Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Selective Hydrogenation of Aromatic Furfurals into Aliphatic Tetrahydrofurfural Derivatives

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EXPERIMENTAL SECTION

Materials:

Furfural (98%), furfuryl alcohol (98%), 2-methyltetrahydrofuran (99%), 5-hydroxymethylfurfural (98%), 2,5-bishydroxymethyl tetrahydrofuran (98%), γ-valerolactone (98%), $PdCl_2$ (Pd 59.8%), and sodium borohydride (A. R.) were purchased from J&K Scientific Ltd. Tetrahydrofurfural was provided by Fluorochem Ltd. Silicon dioxide (A. R.), magnesium chloride (A. R.), aluminium nitrate (A. R.), aluminium chloride (A. R.), sodium hydroxide (A. R.) and sodium carbonate (A. R.) were provided by Sinopharm Chemical Reagent Co., Ltd. Tetrahydrofuran (A. R.) was supplied by Beijing Chemical Company. Magnesium nitrate (A. R.) was purchased from Innochem technology Co., Ltd. Hydrogen (>99.99%) was provided by Beijing Analytic Instrument Company. Zirconium dioxide (99+%) was supplied by Alfa Aesar and titanium dioxide was purchased from Acros Organics. All chemicals were used without further purification.

Layered double hydroxide preparation:

Layered double hydroxide with carbonate ions in the interlayers was prepared by co-precipitation method according to the reported method with some modification. The molar ratio of Mg^{2+}/Al^{3+} was 3:1. Generally, a solution (25 mL) of 6 M NaOH was introduced to the mixed metal nitrate solution (25 mL) of 1.2 M $Mg(NO_3)_2{\cdot}6H_2O$ and 0.4 M $Al(NO_3)_3{\cdot}9H_2O$ dropwise under vigorous stirring condition. It usually took 30 minutes for the nucleation. After aging for 24 h with vigorous stirring at room temperature, the mixture was filtered and washed with deionized water, and then lyophilized in the vacuum freeze drier at -50^{o}C. The white powder was ground evenly with a pestle, and LDH-MgAl-NO_3 was obtained.

Catalyst preparation:

The Pd/LDH and Pd/Oxide catalysts were prepared by impregnation method. 400 mg support was added in 40 mL aqueous solution of H_2PdCl_4 (0.113 mmol). After stirring for a while, the Pd precursors were reduced by dropping 0.5% freshly prepared aqueous solution of $NaBH_4$ (1.13 mmol, 20 mL) over 5 min. Then the dispersion was stirred for 2 h at room temperature and then the catalysts were obtained by filtration, followed by washing with ultra-pure water (3×20 mL) to remove excess chemicals. Finally, the catalysts were dried at 60°C in a vacuum oven overnight. The Pd contents of different catalysts are shown in Table S1.

The LDH-MgAl-NO_3 was calcined at 500 ^{o}C for 3 h to obtain the corresponding metal oxides MgO-Al_2O_3, and afterward stirred in water for 24 h to restore the structure of LDH.

Catalyst characterization:

The catalysts were characterized by different techniques. Hitachi-HT7700 electron microscope was applied to take a set of transmission electron microscopy (TEM) images, which was operated at 100.0 kV, 10.00 μA. Powder X-ray diffraction (XRD) patterns were obtained by Rigaku D/max-2500X-ray diffractometer (excitation source: Cu Kα radiation, $\lambda = 0.15406$ nm; tube voltage: 40 kV; tube current: 200 mA). The Pd loadings in the catalysts were determined by ICP-AES (VISTA-MPX). The EXAFS analysis was supported by beamline BL14W1 (Shanghai Synchrotron Radiation Facility). FT-IR spectra of the aldehyde group absorbed on the catalysts were recorded with a TENSOR 27 spectrometer. 50 mg Pd/LDH-MgAl-NO_3 catalyst was pretreated by dispersing in propyl aldehyde solution of water, EtOH, THF and n-hexane (200 μL in 5 mL solvent) at 30 °C respectively and stirred for 24 h. Similarly, 50 mg supports were pretreated by dispersing in propyl aldehyde solution of water or n-hexane (200 μL in 5 mL solvent) at 30 °C and stirred for 24 h. The suspension was centrifuged and washed using the correspoding solvent to remove the physical absorbed species, and then the samples were dried at 80°C. The samples were blended with KBr for IR characterization.

