Supporting Information

Cascade upgrading of gamma-valerolactone to biofuels

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1. Experimental

1.1 Supports synthesis

The typical process of HY synthesis was as following[1]: The sodium of Zeolite Na-Y (SiO_2/Al_2O_3-weight ratio of 3, Sigma-Aldrich) was exchanged with an aqueous solution of NH_4Cl (1 M) at 80 °C for 4 h. This process was repeated three times. The obtained zeolite NH_4Y was washed with distilled water. Subsequently, the powder material was dried in air at 80 ^oC for 12 h and then calcined at 550 °C for 12 h (heating rate 2 ^oC/ min).

The typical process of the MCM-41 synthesis was performed as following[2,3]: 10.0 g CTAB were firstly dissolved in 250 mL water and stirred at 40 °C until a clear solution was obtained. After that, 20.2 mL TEOS was added into the solution, followed by the drop wise addition of NaOH (2 M) and H_2SO_4 (96%) to adjust the pH value of ~11. This solution was then transferred into several vessels with Teflon-line and treated at 180 °C for 48 h in an oven. The obtained gel was washed for three times with pure water, and then separated by centrifugation and dried at 100 ^oC for 12 h. Finally, the solid material was calcined at 550 ^oC for 6 h in a furnace with the heating rate of 120 ^oC/h.

For the synthesis of ZrMCM-41 (Si/Zr=20), zirconium n-butyl oxide (20% in 80% butanol) was used as Zr resources. For the synthesis of TiMCM-41 (Si/Ti=20), titanium (IV) tert-butoxide was used as the Ti resources. All the other procedures were very similar to the process of MCM-41 synthesis.

1.2 Preparation of Pd loaded on different supports

Five supported Pd catalysts were prepared via a wet impregnation method. The required amount of precursor solution (20 mL) was prepared with deionized water (the conductivity at 25 ^oC was 0.056 s/m) in a 50-mL round bottom flask, where a magnetic stirring bar inside was used to stir the solution. The round bottom flask was kept at room temperature and the mixture was then stirred using the speed of 1000 rpm. After 1 h, the support was slowly added to the solution, with the agitation speed 1000 rpm at room temperature for another 1 h. After mixing of the support with the impregnation solution, the temperature was raised to 70 ^oC and kept for 12 h, where the temperature was controlled by a thermocouple in an oil bath. The 12 h will allow slow impregnation and well dispersion of the metal precursor. The resulted solution went through centrifugation and the left solvent was removed. The obtained powder was then reduced directly at 350 ^oC with a heating ramp of 2 ^oC/min and then kept under a flow of 10 vol.% H_2/N_2 for 2 h. The catalyst sample was automatically cooled to room temperature a rapid manner and the resulted catalyst was kept in Ar environment.

1.3 Characterization of different supports and metal catalyst

The different mesoporous supports, fresh and spent metal Pd catalysts were characterized by powder X-ray diffraction (XRD), X-Ray Photoelectron spectroscopy (XPS), energy-dispersive

X-ray analysis (EDX), Nitrogen sorption isotherms (N_2-BET), transmission electron microscopy (TEM) and Temperature-programmed desorption of ammonia (NH_3-TPD).

TEM analysis was used to investigate structural features of the catalysts with a Philips CM 20 instrument at 120 KV. Scanning electron microscopy (SEM) was obtained with FEI Helios - FIB operating at an acceleration voltage of 20 kV. The powder X-ray diffraction (XRD) patterns for qualitative phase analysis were collected on a Bruker AXS D8-Advanced diffractometer with Cu Kα radiation (λ = 1.5418 Å) to record a data set in a continuous scan mode in the range of 5 - 95° with intervals of 0.05°.

XPS measurements were performed with a *Kratos HSi* spectrometer with a hemispherical analyzer and a monochromatized Al$K\alpha$ X-ray source (E = 1486.6 eV), operated at 15 kV and 15 mA. For the narrow scans, analyzer pass energy of 40 eV was applied. The hybrid mode was used as lens mode. The base pressure in the analysis chamber was 6×10^{-10} Torr. To account for charging effects, all spectra are referred to Si 2p at 103.45 eV.

Nitrogen adsorption data have been measured on an *ASAP 2010* sorption analyzer (*Micromeritics*) at 77 K. The samples have been activated under a vacuum of 0.01 mbar at 200 °C for 10 h prior to measurements. Data evaluation was performed with the *Autosorb 1.52* software package (*Quantachrome*). The BET surface area was calculated from the adsorption branch and NLDFT method was used to calculate the pore size.

Temperature-programmed desorption of ammonia (NH_3-TPD) analysis was carried out in an AutoChem II 2920 apparatus (Micromeritics, USA) to estimate the amount and strength of acid sites. The sample was fluxed with a He flow at temperatures up to 500 ^{o}C, maintained for 1 h at this temperature, and then was allowed to cool down to room temperature and exposed to flowing NH_3 (15% in He) for 0.5 h. Afterwards, the system was purged for 0.5 h with helium to eliminate the excess NH_3 gas. The temperature of the sample was then raised linearly (10 ^oC/ min) from room temperature to 600 ^oC. The desorbed NH_3 was monitored by means of a thermal conductivity detector and quantified by comparing the areas under the curve of the respective thermograms with those obtained from previous calibration using known amounts of NH_3.

