Supporting information

Upcycling of Polyethylene Terephthalate to 1,4-cyclohexanedimethanol in Water

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Section 1 Experimental Section

Section 1.1 Materials

Poly(ethylene terephthalate) granules (PET, 99%, <200 μm, Guangzhou YOUSU 3D Technology Co., Ltd.), Pd/C (5 wt. %, Sigma-Aldrich (Shanghai) Trading Co., Ltd.), Pt/C (5wt.% Shanghai Macklin Biochemical Technology Co., Ltd.), $RuCl_3$ (97%, Bide Pharmatech Co., Ltd.), $SnCl_2{\cdot}2H_2O$ (≥99.99%, Shanghai Aladdin Biochemical Technology Co., Ltd.), Ni $(NO_3)_2{\cdot}6H_2O$ (≥98.0%, Sinopharm Chemical Reagent Co., Ltd.), Co $(NO_3)_2{\cdot}6H_2O$ (99%, Shanghai Aladdin Biochemical Technology Co., Ltd.), Cu $(NO_3)_2{\cdot}3H_2O$ (99% ~102%, Sinopharm Chemical Reagent Co., Ltd.), Pd $(OCOCH_3)_2$ (Shanghai Aladdin Biochemical Technology Co., Ltd.), Pd $(NO_3)_2(NH_3)_4$ (98%, Shanghai Adamas Reagent Co., Ltd.), (NH_4) H_2PO_4 (≥99%, Shanghai Aladdin Biochemical Technology Co., Ltd.), 1,4-Cyclohexane dicarboxylic acid (cis-and trans-mixture) (CHDA, 99%, Shanghai Macklin Biochemical Technology Co., Ltd.), 1,4-Cyclohexanedimethanol (cis-and trans-mixture) (CHDM 99%, Shanghai Macklin Biochemical Technology Co., Ltd.), Terephthalic acid (TPA, 99 %, Shanghai Adamas Reagent Co., Ltd.), Bis(2-Hydroxyethyl) terephthalate (BHET, 98%, Shanghai Adamas Reagent Co., Ltd.), acetonitrile (ACN, 99.9%, Shanghai Macklin Biochemical Technology Co., Ltd.) were used.

Section 1.2 Preparation of catalysts

Activated carbon (C), SiO_2, Al_2O_3, H-ZSM-5 (Si/Al 25), H-Beta (Si/Al 12.5), H-Beta (Si/Al 20), ZrO_2 and CeO_2 were used as catalyst support. SiO_2, Al_2O_3, H-ZSM-5 and H-Beta were commercially purchased and calcined in flowing air at 550 ^oC for 3h prior to use. Activated carbon was thermally treated at 400 ^oC under flowing H_2 before use. ZrO_2 and CeO_2 were home synthesized. ZrO_2 was prepared by hydrothermal method. Typically, 0.128 mol Zr $(NO_3)_2{\cdot}2H_2O$ and 1.28 mol urea were dissolved in 320 ml deionized water and stirred evenly. The mixture was transferred to a PTFE-lined stainless steel autoclave. Then, the autoclave was placed in an oven for hydrothermal reaction at 140 ^oC for 20 h. Afterwards, the precipitates were centrifugally separated and washed with deionized water and ethanol for several times until the centrifuge supernatant was pH neutral. The precipitates were dried in an oven at 80 ^oC and then calcined in air flow at 500 ^oC for 4 h. After calcination, the ZrO_2 powder was obtained and ready for use. CeO_2 was prepared by a similar hydrothermal synthesis process, except for the use of different reagents, i.e. 0.64 mol urea and 0.042 mol (NH_4) Ce $(NO_3)_2$ dissolved in 640 ml of deionized water. The subsequent operations are the same as those for the preparation of ZrO_2.

Carbon-supported ruthenium (Ru/C), nickel (Ni/C), cobalt (Co/C), copper (Cu/C), palladium (0.5 wt.% Pd/C) and Ru-Sn/C were prepared by the impregnation method. In brief, a certain amount of precursor ($RuCl_3$,

Ni $(NO_3)_2 \cdot 6H_2O$, Co $(NO_3)_2 \cdot 6H_2O$, Cu $(NO_3)_2 \cdot 3H_2O$ or $SnCl_2 \cdot 2H_2O$) was dissolved in water, followed by the introduction of pretreated activated carbon. The paste was stirred at room temperature for 10 h and then dried in an oven at 80 ^oC overnight. The mixture was then reduced in flowing H_2 at 350 ^oC for 5 h. Besides these home-synthesized catalysts, commercial catalysts, including carbon-supported palladium (5 wt. % Pd/C) and carbon-supported platinum (5 wt. % Pt/C), were also used in this work.

