15.** GPC spectrogram of PTMEG in comparison to blank (THF used as mobile phase).



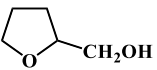
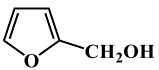

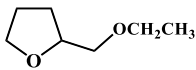



**Figure S16.** The IR spectra of adsorbed pyridine on (a) PWA and (b) PMA.



**Figure S17.** FT-IR spectra of PWA at different activated temperatures.

**Table S1.** Hydrogenation of furfural over different supported catalysts.

Entry	Catalyst	Conv. (%)	Yield (%)					Carbon balance (%)
								
1	Pd/C <sup>a</sup>	100	98	0	0	0	0	98.0
2	Ru/C <sup>a</sup>	65	0	65	0	0	0	100
3	Rh/C <sup>a</sup>	54	0	54	0	0	0	100
4	Cu-K/SiO <sub>2</sub> <sup>a</sup>	100	0	100	0	0	0	100
5	Ni/SiO <sub>2</sub> <sup>b</sup>	100	80.2	0	0	19.7	0	95.8
6	Ni-Cu/SiO <sub>2</sub> <sup>c</sup>	100	38.2	0	30.2	22.6	7.0	99.9
7	Ni/SiO <sub>2</sub> <sup>d</sup>	100	99.6	0	0	0	0	99.6
8	Ni/SiO <sub>2</sub> + Cu-K/SiO <sub>2</sub> <sup>e</sup>	100	100	0	0	0	0	100
9	Ni/SiO <sub>2</sub> + Cu-K/SiO <sub>2</sub> <sup>e</sup>	100	99.4	0	0.6	0	0	94.1
10	Ni/SiO <sub>2</sub> + Cu-K/SiO <sub>2</sub> <sup>e</sup>	100	99.2	0	0.8	0	0	94.2
11	Ni/SiO <sub>2</sub> + Cu-K/SiO <sub>2</sub> <sup>e</sup>	100	99.2	0	0.8	0	0	94.2
12	Ni/SiO <sub>2</sub> + Cu-K/SiO <sub>2</sub> <sup>e</sup>	100	99.2	0	0.8	0	0	94.2
13	Ni/SiO <sub>2</sub> + Cu-K/SiO <sub>2</sub> <sup>e</sup>	100	99.2	0	0.8	0	0	94.2

<sup>a</sup>Reaction conditions: FA 1.5 g, ethanol 28.5 g, catalyst 0.2 g, 100°C, 6 MPa H<sub>2</sub>, 2 h. <sup>b</sup>Reaction conditions: FA 1.5 g, ethanol 28.5 g, 0.2 g Ni/SiO<sub>2</sub>, 140°C, 6 MPa H<sub>2</sub>, 2 h. <sup>c</sup>FA 3 g, ethanol 27 g, Ni-Cu/SiO<sub>2</sub> (preparation by hydrothermal method) 0.2 g, 140°C, 6 MPa H<sub>2</sub>, 3 h. <sup>d</sup>FFA 3 g, ethanol 27 g, 140°C, 6 MPa H<sub>2</sub>, 3 h. <sup>e</sup>Six-run recycling tests. Reaction conditions: FA 3 g, ethanol 27 g, 0.2 g Ni/SiO<sub>2</sub>, 0.2 g Cu-K/SiO<sub>2</sub>, 140°C, 6 MPa H<sub>2</sub>, 3 h.

**Table S2.** Physical Properties of Cu-K/SiO<sub>2</sub> and Ni/SiO<sub>2</sub> catalysts.

Catalyst		Metal Loading	Particle size	Pore diameter	S <sub>meso</sub>	S <sub>micro</sub>	V <sub>meso</sub>	V <sub>micro</sub>
		ICP						
		/wt%	/nm	/nm	/m <sup>2</sup> ·g <sup>-1</sup>	/m <sup>2</sup> ·g <sup>-1</sup>	/cm <sup>3</sup> ·g <sup>-1</sup>	/cm <sup>3</sup> ·g <sup>-1</sup>
Cu-K/SiO <sub>2</sub>	Reduction	71	4.3 ± 0.8	2.969	279	0	0.25	0
	Used	64	4.1 ± 0.9	2.971	219	17	0.22	0
Ni/SiO <sub>2</sub>	Reduction	50	2.7 ± 0.4	2.974	219	0	0.52	0
	Used	43	2.6 ± 0.5	3.122	162	0	0.49	0

**Table S3.** The thermodynamic constant at different temperature of tetrahydrofurfuryl alcohol hydrodeoxygenation reaction.

