

## Supporting Information

### **Reductive etherification of furfural via hydrogenolysis with Pd-modified aluminum phosphate and formic acid**

*Wenting Fang, Jonas Egebo, Leonhard Schill, Hua Chen and Anders Riisager\**

Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical  
University of Denmark, DK-2800 Kgs. Lyngby, Denmark.

\* E-mail: ar@kemi.dtu.dk, Tel.: (+45) 4525 2233

## Experimental

### Chemicals

Phosphoric acid (85% H<sub>3</sub>PO<sub>4</sub>, ≥99.8%), aluminum isopropoxide (Al(O-*i*-Pr)<sub>3</sub>, ≥98%), triethylamine (Et<sub>3</sub>N, ≥99%), furfural (FF, 99%), furfuryl alcohol (FAL, 98%), ethanol (≥99.8%), 1-propanol (≥99.9%), 2-propanol (≥99.5%), 1-butanol (≥99.4%), 2-butanol (99.5%), 2-methyl-1-propanol (99.5%), 1-pentanol (≥99%), 1-hexanol (≥99%), 1-octanol (≥99%), formic acid (HCOOH, FA, 99%), palladium nitrate dihydrate (Pd(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, 99%), palladium chloride (PdCl<sub>2</sub>, 99%), dimethyl sulfoxide (DMSO, ≥99.9 %), and methanol-d<sub>4</sub> (MeOD, ≥99.8%), were purchased from Sigma-Aldrich. All chemicals were used as received.

### Catalyst Synthesis

The APO-5 catalysts were prepared as described in literature<sup>1,2</sup> using a gel composition with 1.5Al<sub>2</sub>O<sub>3</sub>:1P<sub>2</sub>O<sub>5</sub>:1Et<sub>3</sub>N:45H<sub>2</sub>O. Al(O-*i*-Pr)<sub>3</sub> (21.45 g, 0.105 mol) was added to 23 mL distilled water and the mixture vigorously stirred for 0.5 h. Then a solution of 85% H<sub>3</sub>PO<sub>4</sub> (8.07 g, 0.07 mol) and 5 mL distilled water was added dropwise and the resulting solution stirred for 2 h. Et<sub>3</sub>N (4.9 mL) was subsequently added slowly and the mixture stirred for another 1 h. Hereafter was the solution transferred to an autoclave, which was tightly closed and kept at 180°C under autogeneous pressure for 73 h. After reaction the autoclave was cooled to room temperature and the product collected by filtration, washed with distilled water several times, oven dried at 110°C for 12 h and finally calcined at 550°C for 7 h. The synthesized zeolite was denominated as APO-5.

Palladium-loaded APO-5 catalysts were prepared by wet-impregnation using appropriate amounts of Pd(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O dissolved in deionized water. The mixture of the Pd solution and APO-5 was kept in a close system at room temperature for 12 h, whereafter the catalyst was dried at 110°C for 12 h followed by calcination at 400°C for 2 h under a flow of formier gas (50 mL/min, H<sub>2</sub>/N<sub>2</sub>:10/90 v/v). The Pd-loaded APO-5 catalysts were denominated as Pd-x (x = wt.% Pd metal).

### Catalyst Characterization

Powder X-ray diffraction (XRD) was carried out on a Huber G670 diffractometer with Cu-Kα radiation (λ = 0.154056 nm) with 2θ ranging from 3-100°.

Brunauer-Emmett-Teller (BET) surface area and porosity analysis were measured by N<sub>2</sub> physisorption performed at -196°C by a Micromeritics ASAP 2020 instrument. The samples (0.1 g) were degassed at 250°C for 4 h before the measurement.

X-ray fluorescence (XRF) spectra were obtained on a PANalytical epsilon3-XL instrument. Samples were prepared by fusing them into disks using a Claisse LeNeo fluxer oven.

X-ray photoelectron spectroscopy (XPS) of samples was evaluated ex-situ with a Thermo Scientific system at room temperature using AlK $\alpha$  radiation (1484.6 eV) and a spot size of 400  $\mu$ m. A flood gun was used to reduce sample charging effects and the obtained spectra were further corrected by setting the C1s binding energy to 284.8 eV. Each Pd 3d scan was performed 30 times. Data processing was done using the Avantage 4.87 software. Signals were corrected using a "Smart" background.