Pd/CeO_2, Pd/ZrO_2, Pd/SiO_2, Pd/Al_2O_3 and Pd (Imp)/H-ZSM-5 (Si/Al 25) were synthesized by impregnation method. A certain amount of Pd $(OCOCH_3)_2$ was dissolved in acetone, and then the oxide support was added. The mixture was stirred at room temperature for 10 h and dried overnight in an oven at 80 ^oC. It was then calcined in flowing air at 350 ^oC for 3 h followed by reduction in flowing H_2 at 400 ^oC for 3 h.

Pd (IE)/H-ZSM-5 (Si/Al 25), Pd (IE)/H-Beta (Si/Al 12.5) and Pd (IE)/H-Beta (Si/Al 20) were synthesized by ion-exchange method. Pd $(NO_3)_2(NH_3)_4$ was dissolved in deionized water and the solution was dropped into a turbid solution of zeolite. The mixture was stirred overnight and then the precipitate was centrifugally separated. After washing with water for several times, the precipitate was dried in the oven at 60 ^oC Subsequently, it was calcined in flowing air at 500 °C for 2 h and then reduced in flowing H_2 at 350 ^oC for 2 h.

Section 1.3 Characterization of catalysts

The X-ray diffraction (XRD) patterns were collected on Rigaku Ultima IV diffractometer using Cu Kα1 X-ray source (λ = 1.5406 Å) operated at 35 kV and 25 mA. The scanning speed was 15°/min from 5° to 90°.

The metal loadings in the catalysts were analyzed by inductively coupled plasma optical emission spectrometer (ICP-OES) using PerkinElmer Optima 8300 instrument. The catalysts were digested in nitric acid (65 wt. %) at 80 ^oC overnight and then diluted with deionized water to a desired volume before analysis.

The transmission electron microscopy (TEM) images and EDS mappings were performed on an FEI Talos F200X G2 microscope. The sample was dispersed with ethanol, and a dilute suspension was deposited on the carbon grid for characterization.

The temperature-programmed desorption of NH_3 (NH_3-TPD) and CO_2 (CO_2-TPD) and temperature programmed reduction in H_2 (H_2-TPR) were performed on a chemical adsorption instrument equipped with a TCD detector (DAS-7200, Huasi Instrument). In the NH_3-TPD experiment, 100 mg catalyst was put into a quartz reactor and pretreated in flowing He at 500 °C. After cooling to 100 °C, it was exposed to flowing NH_3 for 30 min and then purged under flowing He for 30 min. Afterwards, it was heated from 100 °C to 600 °C with a heating rate of 10 °C /min and kept for 30 min. In the CO_2-TPD experiment, 100 mg sample was placed in a

quartz tube, which was pretreated at 500 °C for 30 min in flowing He. After cooled to 30 °C, it was exposed to flowing CO_2 for 30 min and then purged under flowing He for 30 min. Afterwards, it was heated from 30 °C to 800 °C with a rate of 10 °C/min and kept for 40 min. In the H_2-TPR experiment, the 50 mg sample was placed in a quartz tube, which was pretreated at 300 °C for 30 min in flowing N_2. The reduction reaction was carried out in a flow of H_2/N_2 (5/95) from 30 ^oC to 900 ^oC with a heating rate of 10 ^oC/min.

Section 1.4 Catalytic reactions

The reactions of PET were carried out in a stainless steel autoclave equipped with magnetic stirring. In a typical reaction, 300 mg reactant, 50 mg catalyst, and 25 ml deionized water were loaded into the autoclave. After purging with N_2, followed by H_2, the autoclave was pressurized with H_2 (e.g. 3 MPa). Under a stirring rate of 600 rpm, the autoclave was heated to the desired reaction temperature (e.g. 200 ^oC) and maintained for a certain period. After reaction, it was quenched by placing the autoclave into a cold water bath.

