Electronic Supplementary Information (ESI)

Complete Utilization of Waste Lignin: Preparation of Lignin-derived Carbon Supports and Conversion of Lignin-derived Guaiacol to Nylon Precursors

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Table S1. Composition of the main products produced after the hydrothermal reaction of lignin.

	Guaiacol (mol %)	Creosol (mol %)
Kraft lignin[a]	45.9	8.1
Klason lignin[b]	33.6	25.0

[a]The amount of guaiacol produced: 0.07 g; minor products (< 6%) of kraft lignin: 1,2-dimethoxy benzene, 2-methoxy-6-methyl phenol, xylene.

[b] The amount of guaiacol produced: 0.04 g; minor products (< 5%) of Klason lignin: 2-methyl-2-cyclopentene-1-one, xylene.

Table S2. Surface properties of catalysts determined by N_2 physisorption by the BET method.

Catalyst	S_{BET} ($m^2\ g^{-1}$)	V_p ($cm^3\ g^{-1}$)	D_p (nm)
AC	868.1	0.7	3.1
LPC	626.0	3.4	21.5
LC	236.4	0.1	2.2
MoO_2/AC	824.5	0.7	3.3
MoO_2/LPC	510.4	1.8	14.0
MoO_2/LC	258.6	0.2	3.6
Pd/AC	871.8	0.7	3.1
Pd/LPC	504.6	2.1	16.5
Pd/LC	391.2	0.2	2.0

S_{BET}: Surface area of catalyst per unit mass

V_p: Total pore volume per unit mass

D_p: Mean pore diameter

Table S3. The amount of Mo or Pd in catalyst determined by ICP-OES.[a]

Catalysts	wt % of metal
MoO_2/AC	10.69
MoO_2/LC	10.28
MoO_2/LPC	9.55
Pd/AC	0.86
Pd/LC	0.74
Pd/LPC	0.81

[a]Preparation of ICP stock solution: To dissolve MoO_2, 40 mg of MoO_2 supported carbon catalyst was poured into a 25 mL flask and dissolved in 10 mL of an acid solution, a mixture of HCl, HNO_3, and HF in a ratio of 1:3:1. Sonication was performed to completely dissolve the catalyst in the solution and placed in a fume hood for 3 days. The solution was diluted with additional deionized water to make a total of 25 mL solution. The carbon support not dissolved in the solution was removed by filtration. For Pd supported carbon catalyst, 40 mg of the catalyst was dissolved in 10 mL of aqua regia, a mixture of HCl and HNO_3 in a ratio of 1:3.

Table S4. Catalytic results of HDO of guaiacol.[a]

Catalysts	Conv. (%)	Selectivity (%)				Yield (%)			
		BNZ[b]	ANI	PHE	CRS	BNZ	ANI	PHE	CRS
MoO_2/AC	81.7	6.5	4.7	76.5	12.3	5.3	3.9	62.5	10.0
MoO_2/LPC	98.4	2.6	7.5	73.7	16.1	2.6	7.4	72.6	15.9
MoO_2/LC	12.2	19.2	*n.d.*[c]	64.4	16.5	2.3	*n.d.*	7.9	2.0

[a] Reaction conditions: guaiacol 0.25 g (2 mmol), catalyst 0.2 g, toluene 20 mL, decane 0.2 mL, reaction temperature 320 °C, initial H_2 pressure 30 bar, and reaction time time 2 h.
[b]BNZ: benzene, ANI: anisole, PHE: phenol, CRS: creosol.
[c]*n.d.* means "not detected."

Table S5. Catalytic results of phenol hydrogenation.[a]

Catalysts	Conv. (%)	Selectivity (%)[c]		Yield (%)	
		CYON	CYOL	CYON	CYOL
Pd/AC	42.5	92.5	7.5	39.3	3.2
Pd/LPC	79.4	85.1	14.9	67.6	11.8
Pd/LC	57.7	82.5	17.5	47.6	10.1

[a]Reaction conditions: guaiacol 0.25 g (2 mmol), catalyst 0.2 g, DI water 20 mL, reaction temperature 80 ^{o}C, initial H_2 pressure 5 bar, and reaction time 3 h.