Ammonia and carbon dioxide temperature-programmed desorption (NH<sub>3</sub>-TPD and CO<sub>2</sub>-TPD) were performed on a Micromeritics AutoChem II 2920 machine. Initially, the samples (0.1 g) were exposed to He gas flow (25 mL/min) and heated up to 600°C followed by cooling to 100/50°C. Then NH<sub>3</sub>/CO<sub>2</sub> adsorption were conducted by purging with NH<sub>3</sub>/CO<sub>2</sub> gas mixture for 1 h, whereafter physically adsorbed gas was removed by purging with He gas for another 1 h. Desorption of NH<sub>3</sub>/CO<sub>2</sub> was eventually conducted in the temperature range 100/50-600°C with a heating ramp of 10°C/min and the amount of liberated gas was quantified by a thermal conductivity detector (TCD) and calibration curves.

Temperature-programmed reduction (TPR) was performed on a Micromeritics AutoChem II 2920 machine. Before measurement, metallic Pd was oxidized in flowing air to allow reduction to metallic Pd by hydrogen. Initially, the sample (0.1g) was calcined under an air flow (25 mL/min) with a heating ramp of 10°C/min to 400°C, followed by a temperature hold at 400°C for 5 h. After cooling to 50°C the gas switched to H<sub>2</sub> then followed by a temperature ramp to 600°C at 10°C/min.

Fourier transformed infrared (FT-IR) spectra of fresh and adsorbed FF catalysts were recorded on a Perkin Elmer 100 FT-IR spectrometer equipped with a Universal ATR sampling accessory. The catalyst with adsorbed FF was prepared by the following method before the measurements: Pd-2 (50 mg), FF (96 mg, 1 mmol) and methanol (1 mL) were mixed and shaken vigorously for 5 min followed by oven drying at 80°C for 2 h to remove the methanol.

Scanning electron microscopy (SEM) images of samples were recorded on an AFEG 250 Analytical ESEM at 5 kV.

Transmission electron microscopy (TEM) images of samples were recorded on a Tecnai T20 G2 microscope operated at an acceleration voltage of 200 kV. TEM samples were prepared by

ultrasonically dispersing samples in ethanol for 5 min, and two drops of the solution was deposited onto a carbon-coated copper grid.

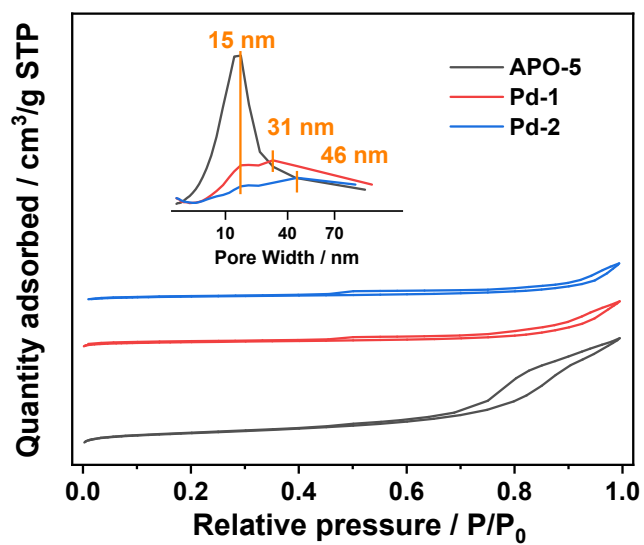
### **Catalyst Activity Tests**

The reductive etherification of FF was performed in 15 mL ACE pressure tubes in an oil bath with a magnetic stirrer. A mixture of FF (96 mg, 1 mmol), catalyst (50 mg), ethanol (5-x mL), FA (x = mL of FA) was placed into the tube and the tube placed in an oil bath (600 rpm) with a designated temperature for the reaction. After a specified reaction time, the tube was cooled to room temperature and liquid samples of the reaction mixture was filtered and analyzed by <sup>1</sup>H NMR (Bruker 400 MHz spectrometer, room temperature, MeOD) using DMSO as an internal standard.