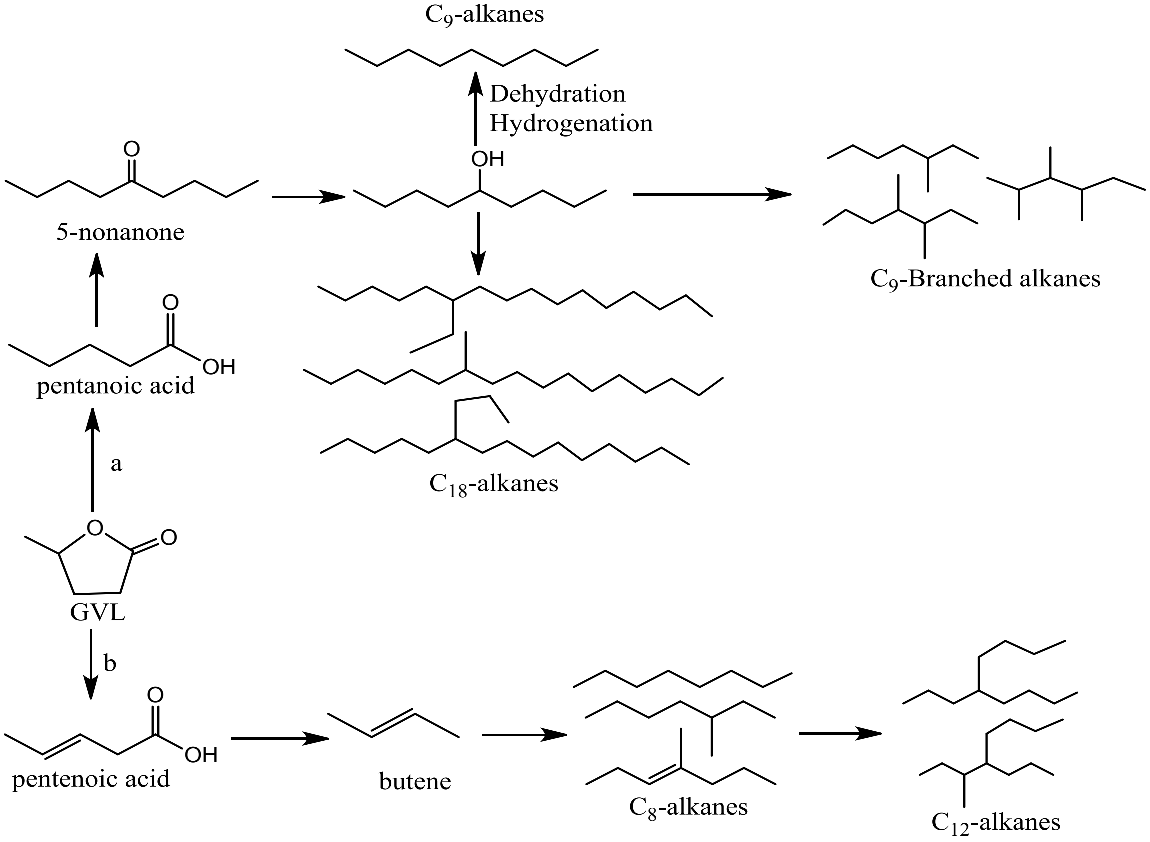
1.4 Cascade upgrading of γ-valerolactone

The cascade upgrading of γ-valerolactone was performed in a 20 mL vessel (Parr Company). 2.2 g *γ*-valerolactone reactant was added into 5 mL octane, where a magnetic stirring bar inside was used to stir the solution for 10 min. 0.1 g catalyst was added inside for another stirring of 5 min. To remove the air inside, the vessel was flushed with Ar for several times before H_2 was introduced inside. t_0 was defined for the moment at which the inner temperature of the autoclave reached desired temperature (this took around 20 minutes). After reaction, the autoclave was cooled down to room temperature in a controlled manner using an ice water bath. Through the measurement of the weight of the vessel before and after reaction, there is no clear difference was found, which suggested no loss during the reaction. The product mixture was firstly centrifuged for 0.5 h at the speed of 4500 rpm, and then filtrated by membrane. The subsequent aqueous samples were analysis by GC (Agilent 7890B, column: 30 m SE-54 G/17, FID). The column temperature was raised from 30 to 250 °C with a heating rate of 5 °C/min. The injector temperature was set to 350 °C, which was loaded with a sampling volume of 1 μL. The left gas was collected by gas bag and measured by GC (Agilent 7890B, column: 30 m MoleSieve 5A, TCD) with a sampling volume of 2 μL.