[b]CYON: cyclohexanone, CYOL: cyclohexanol.

[c]The products were extracted using 20 mL of ethyl acetate.

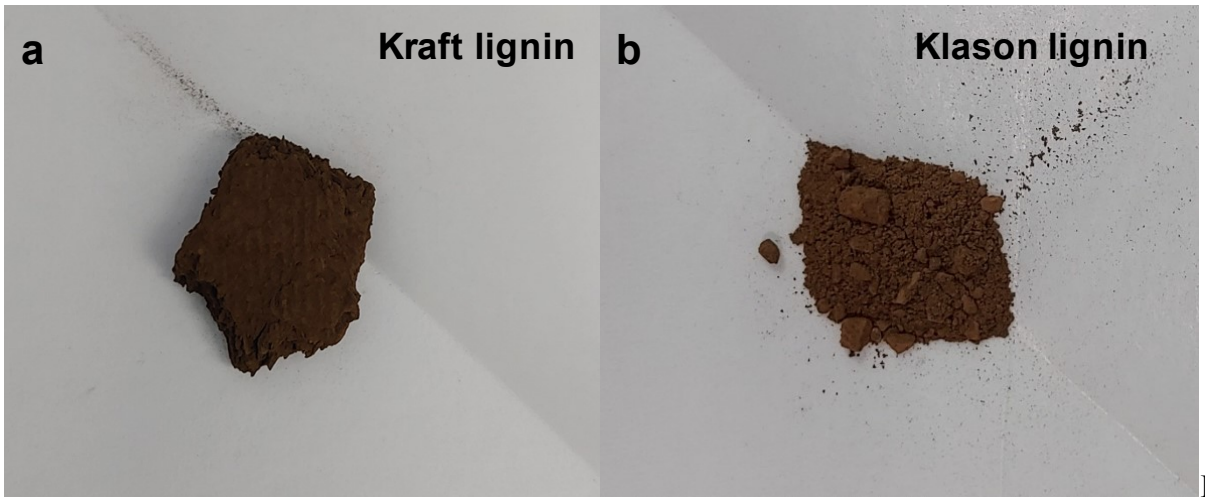

Fig. S1. Photographs of industrially released (a) kraft lignin and (b) Klason lignin, which were supplied directly from domestic companies in Korea.

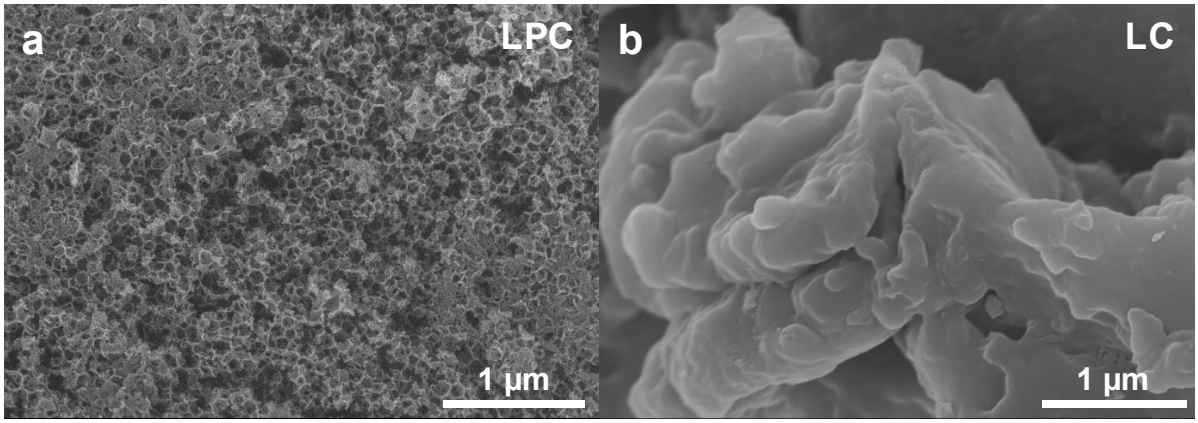

Fig. S2. SEM images of (a) LPC and (b) LC.