To analyze the product, 16.6 ml CH_3CN and 0.235 g (NH_4) H_2PO_4 were added to the reaction solution to dissolve the products. The solution was then analyzed by a liquid chromatograph (Shimadzu, LC-20AD) equipped with a UV detector and an Eclipse Plus C18 column (4.6 nm×250 mm×5 um, Agilent) using 50 mmol (NH_4) H_2PO_4 (60%): CH_3CN (40%) as mobile phase at 40 ^oC. The CHDM was determined on a gas chromatograph (Shimadzu, GC-2014) equipped with an FID detector and a DB-Wax UI column (30 m×250 mm×0.25 um, Agilent) using cyclohexanol as an internal standard. The CHDM could be isolated and purified from water solution after reaction by vacuum distillation at 55^oC, <32torr. The conversion of PET, the yield of the product and the selectivity of the product were calculated using the following equations (1), (2) and (3):

$$\text{Conversion of PET (\%)} = \left(1 - \frac{\text{Mass of unreacted PET}}{\text{Mass of loaded PET}}\right) \times 100\% \quad (1)$$

$$\text{Yield of product (\%)} = \frac{\text{Moles of product}}{\text{Moles of terephthalate in loaded PET}} \times 100\% \quad (2)$$

$$\text{Selectivity of product (\%)} = \frac{\text{Yield of product}}{\text{Conversion of PET}} \times 100\% \quad (3)$$

Section 2 Supplementary Figure

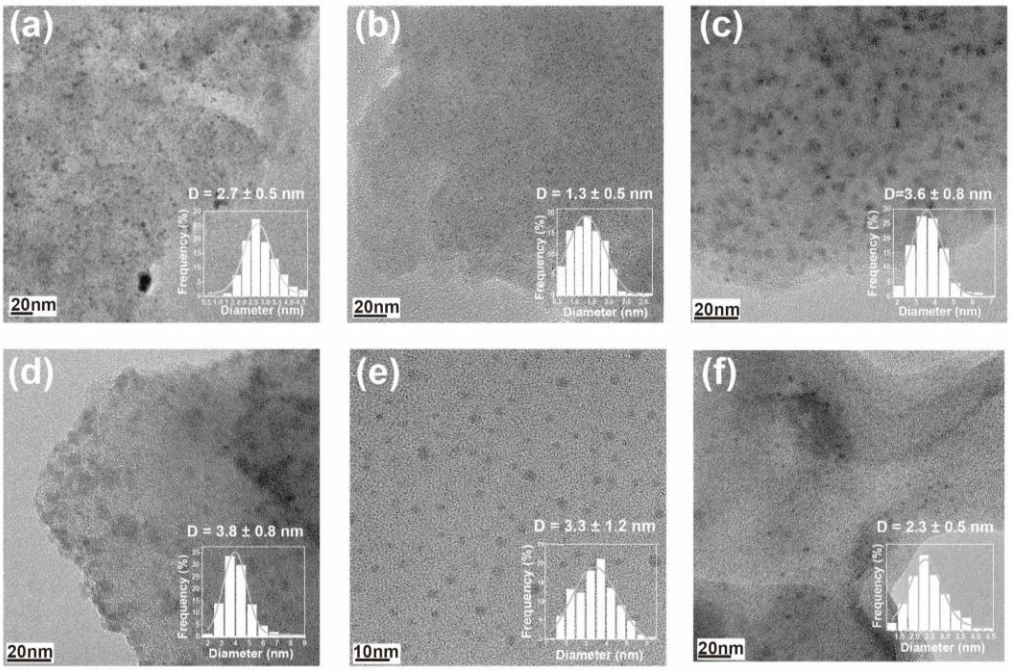


Figure S1 TEM images of (a) 5 wt.% Pd/C, (b) 3 wt.% Ru/C, (c) 5 wt.% Ni/C, (d) 5 wt.% Co/C, (e) 5 wt.% Cu/C and (f) 0.5 wt.% Pd/C.