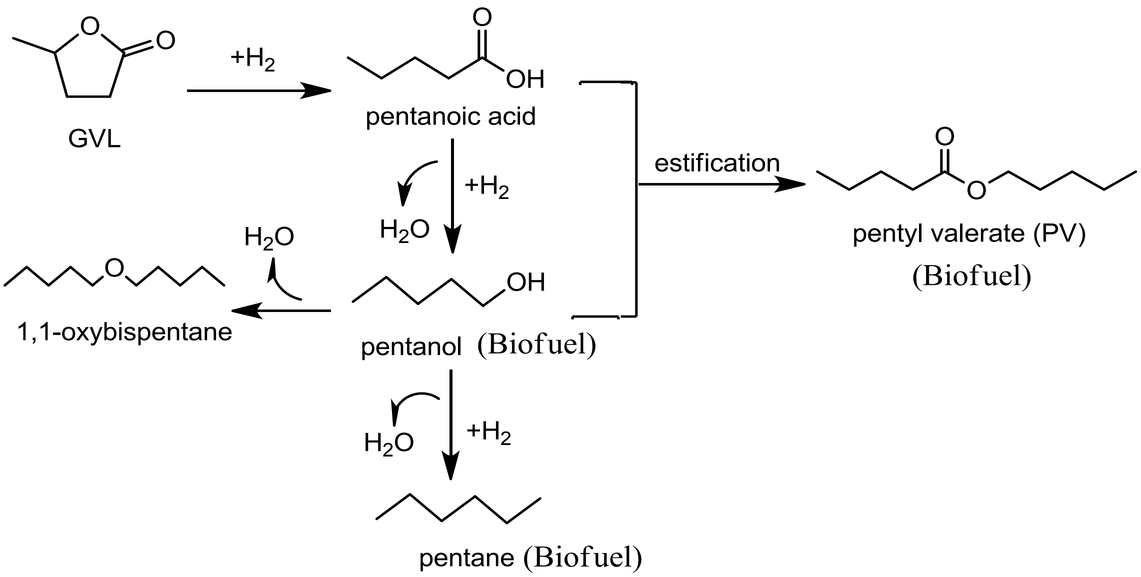
1.5 Stability tests

To check the recyclability of the resulting catalysts, recycling experiments were done with a 5% Pd/HY catalyst under the test condition of 260 °C, 12 h and 80 bars. After reaction, the catalyst was recycled through the centrifugation for 30 min and then dried in 90 °C oven for 12 h.

To get rid of the possible carbon deposit on the catalyst surface, the spent catalyst was reduced at 350 °C with a rising rate of 2 °C/min and kept at 350 °C for 1 h under the air enviroment, then reduced under a flow of 10 vol.% H_2/N_2 for 1 h.



Scheme S1. Routes for the transformation of GVL into liquid alkanes.[4]



Scheme S2. Reaction network on the hydrogenation of GVL.[5]

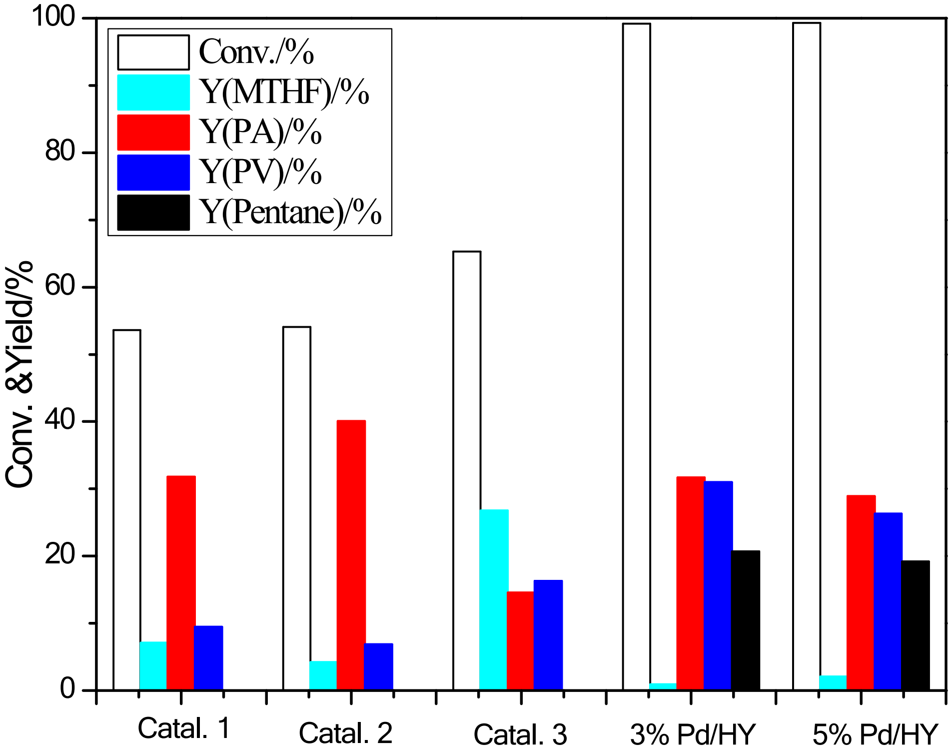


Fig. S1. Evaluation of different catalysts in the hydrogenation of GVL in octane solvent.[a]

a Reaction conditions: *m*(GVL) = 2.20 g, *m*(catalyst) = 0.10 g, *V*(octane) = 5 mL, p_{H2} = 40 bars, *T* =260 °C, *t* =12 h, stirring speed = 1000 rpm. Catal. 1: 5% Pd/MCM-41; Catal. 2: 7% Pd/MCM-41; Catal. 3: 5% Pd/ZrMCM-41; PA: pentanoic acid; ether: 1,1-oxybispentane; PV: pentyl valerate.