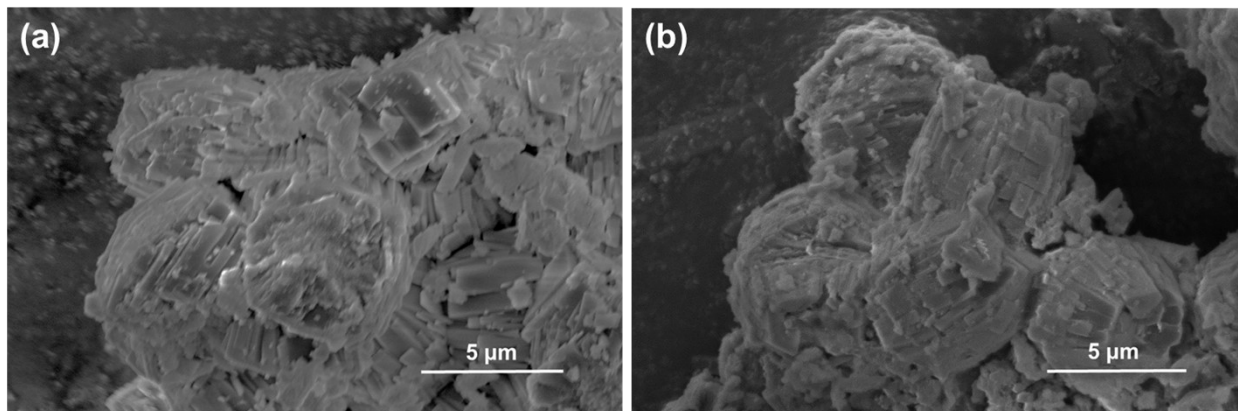
### **Catalyst Leaching and Reusability Test**

Leaching and catalyst recyclability was examined for the Pd-2 catalyst after separate reactions performed for 4 h at 140 °C. For the leaching test, the reaction mixture was rapidly cooled to room temperature, the catalyst removed by filtration, and the solution then reheated to 140 °C for another 20 h. For the reusability test, the catalyst was collected *via* filtration after the reaction, and then directly used in a next reaction run. The collected reaction mixtures were analyzed as described above.

## Supplementary figures



**Fig. S1.** N<sub>2</sub> adsorption-desorption isotherms (inset: BJH mesopore size distribution) of APO-5, Pd-1, and Pd-2.