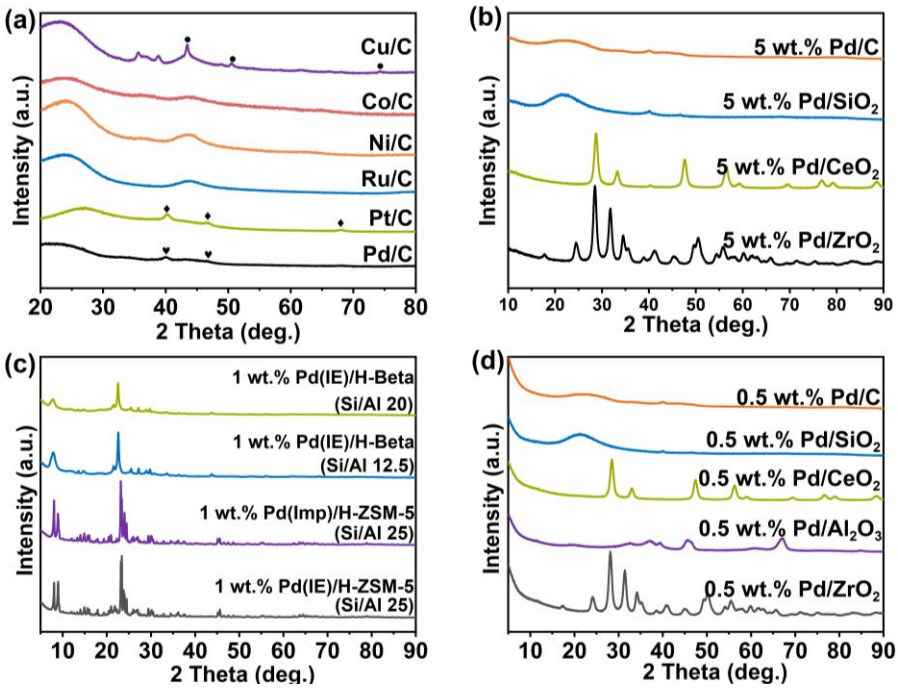


Figure S2 XRD patterns of catalysts. (a) Cu/C, Co/C, Ni/C, Ru/C, Pt/C and Pd/C. (b) 5 wt.% Pd/C, 5 wt.% Pd/SiO_2, 5 wt.% Pd/CeO_2 and 5 wt.% Pd/ZrO_2. (c). 1 wt.% Pd (IE)/H-Beta (Si/Al 20), 1 wt.% Pd (IE)/H-Beta (Si/Al 12.5), 1 wt.% Pd (Imp)/H-ZSM-5 (Si/Al 25) and 1 wt.% Pd (IE)/H-ZSM-5 (Si/Al 25). (d) 0.5 wt.% Pd/C, 0.5 wt.% Pd/SiO_2, 0.5 wt.% Pd/CeO_2, 0.5 wt.% Pd/Al_2O_3 and 0.5 wt.% Pd/ZrO_2.