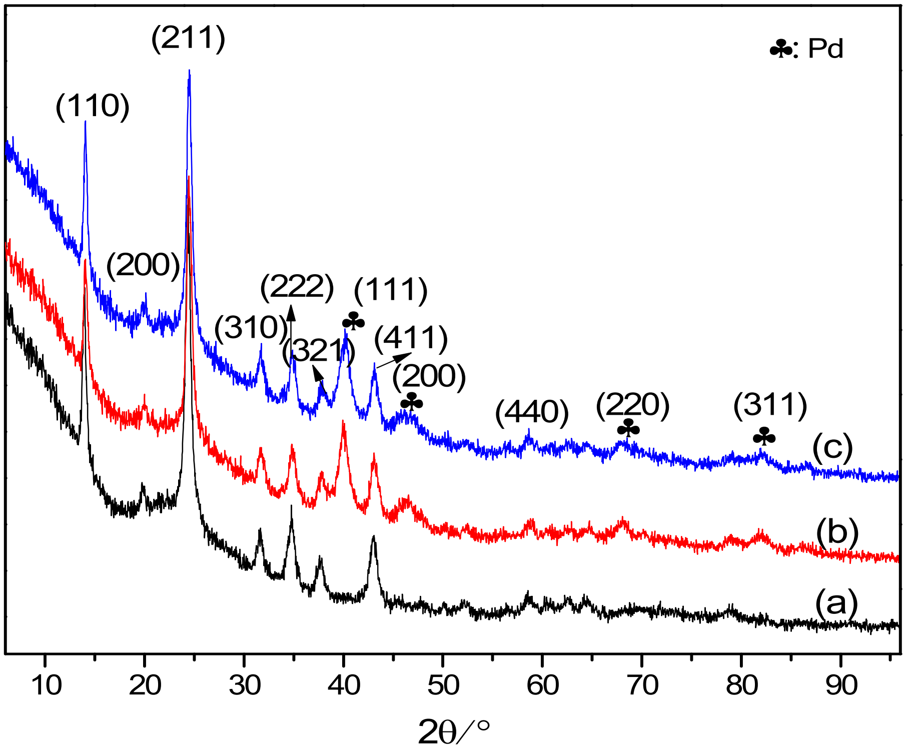


Fig. S2. XRD analysis of the resulting HY and supported metal samples: (a) HY (b) 3% Pd/HY (c) 5% Pd/HY.

The particle sizes (*L*) for each sample were calculated using the Scherrer Equation (1), where λ corresponds to the Cu $K\alpha$ radiation, and β is the full width at half-maximum for a reflection maximum, located at 2θ). The average particle sizes of 3.5 nm and 4.7 nm are calculated in the case of 3% and 5% Pd/HY, respectively.

$$L = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

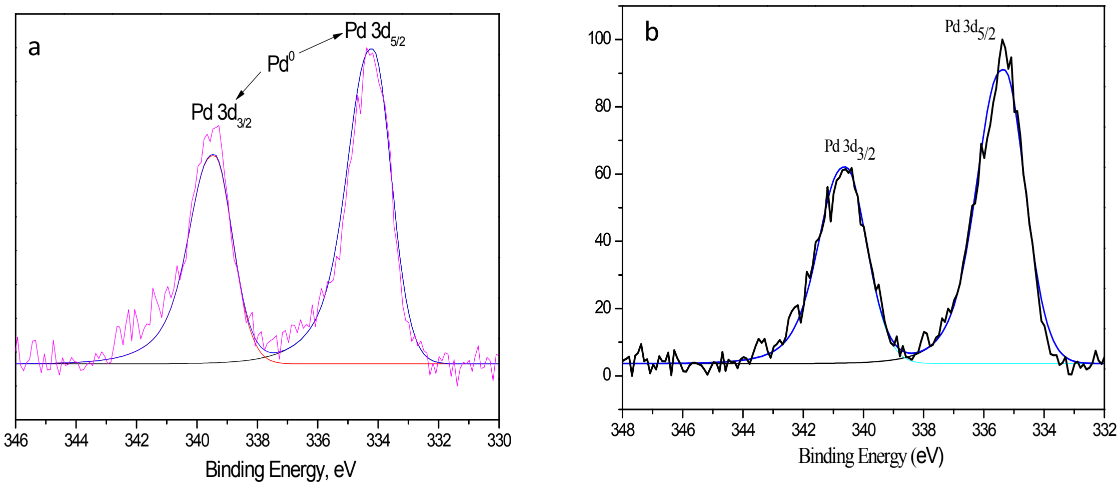


Fig. S3. XPS analysis of the resulting Pd catalysts with 3% (a) and 5% (b) loading.

For the supporting metal nanoparticles, the surface was very sensitive due to the thermal dynamic. XPS was used to investigate the oxidation state of Pd on the surface case shown in Fig. S3. As expected, the presence of two prominent sets of Pd (3d) peaks, corresponding to the $3d_{3/2}$ and $3d_{5/2}$ orbital states, demonstrated that Pd was present on the surface in the reduced form. The peak regions of Pd can be fitted with two sets of peaks at 340.6 eV ($3d_{3/2}$) and 335.3 eV ($3d_{5/2}$). Besides, the very weak peak was observed at 341.7 eV and 336.5 eV, which was possible due to the interaction between of Pd and the oxygen from the HY support.