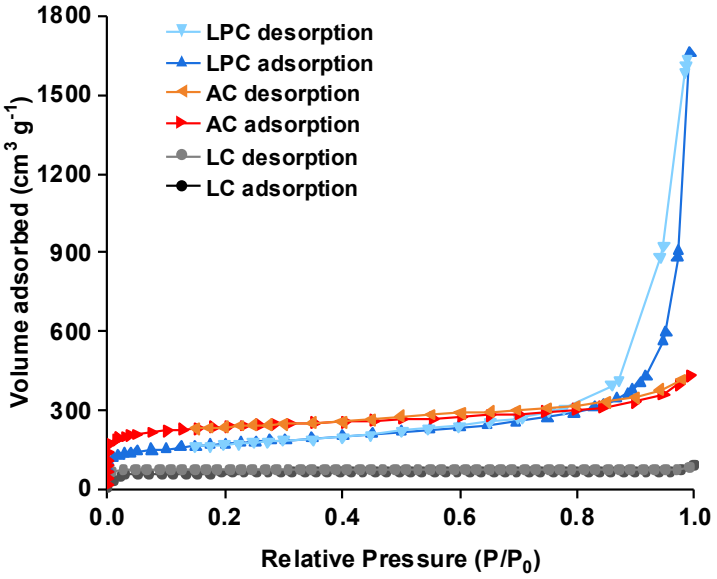

Fig. S3. N_2 adsorption-desorption isotherms of LPC, LC, and AC.

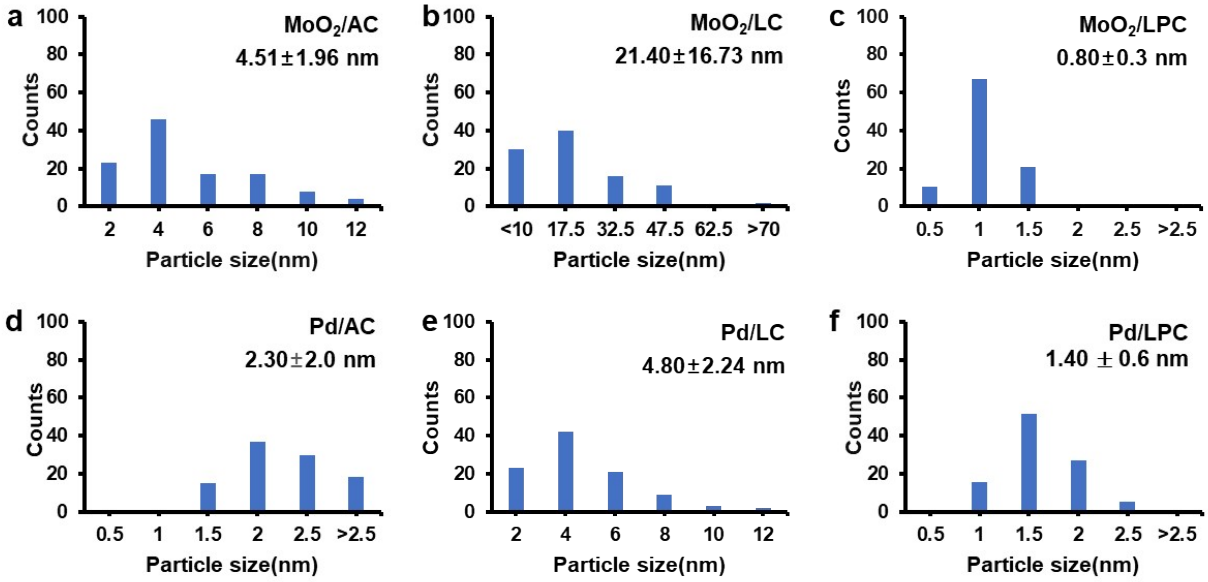

Fig. S4. Particle size histograms of (a-c) MoO_2 and (d-f) Pd supported carbon catalysts: (a) MoO_2/AC, (b) MoO_2/LC, (c) MoO_2/LPC, (d) Pd/AC, (e) Pd/LC, and (f) Pd/LPC.