**Fig. S2.** SEM images of APO-5 and Pd-2.

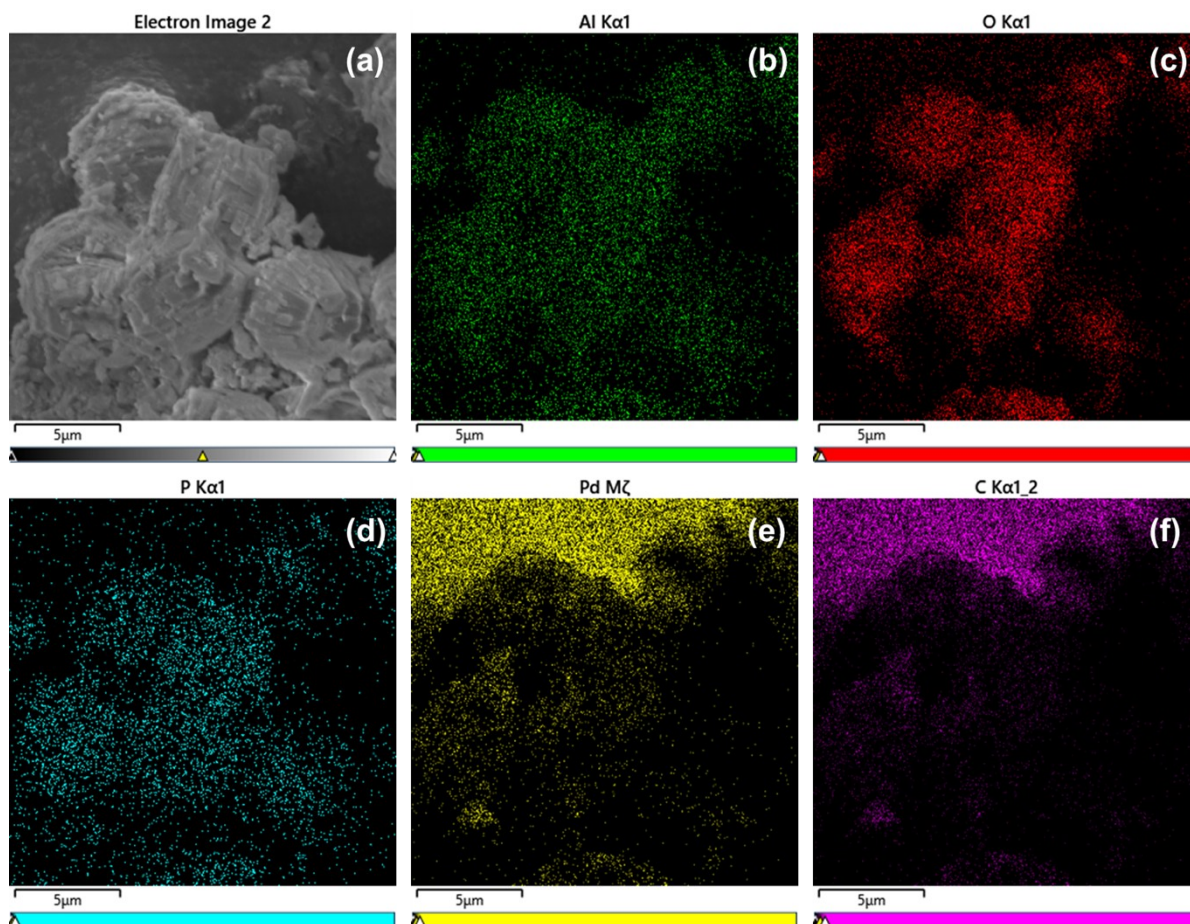


Fig. S3. EDS mapping of Pd-2.