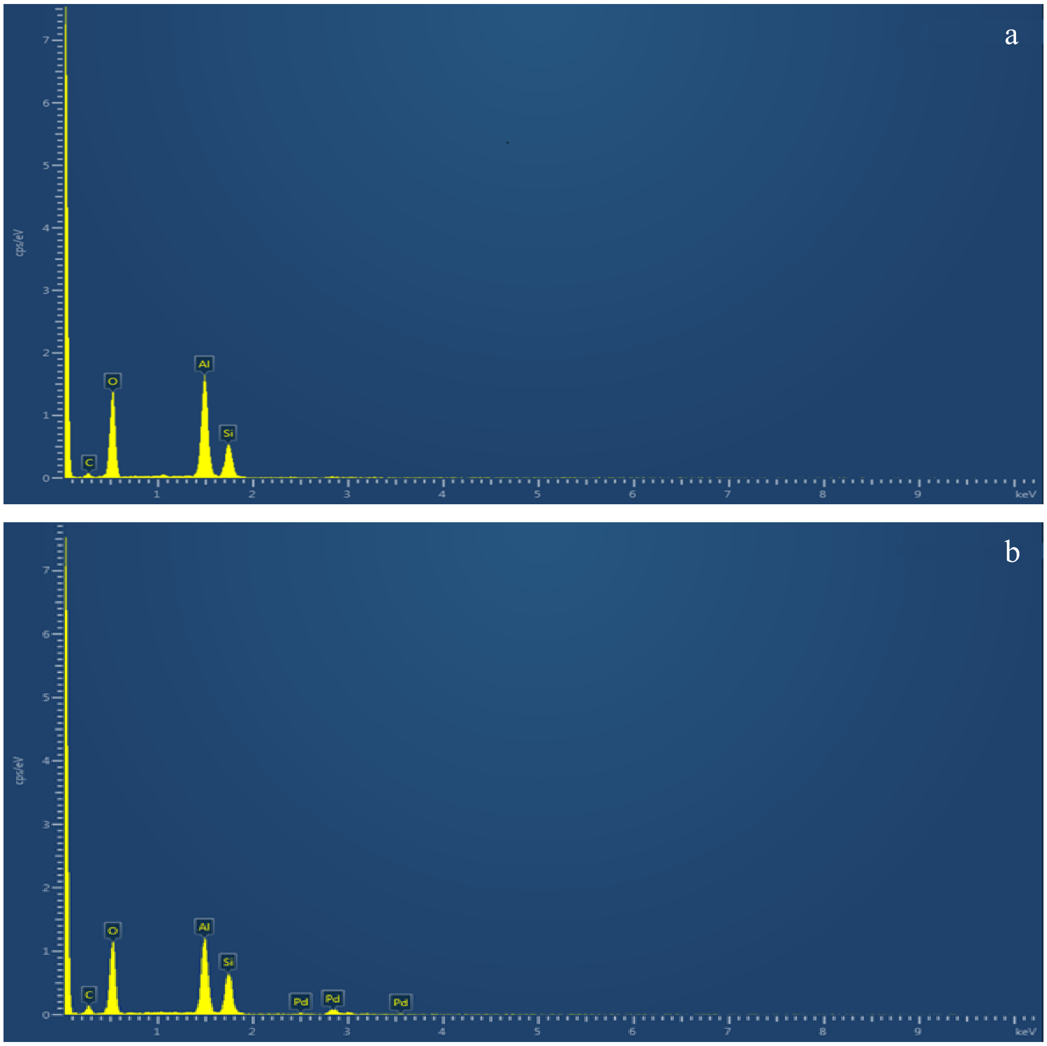


Fig. S4. EDX analysis of the HY support (a) and its supported 5% Pd catalyst (b).