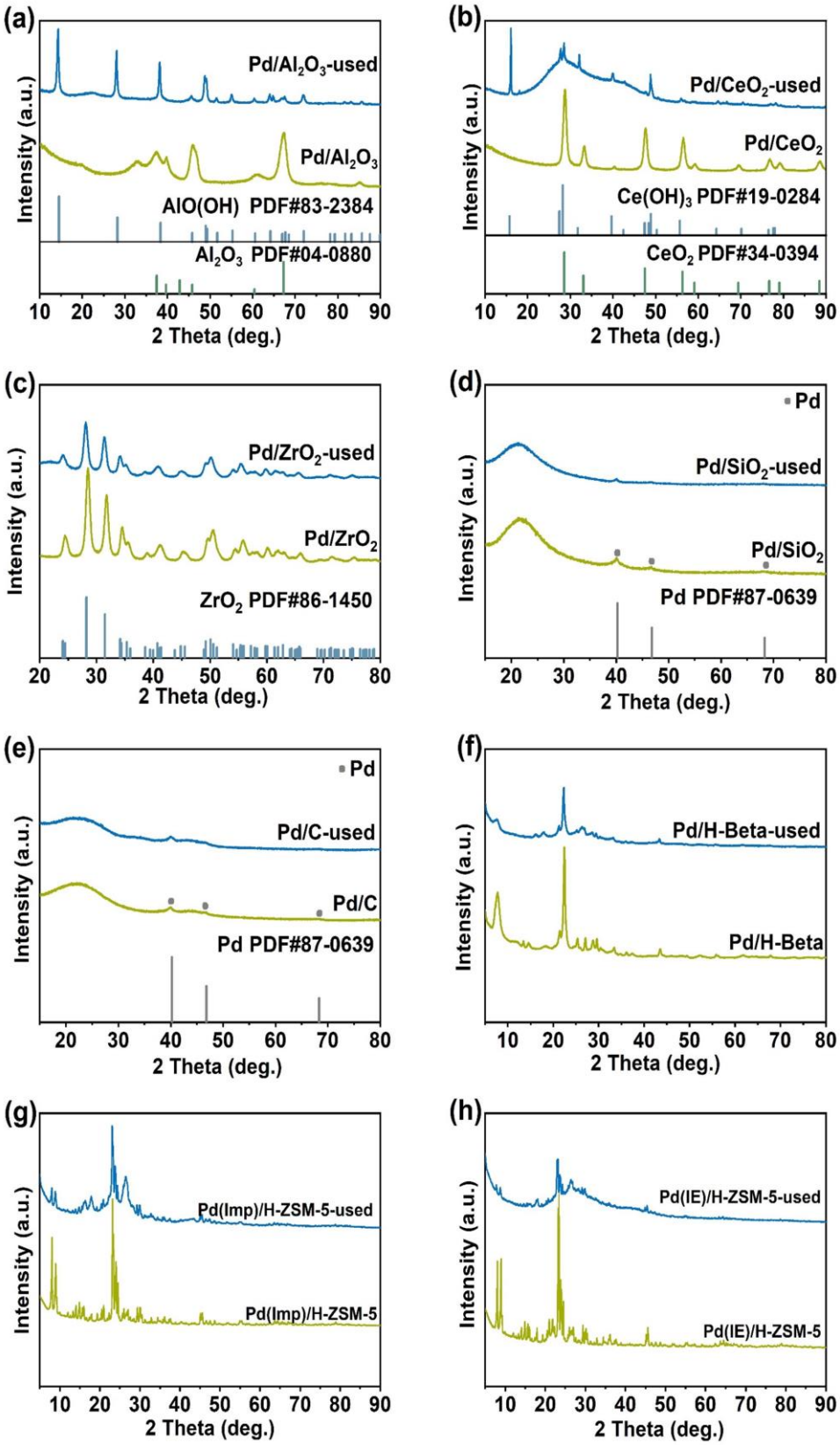


Figure S3 XRD patterns of Pd/Al_2O_3, (b) Pd/CeO_2, (c) Pd/ZrO_2, (d) Pd/SiO_2, (e) Pd/C (f) Pd/H-Beta, (g) Pd (Imp)/H-ZSM-5 and (h) Pd (IE)/H-ZSM-5 before and after reaction. Reaction conditions: 300 mg PET, 50 mg catalyst, 25 ml H_2O, 200 ^oC, 3 MPa H_2, 5 h.

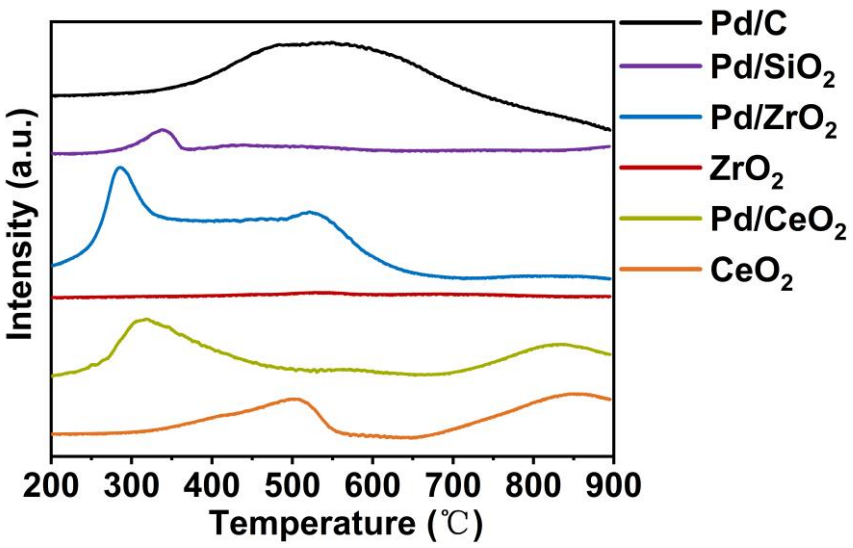


Figure S4 H_2-TPR profiles of catalysts.

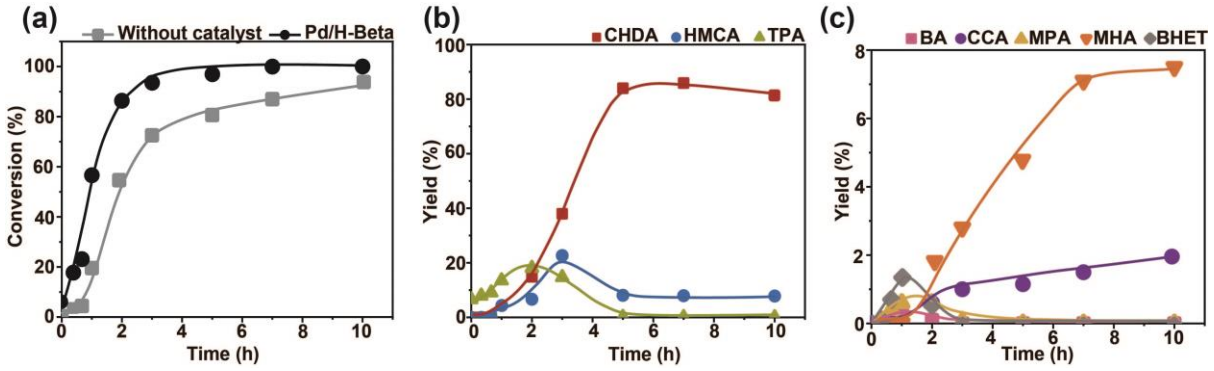


Figure S5 (a) PET conversion over time in presence and absence of Pd (IE)/H-Beta (Si/Al 12.5). (b, c) The product yield over time in the reaction of PET on Pd (IE)/H-Beta (Si/Al 12.5). Reaction conditions: 300 mg PET, 50 mg Pd (IE)/H-Beta (Si/Al 12.5), 25 ml H_2O, 200 ^oC, 3 MPa H_2.