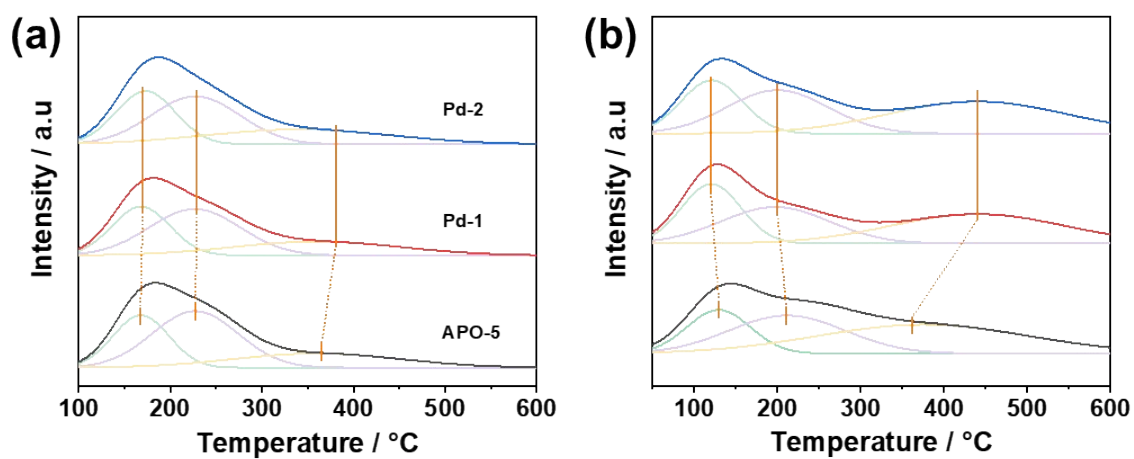
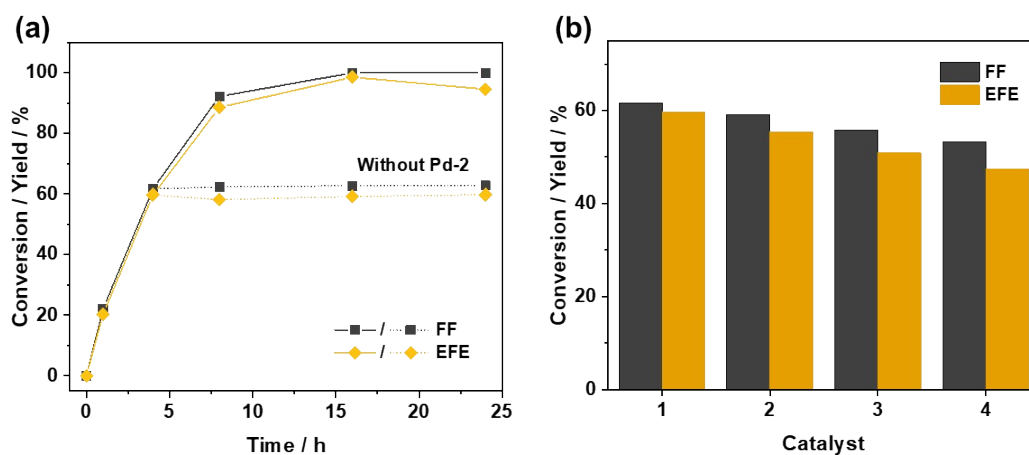
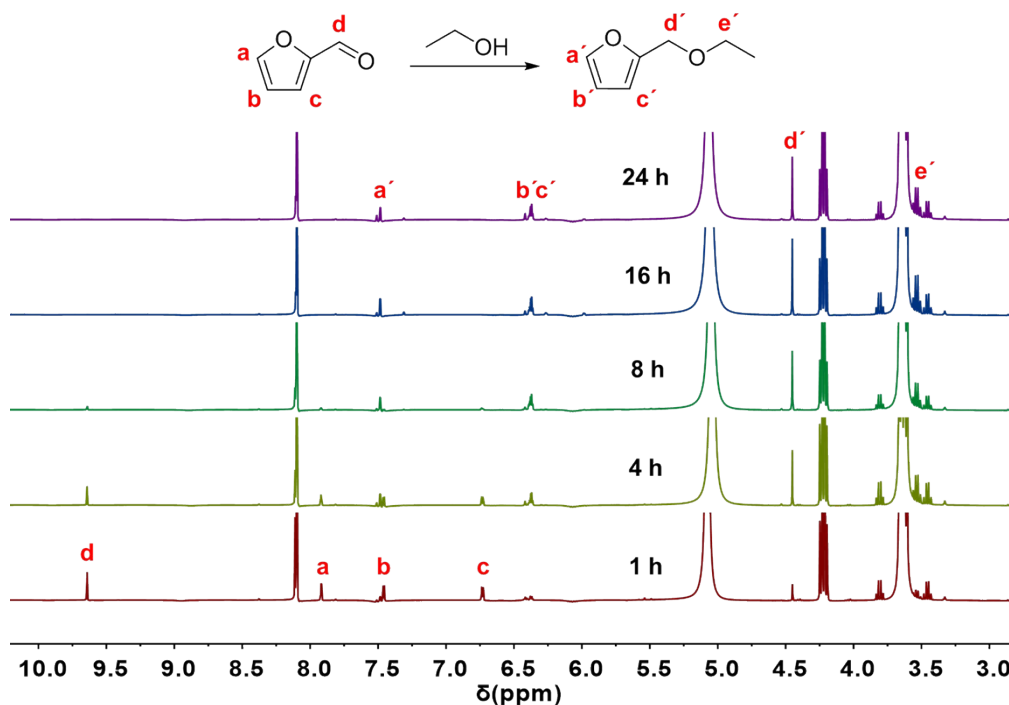


Fig. S4. (a) NH<sub>3</sub>-TPD and (b) CO<sub>2</sub>-TPD profiles of APO-5, Pd-1, and Pd-2.