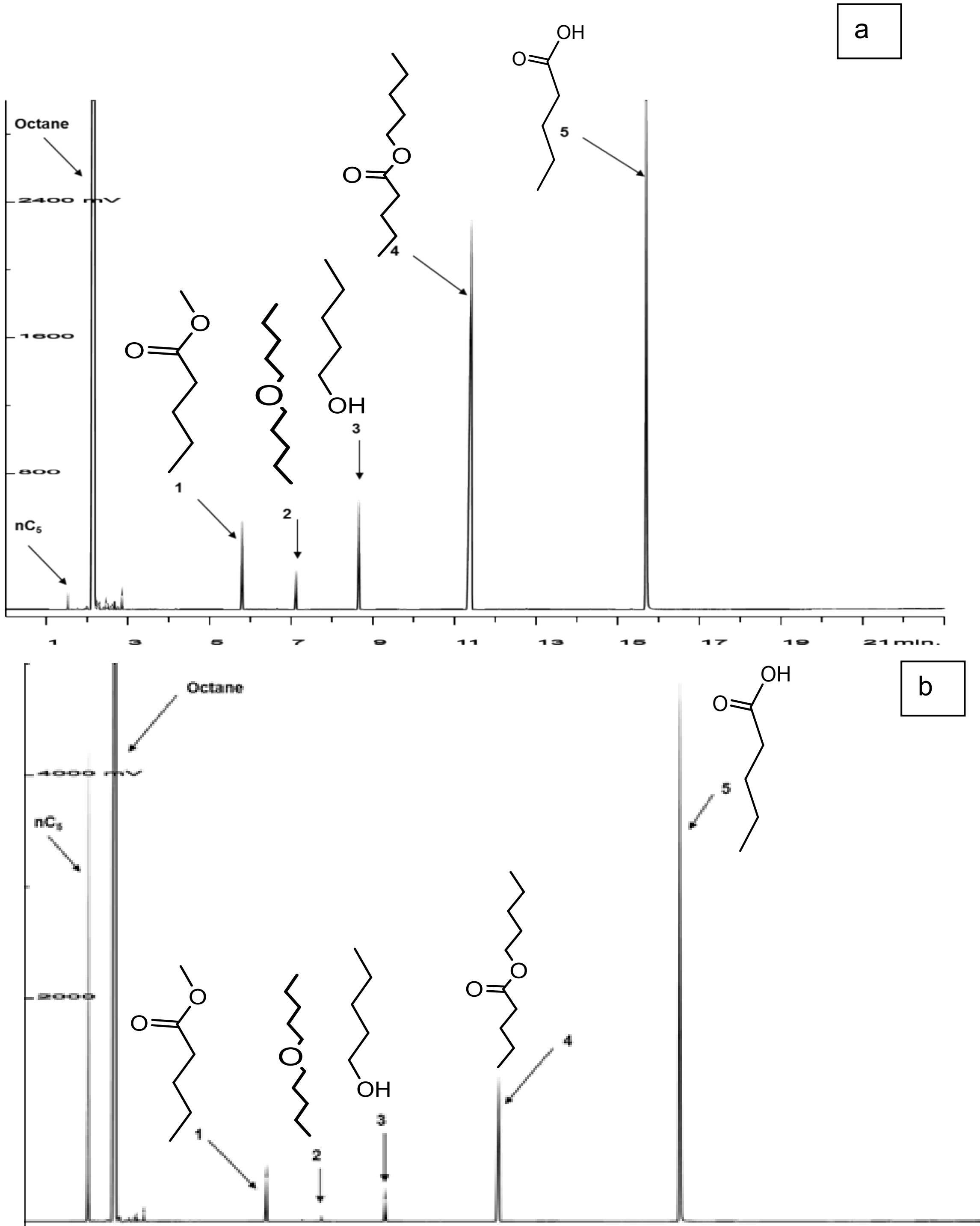


Fig. S5. GC analysis spectrum: (a) the reaction is operated under the condition of at 260 °C, 30 h and 40 bar H_2; (b) the reaction is operated under the condition of 280 ^{o}C, 24 h and 40 bar H_2. 1: methyl valerate; 2: 1,1-oxybispentane; 3: pentanol,;4: pentyl valerate; 5: pentanoic acid. Other products include MTHF, 1,4-pentanediol, *etc*.

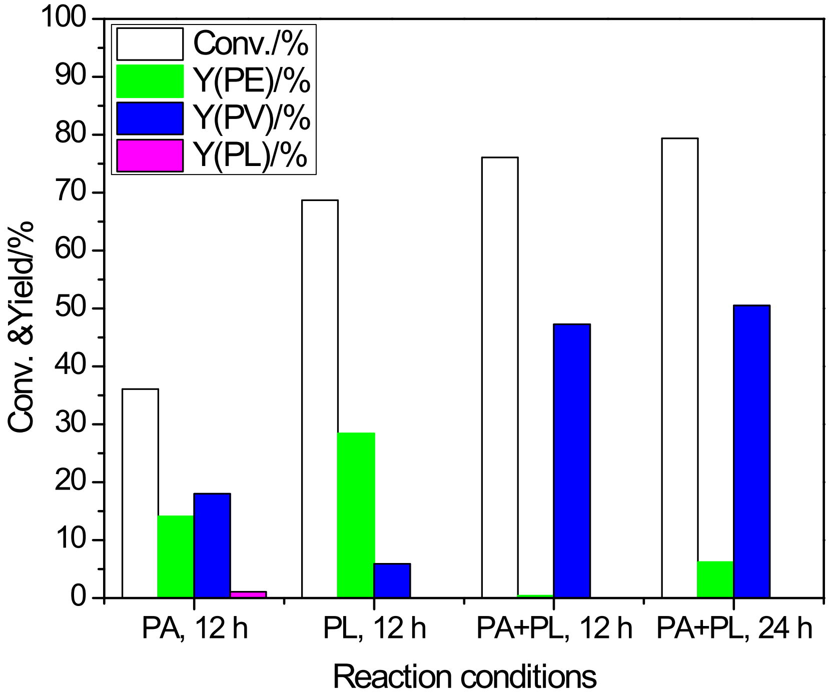


Fig. S6. Different intermediates were used.[a]

[a] *Note: Reaction conditions:* *m*(5% Pd/HY catalyst) = 0.10 g, *V*(octane)= 5 mL, p_{H2}= 40 bar, stirring speed= 1000 rpm; *b*: *m*(PA)= 2.2 g; *c*: *m*(pentanol)= 2.0 g; *d*: *m*(PA)=1.1 g, *m*(pentanol)=1.1 g. PA: pentanoic acid; PL: pentanol; PE: 1,1-oxybispentane ether.