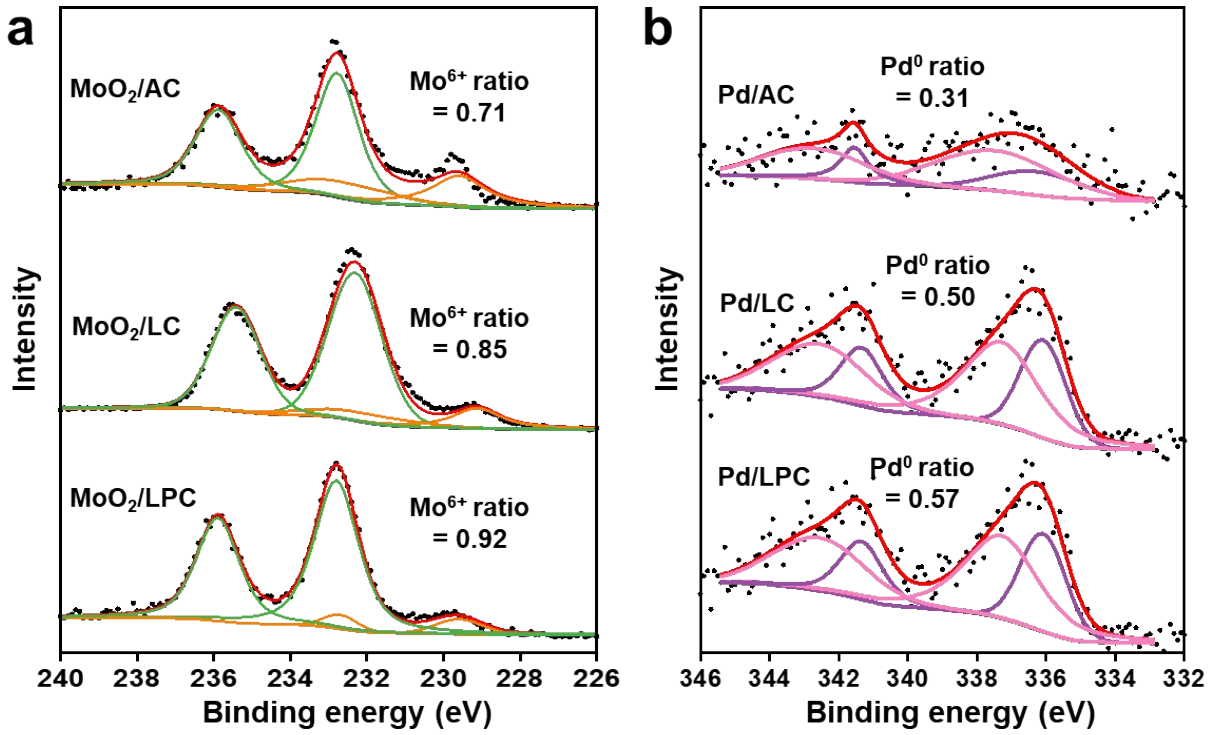

Fig. S5. XPS profiles of (a) Mo 3*d* of MoO_2/LPC, MoO_2/LC, and MoO_2/AC catalysts and (b) Pd 3*d* of Pd/LPC, Pd/LC, and Pd/AC catalysts