**Fig. S5.** (a) Leaching study with the Pd-2 catalyst. Reaction conditions: FF (96 mg, 1 mmol), Pd-2 (50 mg), FA (0.38 mL, 10 mmol), ethanol (4.62 mL), 140°C; (b) Recycling study with the Pd-2 catalyst. Reaction conditions: FF (96 mg, 1 mmol), Pd-2 (50 mg), FA (0.38 mL, 10 mmol), ethanol (4.62 mL), 140°C, 4 h.'



**Fig. S6.** <sup>1</sup>H NMR spectra of the reaction mixtures at different reaction times. Reaction conditions: FF (96 mg, 1 mmol), Pd-2 (50 mg), FA (0.38 mL, 10 mmol), EtOH (4.62 mL), 140°C.

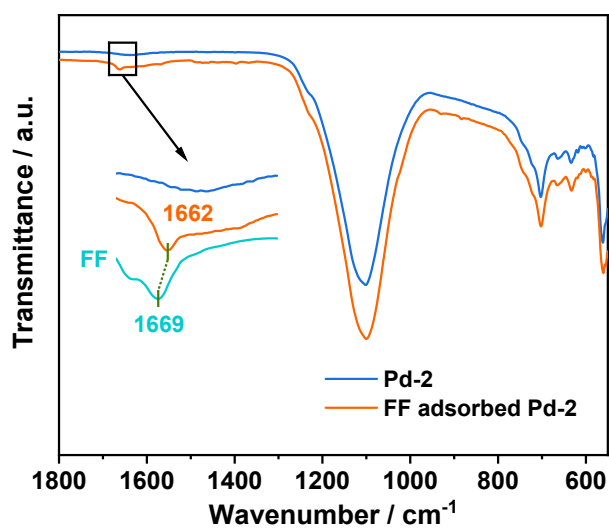


Fig. S7. FT-IR spectra of fresh and FF pre-adsorbed Pd-2.

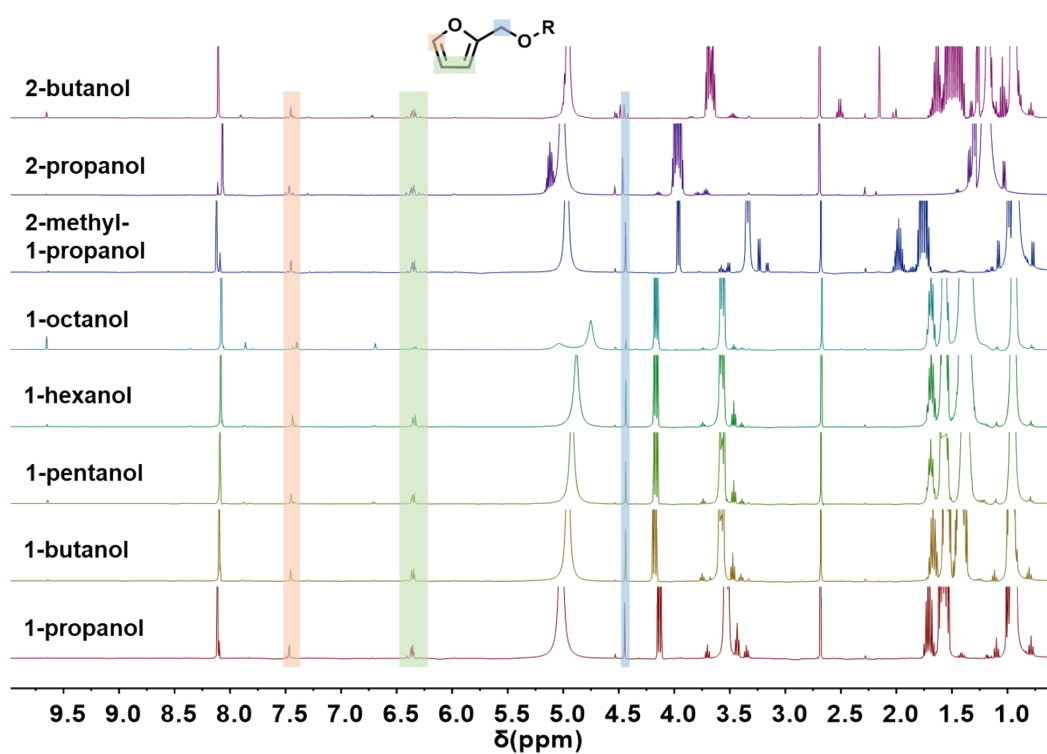


Fig. S8.  $^1\text{H}$  NMR spectra of the products in Table 1.