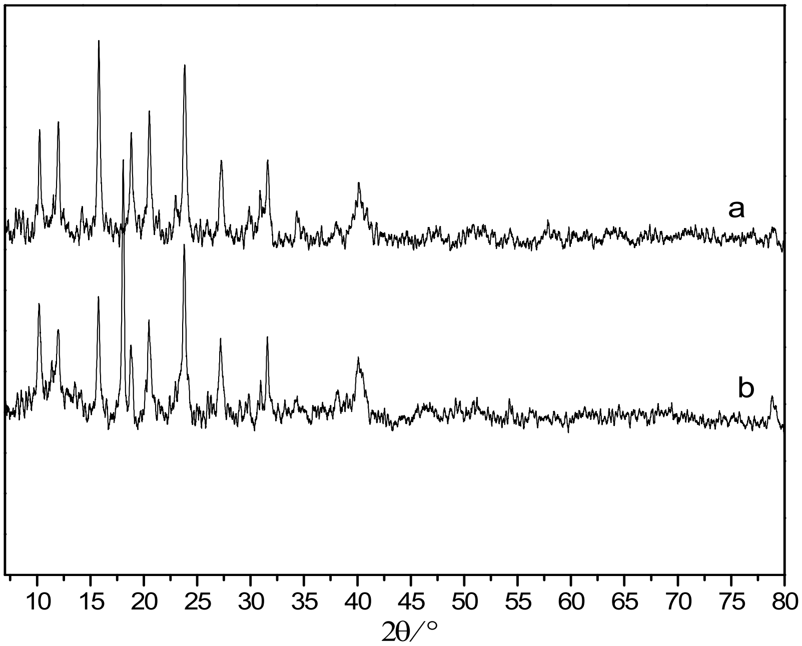


Fig. S7. XRD analysis of the fresh (a) and spent (b) 5% Pd/HY catalyst.

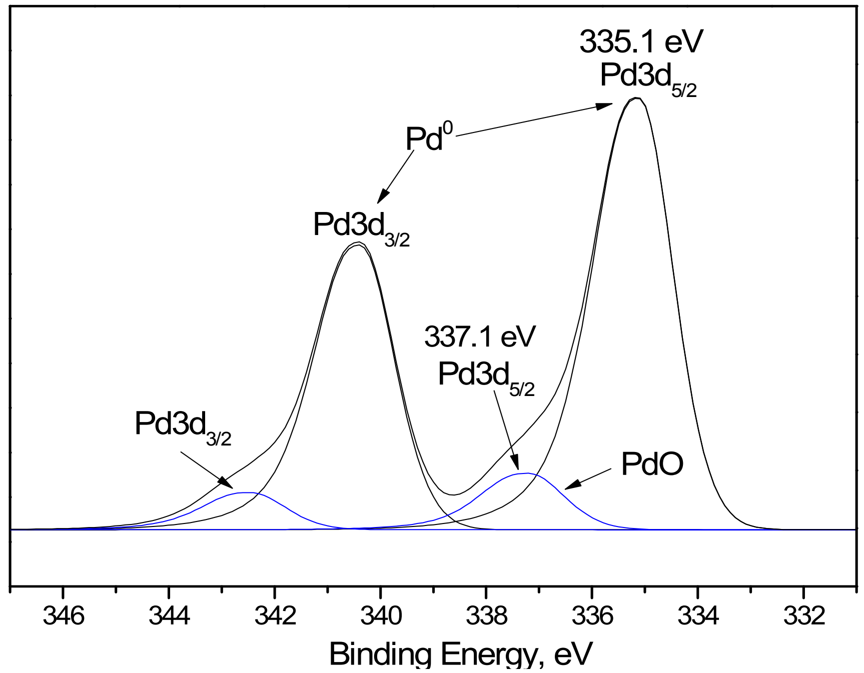


Fig. S8. XPS analysis of the spent 5% Pd/HY catalyst.

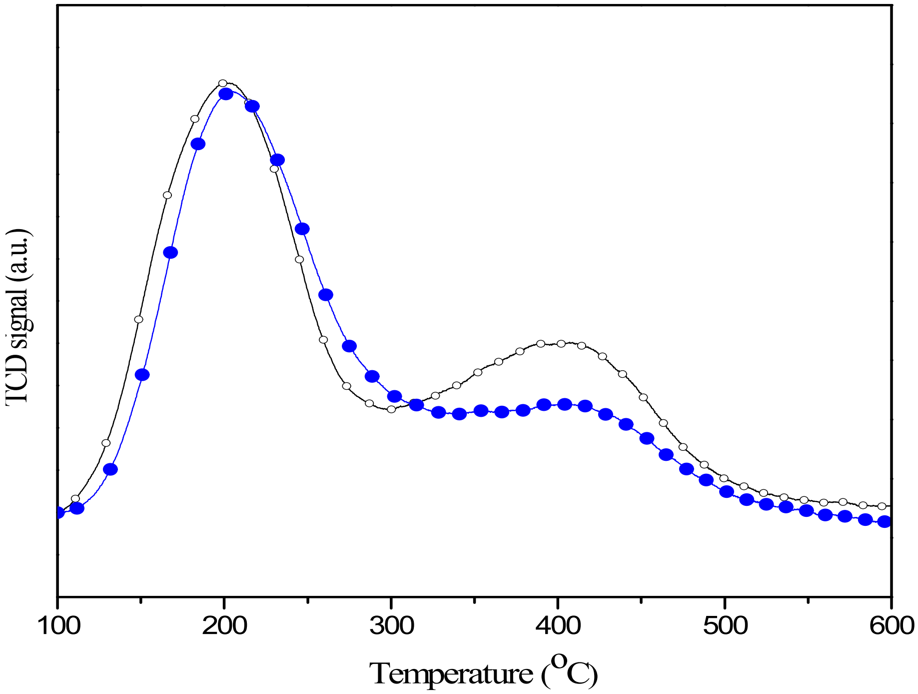


Fig. S9. NH_3-TPD of the fresh (black color) and spent (blue color) 5% Pd/HY catalysts.