T °C	$\Delta H$ kcal	$\Delta S$ cal/K	$\Delta G$ kcal	LogK
280	14.712	54.549	-15.461	6.109
290	14.506	54.179	-16.005	6.212
300	14.294	53.805	-16.545	6.309
310	14.076	53.430	-17.081	6.402
320	13.854	53.052	-17.614	6.490
330	13.627	52.672	-18.142	6.574

**Table S4.** Physical Properties of Ni/ silica spheres catalysts.

Catalyst		Metal Loading ICP /wt%	Particle size /nm	Pore diameter /nm	S <sub>meso</sub> /m <sup>2</sup> ·g <sup>-1</sup>	S <sub>micro</sub> /m <sup>2</sup> ·g <sup>-1</sup>	V <sub>meso</sub> /cm <sup>3</sup> ·g <sup>-1</sup>	V <sub>micro</sub> /cm <sup>3</sup> ·g <sup>-1</sup>
SiO <sub>2</sub>		-	-	52.0	143.7	12.2	0.588	0.006
Ni/SiO <sub>2</sub>	Reduction	50	3.0±0.2	19.2	95.1	0	0.300	0
	Used	48	3.4±0.4	78.5	116.8	25.7	0.288	0.014

**Table S5.** List of economic parameters of Reppe method.

Entry		Consumption (ton/kwh/m <sup>3</sup> )	Unit price (\$/ton or kwh or m <sup>3</sup> )	Total price (\$)
Raw feedstock cost	Acetylene	0.42	219.80 <sup>a</sup>	91.88
	Formaldehyde	2.02	200.00 <sup>a</sup>	404.00
	Hydrogen	0.06	1255.20	79.00
Catalyst cost	Ethnylation catalyst	0.028	1122.37	31.43
	Hydrogenation catalyst	0.018	1247.22	22.45
	Natrium aceticum	0.025	391.94 <sup>a</sup>	9.80
	Sodium hydroxide	0.05	360.59 <sup>a</sup>	18.03
	Sulphuric acid	0.045	95.32 <sup>a</sup>	4.29
Utility&Electricity costs	Electricity	271.00 kwh	0.08	21.27
	Process water	0.65 m <sup>3</sup>	0.78	0.51
	Cooling water	0.58	0.78	0.46
	Steam	12.94	23.54	304.60
Fixed operating costs		-	-	11.36
Capital costs		-	-	173.50
Recycled product	Butanol	0.027	2039.7	-55.07
	Propynol	0.02	6087.72	-121.75
Total				995.76 \$/ton

<sup>a</sup>Taken from reference price by MOLBASE<sup>1</sup>.

**Table S6.** List of economic parameters of Furfural method.

Entry		Consumption (ton/kwh/m <sup>3</sup> )	Unit price (\$/ton or kwh or m <sup>3</sup> )	Total price (\$)
Raw feedstock cost	Furfural	1.10	1183 <sup>a</sup>	1301
	Hydrogen	0.046	1255.2	57.74
Catalyst cost	Copper nitrate	0.0054	3929.6 <sup>b</sup>	21.22
	Nicker nitrate	0.0055	4079.4 <sup>b</sup>	22.44
	Silicon dioxide	0.011	94.14	1.04
	Ammonia water	0.003	117.58 <sup>a</sup>	0.35
Utility&Electricity cost	Electricity	320.00 kwh	0.08	25.12
	Process water	0.34 m <sup>3</sup>	0.78	0.27
	Cooling water	0.43	0.78	0.34
	Steam	4	23.54	94.16
Fixed operating cost		-	-	11.36
Capital costs		-	-	173.50
Recycled product CH <sub>4</sub>		0.86	988.47	-850
<b>Total</b>				<b>858.53\$/ton</b>

<sup>a</sup>Taken from reference price by MOLBASE<sup>1</sup>.  
<sup>b</sup>Taken from study by Consensus Economics Inc<sup>2</sup>.



## Reference

- [1] <https://www.molbase.com/>
- [2] <https://www.consensuseconomics.com/>