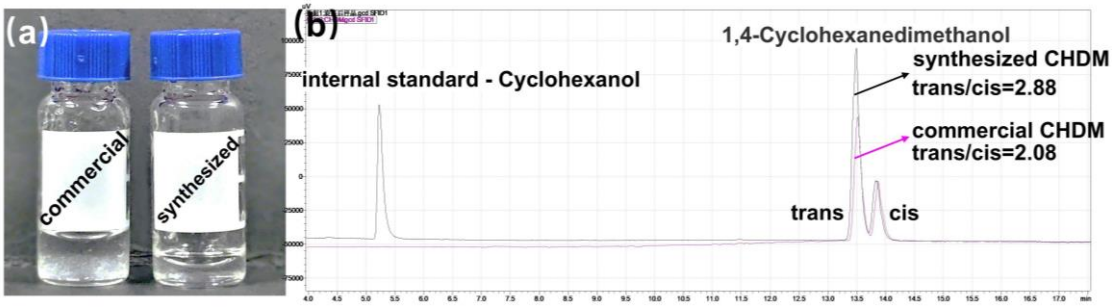


Figure S6 (a) Photograph of commercial CHDM and synthesized CHDM. (b) GC profile of commercial CHDM and synthesized CHDM. The trans and cis isomers of yield CHDM are determined by GC peak area.

Note to Figure S6. Due to the differences in boiling point of water (100 ^{o}C), CHDM (283 ^{o}C) and other byproducts (cyclohexyl methanol (CHM) 181 ^{o}C, 4-methyl-1-cyclohexanemethanol (4-MCHM) 192 ^{o}C), CHDM is separated by distillation under vacuum at 55 ^{o}C, <32 torr. During the process, water solvent as well as the byproducts 4-MCHM and CHM, which have lower boiling points than CHDM, were removed. We get the yielded CHDM with a purity over 99% and an isolated yield of 73.8% accounting from PET feedstock. The commercial CHDM had a trans/cis ratio of 2.08, while the CHDM we synthesized obtained a trans/cis ratio of 2.88.

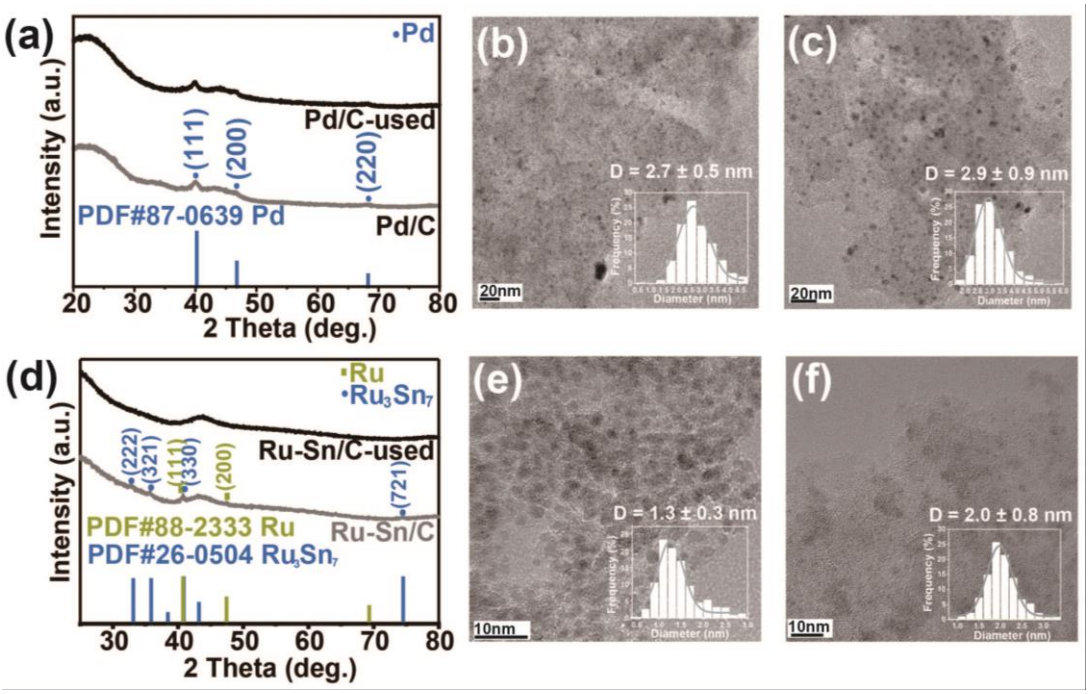


Figure S7 XRD patterns of fresh and used (a) Pd/C and (d) Ru-Sn/C. (b), (c) TEM images of fresh and used Pd/C. (e), (f) TEM images of fresh and used Ru-Sn/C.