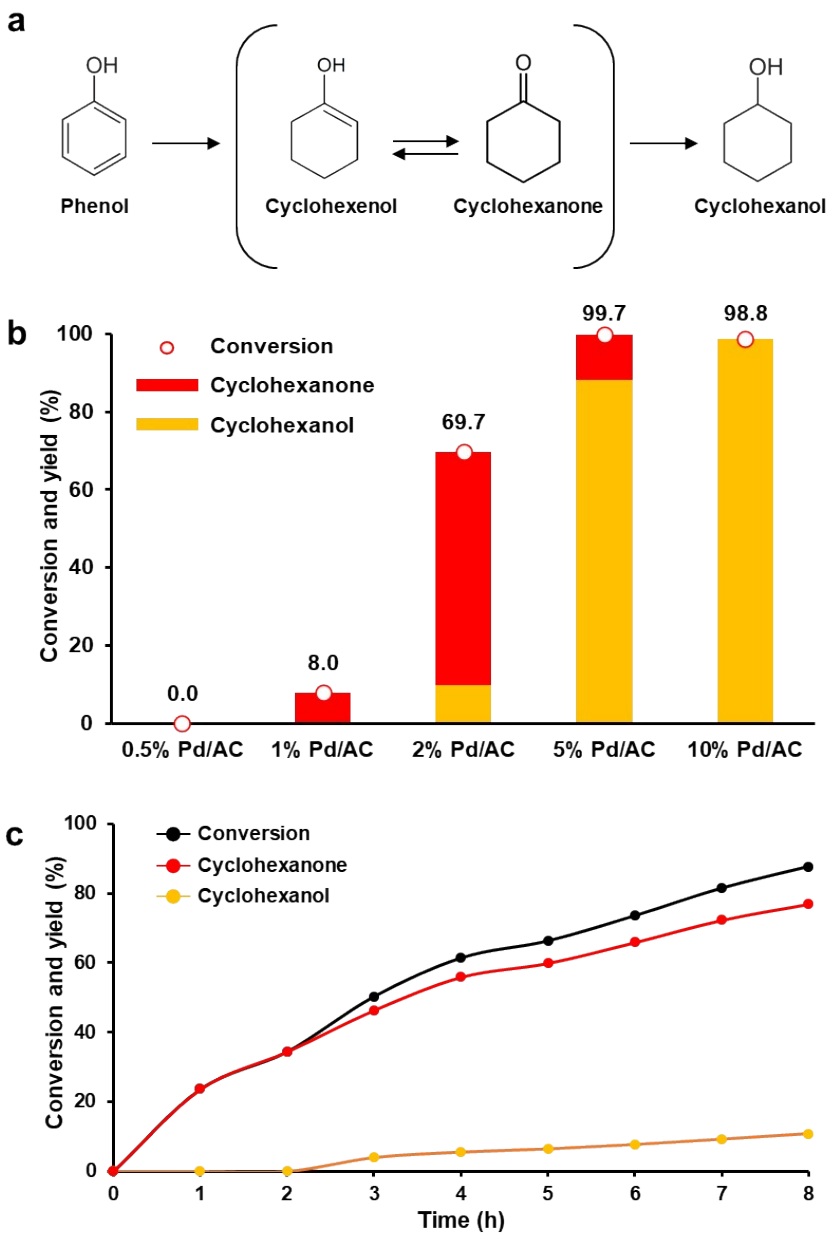

Fig. S6. (a) A reaction pathway of Pd-catalyzed phenol hydrogenation. (b) Conversion and yield of phenol hydrogenation reaction over 3 h as a function of Pd concentration. (c) Changes in phenol conversion and product yield as a function of reaction time for 10 wt% Pd/AC catalysts. Reaction conditions: phenol 0.19 g (2 mmol), DI water 20 mL, catalyst 0.1 g, reaction temperature 80 °C, initial H_2 pressure 5 bar.

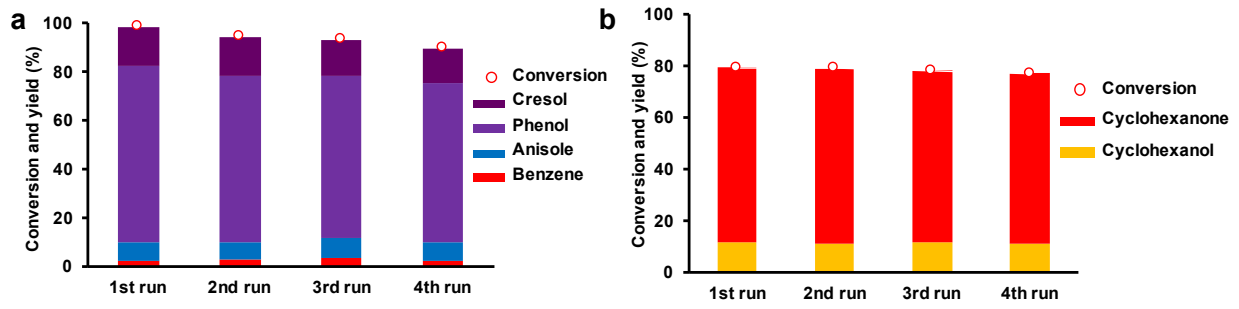

Fig. S7. The recyclability test by 4 consecutive cycles of (a) guaiacol HDO over MoO_2/LPC and (b) phenol hydrogenation over Pd/LPC, presenting the substrate conversion and product yield.