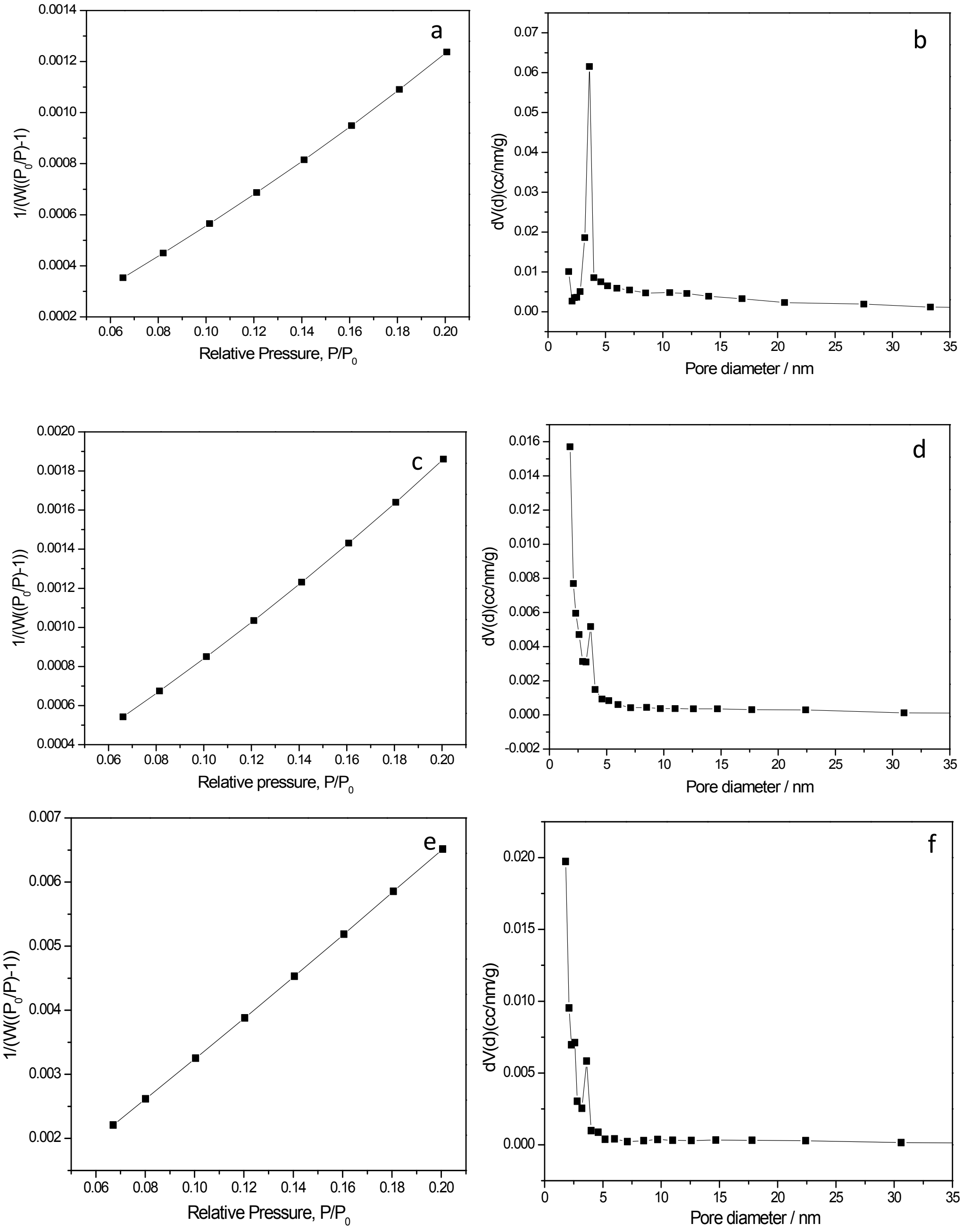


Fig. S10. BET Plot, Size distributions of the HY support (a and b), the fresh (c and d) and reduced (e and f) 5% Pd/HY catalysts.

Table S1. The BET surface area and porosity of the support and its loaded catalysts.

No.	Catalyst	BET surface area (m^2 g^{-1})	Pore diameter (nm)	Micropore area (m^2 g^{-1})	External surface area (m^2/g)	Micropore volume (cm^3 g^{-1})
1	HY	677	1.95	615	62	0.2864
2	Fresh 5% Pd/HY	451	2.12	397	54	0.1849
3[a]	Spent 5% Pd/HY	135	5.03	45	90	0.0201
4[b]	Reduced 5% Pd/HY	429	2.27	378	51	0.1678

Note: *a*, catalyst recycled after the third run. *b*, catalyst was reduced in the fourth run.

References

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