Note to Figure S7. On fresh Pd/C, the Pd particles were well dispersed and nearly spherical, with a particle size of 2.7± 0.5 nm. After the reaction, on the used Pd/C, the Pd particle size grew to 2.9 ± 0.9 nm. Ru-Sn/C also underwent an increase in particle size after reaction from 1.3 ± 0.3 nm to 2.0 ± 0.8 nm. The change of metal particles may be caused by the aggregation of metals under the reductive hydrothermal condition applied in the reaction. Both catalysts have a broad peak of amorphous carbon at 21.6°. For fresh Pd/C, diffraction peaks of Pd (111), Pd (200) and Pd (220) were observed at 40.1°, 46.5° and 68.1° (PDF 87-0639). These peaks were still observable on the XRD of used Pd/C. For fresh Ru-Sn/C, characteristic peaks were observed at 33.2°, 35.9°, 40.9° and 74.5°, corresponding to the (222), (321) and (330), and (721) faces of Ru_3Sn_7 alloy (PDF 26-0504). Besides this Ru_3Sn_7, monometallic Ru particles were also present on Ru-Sn/C, featured by the diffraction peaks at 40.8° and 47.4° (PDF 88-2333). However, these characteristic peaks were not observed in the XRD profile of the used Ru-Sn/C. The disappearance of diffraction peaks is likely related to the loss of Ru and Sn during the reaction.

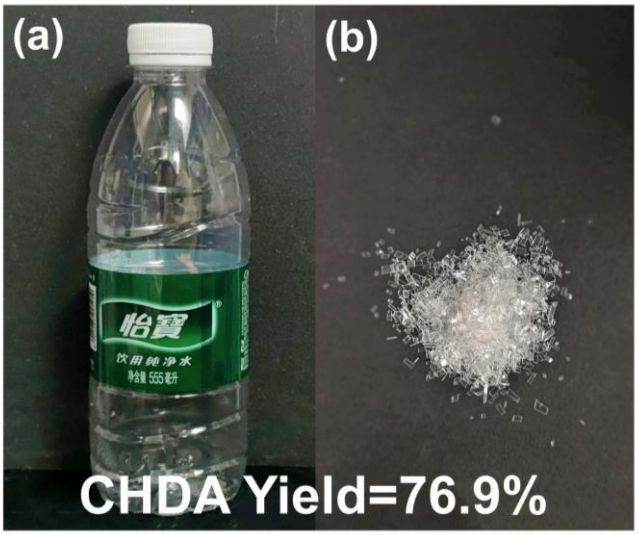
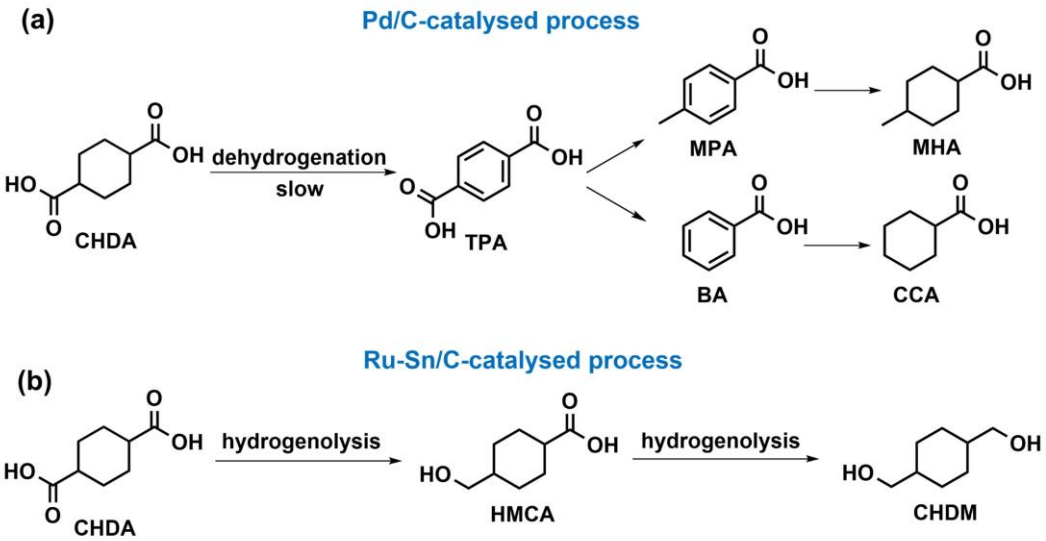
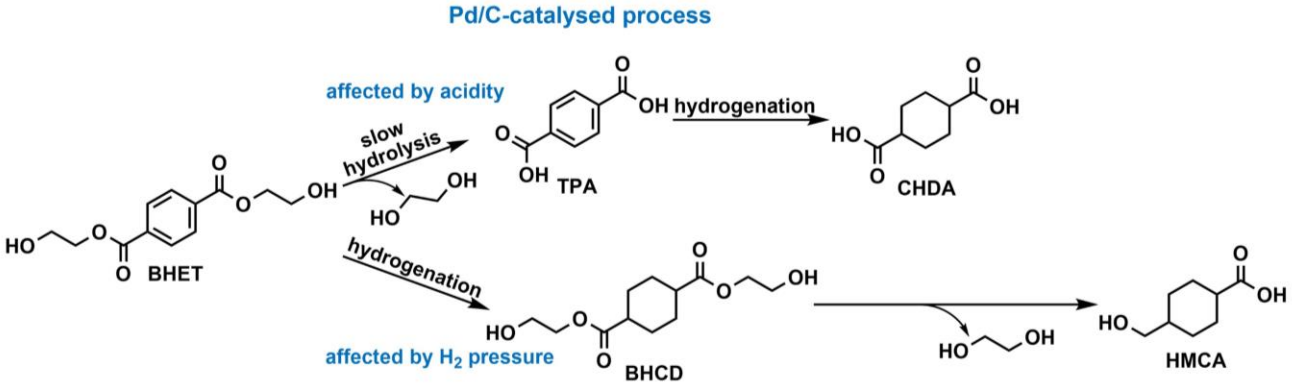