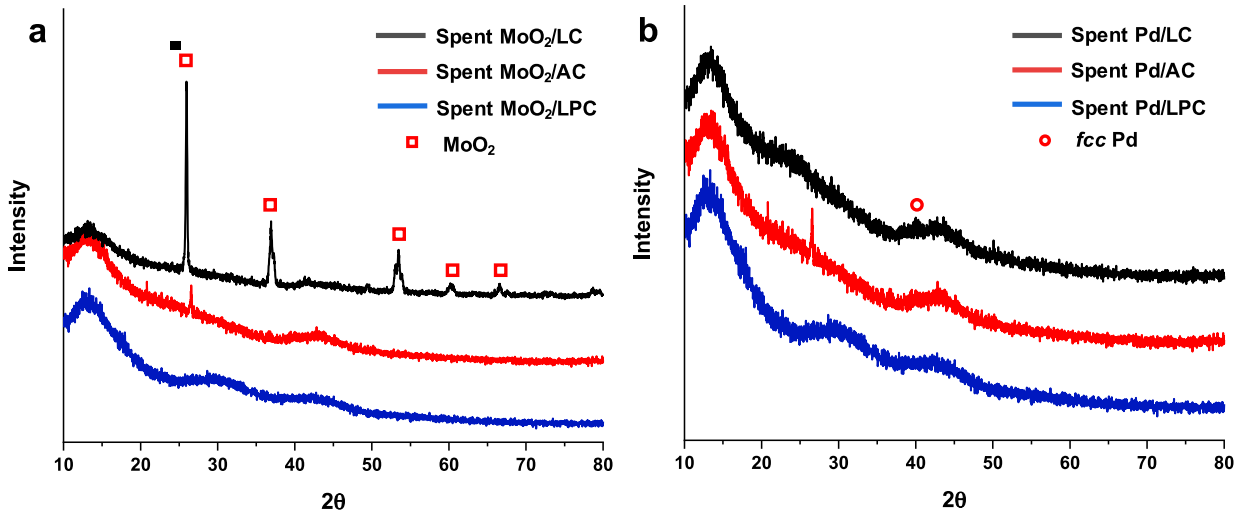

Fig. S8. XRD patterns of the spent catalysts of (a) MoO_2 and (b) Pd obtained after the recyclability test by 4 consecutive cycles. The red boxes and circles represent the MoO_2 (JCPDS #86-0135) and fcc Pd (JCPDS #05-0681) peaks, respectively.