## Supplementary tables

**Table S1.** Textural properties of APO-5 and Pd-loaded APO-5

Sample	Pd-loading (wt.%) <sup>a</sup>	S <sub>total</sub> (m <sup>2</sup> /g) <sup>b</sup>	V <sub>micro</sub> (cm <sup>3</sup> /g) <sup>c</sup>	V <sub>meso</sub> (cm <sup>3</sup> /g) <sup>d</sup>	Acidity (mmol/g) <sup>e</sup>	Basicity (mmol/g) <sup>f</sup>
APO-5	-	192	0.05	0.25	0.29	0.24
Pd-1	1.72	163	0.06	0.10	0.20	0.24
Pd-2	2.45	129	0.05	0.05	0.21	0.24

<sup>a</sup> Determined by XRF. <sup>b</sup> Calculated by the BET method. <sup>c</sup> Estimated by t-plot method. <sup>d</sup> Calculated by subtracting the micropore volume from the total pore volume. <sup>e</sup> Determined by NH<sub>3</sub>-TPD. <sup>f</sup> Determined by CO<sub>2</sub>-TPD.

**Table S2.** Acid characteristics of APO-5 and Pd-loaded APO-5 <sup>a</sup>

Sample	Weak sites		Medium sites		Strong sites		Total acidity (mmol/g)
	T <sub>max</sub> (°C)	Acidity (mmol/g)	T <sub>max</sub> (°C)	Acidity (mmol/g)	T <sub>max</sub> (°C)	Acidity (mmol/g)	
APO-5	173	0.09	239	0.13	371	0.07	0.29
Pd-1	168	0.06	227	0.09	360	0.05	0.20
Pd-2	168	0.06	227	0.10	360	0.05	0.21

<sup>a</sup> Determined by NH<sub>3</sub>-TPD.

**Table S3.** Base characteristics of of APO-5 and Pd-loaded APO-5 <sup>a</sup>

Sample	Weak sites		Medium sites		Strong sites		Total basicity (mmol/g)
	T <sub>max</sub> (°C)	Basicity (mmol/g)	T <sub>max</sub> (°C)	Basicity (mmol/g)	T <sub>max</sub> (°C)	Basicity (mmol/g)	
APO-5	129	0.05	211	0.08	375	0.11	0.24
Pd-1	121	0.07	197	0.08	441	0.09	0.24
Pd-2	121	0.06	200	0.08	440	0.10	0.24

<sup>a</sup> Determined by CO<sub>2</sub>-TPD.

**Table S4.** Catalytic performances <sup>a</sup>

Substrate	Catalyst	Conversion (%) <sup>b</sup>	Yield (%) <sup>b</sup>				Carbon loss (%)
			FAL	DEF	MF	EFE	
FAL	APO-5	41	-	0	0	15	26
FF	Pd/C <sup>c</sup>	18	1	4	0	3	10

<sup>a</sup> Reaction conditions: Substrate (1 mmol), catalyst (50 mg), FA (0.38 mL, 10 mmol), ethanol (4.62 mL), 140°C, 4 h. <sup>b</sup> Quantified using <sup>1</sup>H NMR. <sup>c</sup> 5 wt.% Pd/C (20 mg).

## References

1. W. T. Fang and A. Riisager, *Appl. Catal. B: Environ.*, 2021, **298**, 120575.
2. S.P. Elangovan, V. Krishnasamy and V. Murugesan, *Catal. Letters*, 1996, **36**, 271-277.