Catalytic activity tests:

The reaction was carried out in a 10 mL Teflon-lined stainless-steel autoclave equipped with a magnetic stirrer. The pressure was determined by a pressure transducer (FOXBORO/ICT, Model 93), which could be accurate to ±0.025 MPa. In a typical experiment, 1 mmol (96 mg) of furfural, 2 mL of the solvent (H_2O) and 10 mg of the catalyst were loaded into the reactor. As for the hydrogenation of HMF, 0.5 mmol (63 mg) of HMF, 2 mL of the solvent (H_2O) and 10 mg of the catalyst were put into the reactor. The reactor was sealed and purged with hydrogen to remove the air at room temperature. Then the reactor was placed in a furnace at 30^{o}C. Hydrogen was introduced into the reactor and the stirrer was started with a stirring speed of 800 r.p.m. After the reaction, the reactor was immediately quenched in an ice-water bath and the gas was released. The liquid reaction mixture in the reactor was transferred into a centrifuge tube. The reactor was washed using THF, which was combined with the reaction mixture. The catalyst was separated by centrifugation. The quantitative analysis of the liquid products was conducted using a GC (Agilent 7890B) equipped with a flame ionization detector (FID) and a HP-INNOWax capillary column (0.25 mm in diameter, 30 m in length) with γ-valerolactone as the internal standard. Identification of the products was done using a GC–MS (Agilent 7890B5977A, HP-INNOWax capillary column (0.25 mm in diameter, 30 m in length)) as well as by comparing the retention time to respective standards in the GC traces. The conversion of substrate and the selectivity of the products were calculated from the GC data.

Hydrogen spillover detection:

The hydrogen spillover was detected by WO_3. 1 g of WO_3 and 20 mg of catalyst were mixed and ground. A transparent double-pass quartz tube was employed to hold the sample and then plugged with silica wool. Hydrogen was allowed to flow through the tube at room temperature for 10 min. Then the powder was removed from the tube, and color changes of the samples were observed.

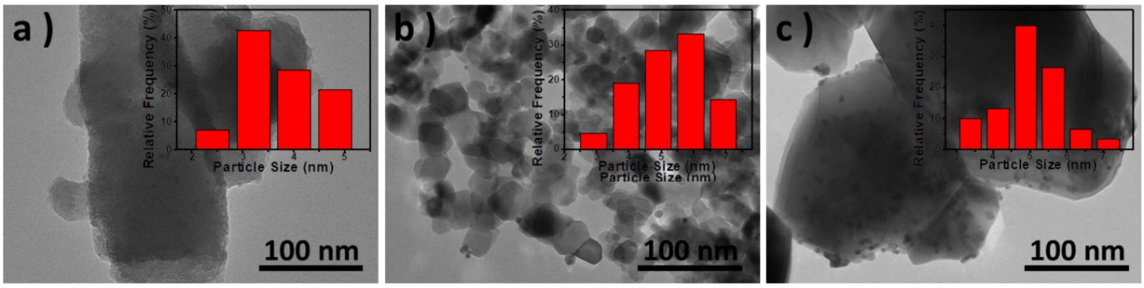


Fig. S1. (a-b) The TEM images of (a) Pd/SiO_2 (b) Pd/TiO_2 and (c) Pd/ZrO_2.

Table S1. The Pd contents of different catalysts.

Entry	Catalysts	Pd %
1	Pd/LDH-MgAl-NO_3	2.76
2	Pd/SiO_2	2.58
3	Pd/TiO_2	2.66
4	Pd/ZrO_2	2.98

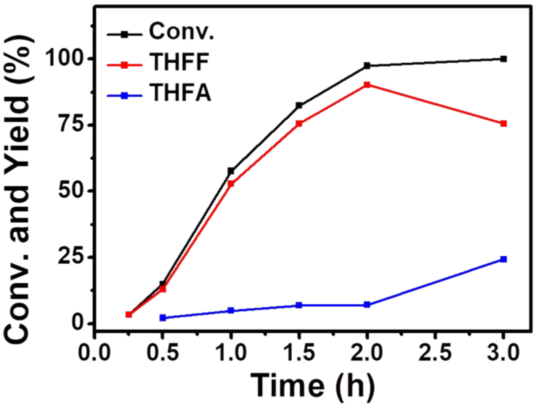


Fig. S2. The effect of the reaction time.