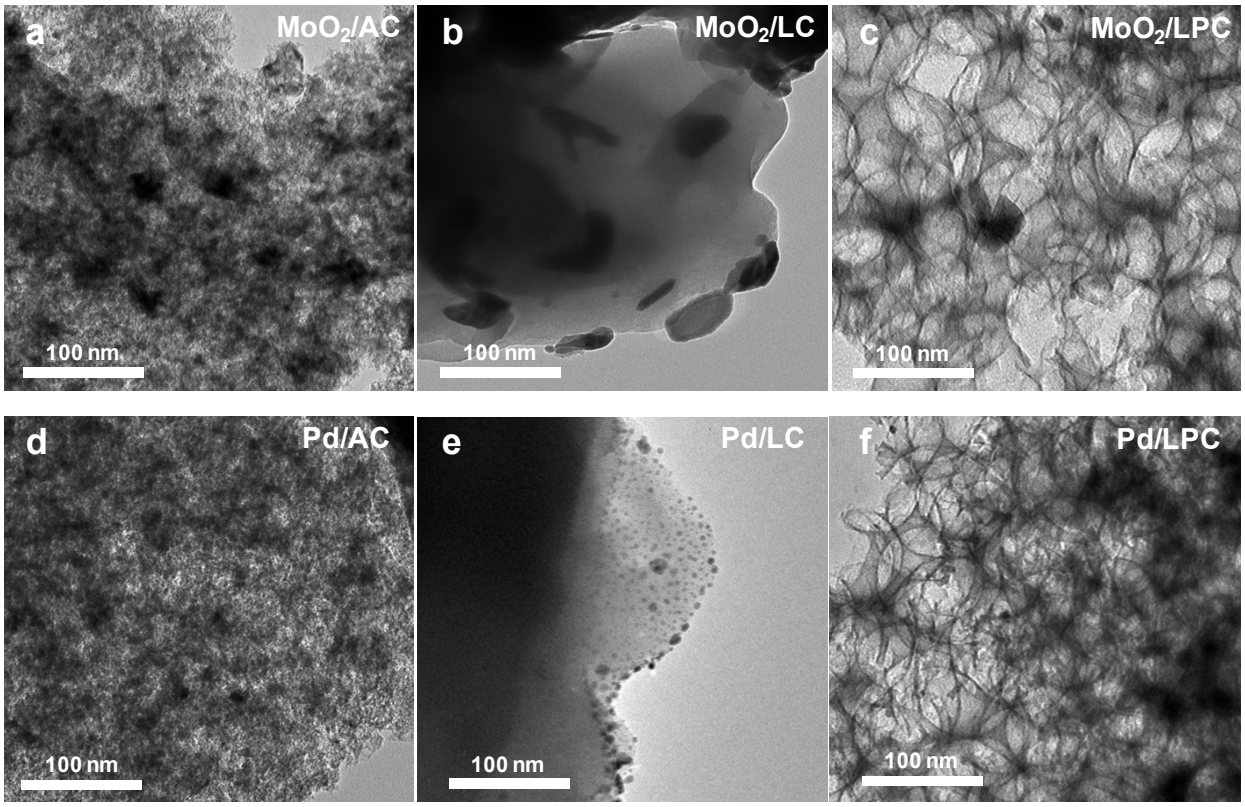

Fig. S9. TEM images of the spent catalysts obtained after the recyclability test by 4 consecutive cycles: (a–c) MoO_2 and (d–f) Pd supported carbon catalysts.

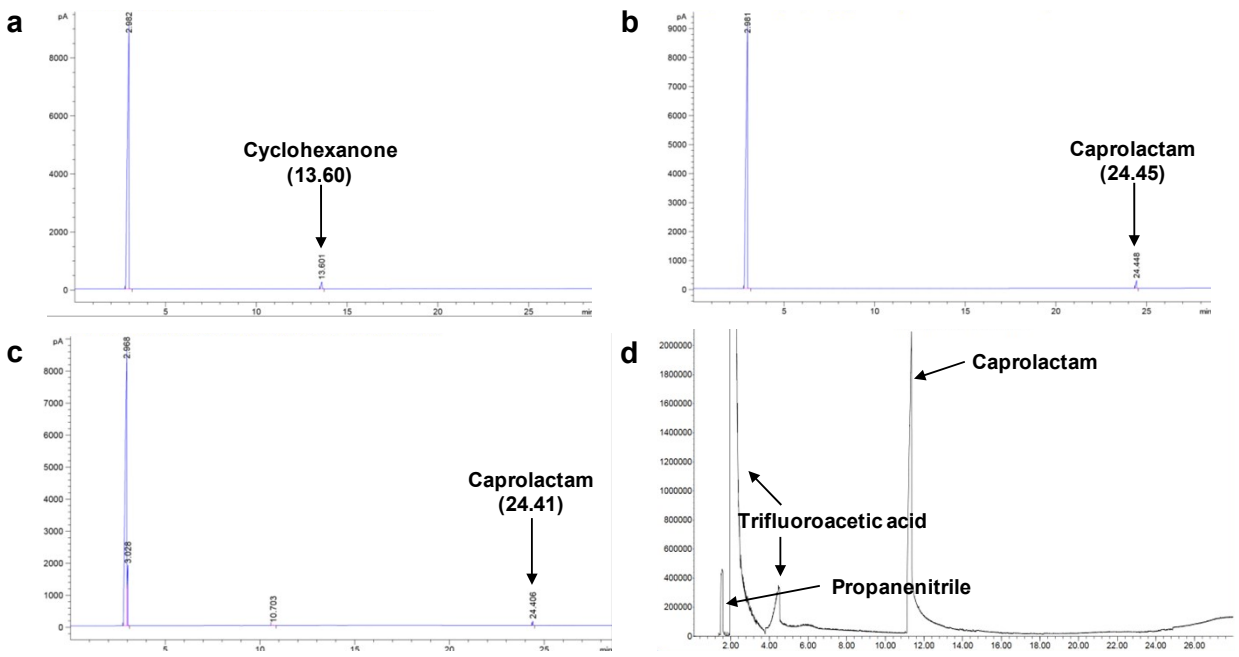

Fig. S10. GC and GC-MS spectra showing caprolactam production after catalytic conversion of cyclohexanone. (a) GC spectrum of a solution containing cyclohexanone and acetonitrile. (b) GC spectrum of a solution containing caprolactam and acetonitrile. (c) GC and (d) GC-MS spectra of a solution taken after 4 h reaction.

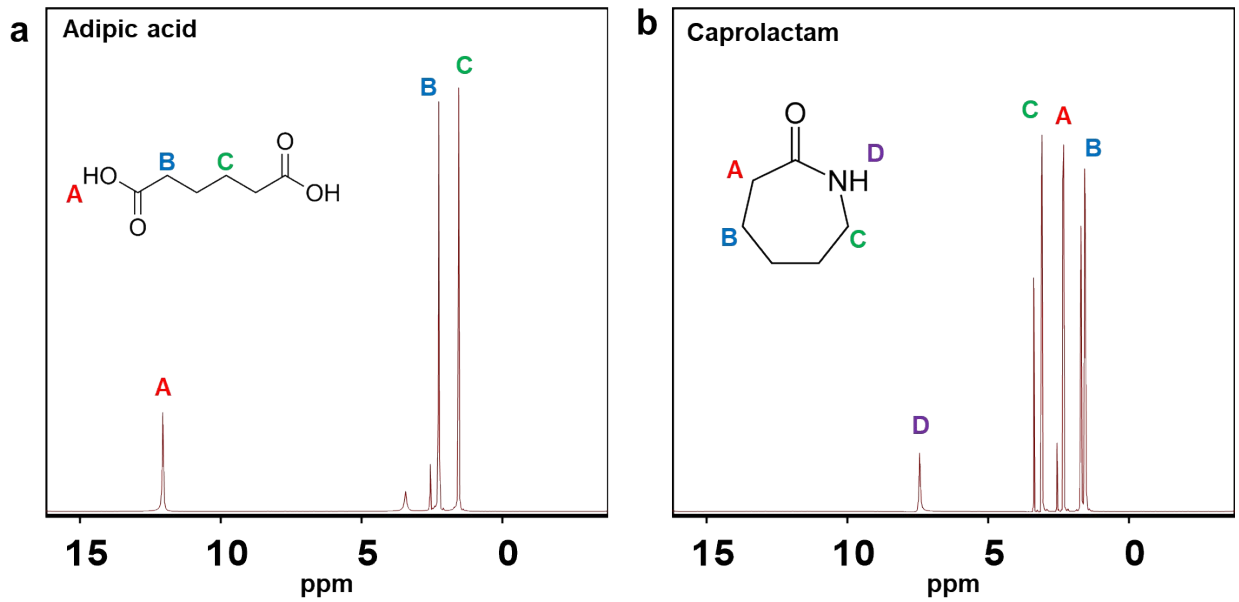

Fig. S11. Solution state ^{1}H NMR spectra of (a) adipic acid and (b) caprolactam dissolved in dimethyl sulfoxide (DMSO-d_6).