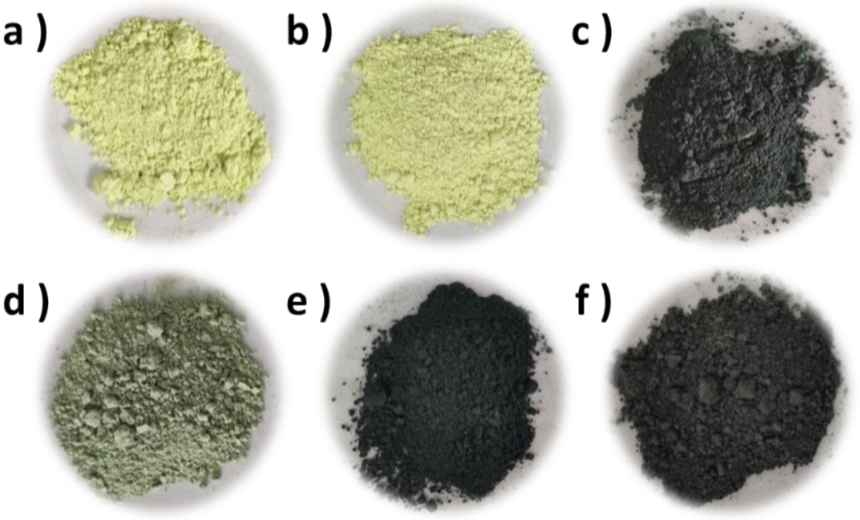


Fig. S3. (a-b) The images of pure WO_3 (a) before and (b) after H_2 treatment. (c-f) The images of H_2 treated mixture of WO_3 and (c) Pd/LDH-MgAl-NO_3, (d) Pd/SiO_2, (e) Pd/TiO_2 and (f) Pd/ZrO_2.

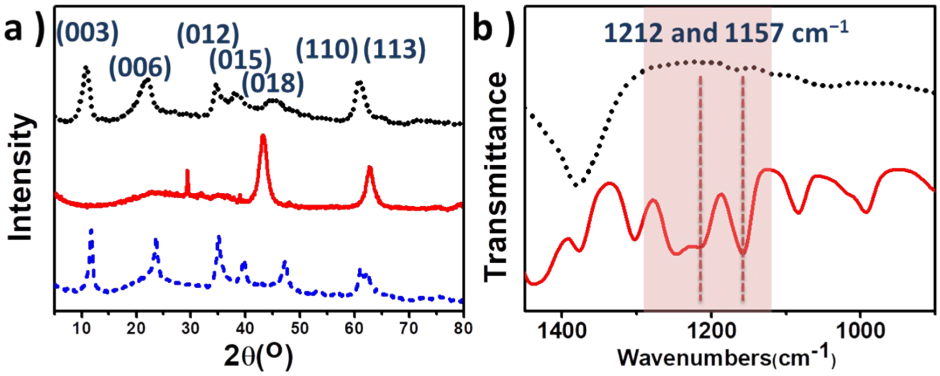
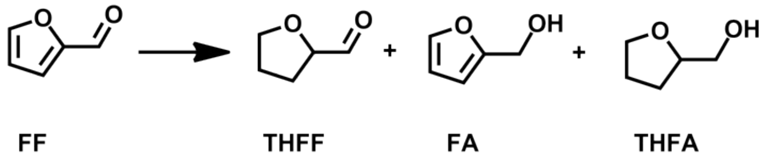


Fig. S4. (a) The XRD patterns of supports. LDH-MgAl-NO_3 (black dot line), MgO-Al_2O_3 (red solid line) and the restored LDH (blue dash line). (e) The FT-IR spectra of aldehyde-modified calcined LDH (MgO-Al_2O_3) supports (stirring in H_2O, black dot line; in n-hexane, red solid line).

Table S2. Results for the selective hydrogenation of FF over different catalysts.



Entry	Cat.	Solvent	t (h)	Conversion (%)	Yield (%)				Selectivity of THFF (%)
					THFF	FA	THFA	others	
1	Pd/MgO-Al_2O_3	H_2O	2	59.7	42.6	0	9.5	7.6	71.4

Reaction conditions: FF (1 mmol), catalyst (10 mg), solvent (2 mL); 30°C; H_2 pressure, 1 MPa; and stirring speed, 800 rpm.