Figure S8 Photograph of (a) PET bottle and (b) the fragments of the PET bottle after processing.



Scheme S1 (a) Reaction pathway of CHDA to produce BA and CHDA to MPA catalyzed by Pd/C. (b) Reaction pathway of CHDA to CHDM catalyzed by Ru-Sn/C.



Scheme S2 Reaction pathway of BHET to CHDA and HMCA catalyzed by Pd/C.

Section 3 Supplementary Tables

Table S1 Physical and chemical properties of catalysts.

Catalyst	Hydrothermal stability[a]	Particle size (nm) [b]	Acid site concentration (mmol/g) [c]	Basic site concentration (mmol/g) [d]
3 wt% Ru/C.	--	1.3± 0.5	--	--
5 wt.% Ni/C	--	3.6± 0.8	--	--
5 wt.% Co/C	--	3.8± 0.8	--	--
5 wt.% Cu/C	--	3.3± 1.2 5.2 (by XRD)	--	--
5 wt.% Pt/C	--	3.8 (by XRD)	--	--
5 wt.% Pd/C	√	2.7± 0.5	0.29	0.22
5 wt.% Pd/CeO_2	×	--	--	--
5 wt.% Pd/ZrO_2	√	--	0.27	0.29
5 wt.% Pd/SiO_2	√	4.0 (by XRD)	0.07	0
1 wt.% Pd (IE)/ZSM-5 (Si/Al=25)	×	--	1.18	--
1 wt.% Pd (Imp)/ZSM-5 (Si/Al=25)	×	--	1.63	--
1 wt.% Pd (IE)/H-Beta (Si/Al=12.5)	×	2.4±0.4	1.21	--
1 wt.% Pd (IE)/H-Beta (Si/Al=20)	×	2.3±0.5	0.73	--
0.5 wt.% Pd/C	√	2.3± 0.5	--	--
0.5 wt.% Pd/ CeO_2	×	--	--	--
0.5 wt.% Pd/ZrO_2	√	--	--	--
0.5 wt.% Pd/SiO_2	√	--	--	--
0.5 wt.% Pd/Al_2O_3	×	--	--	--

[a] Characterized by XRD. [b] Determined by TEM if otherwise not mentioned. [c] Determined by NH_3-TPD. [d] Determined by CO_2-TPD.

Table S2 Conversion and product selectivity of PET reaction on Pd catalysts on different supports. *

Catalyst	PET Conversion (%)	Selectivity (%)							
		CHDA	HMCA	BA	CCA	MPA	MHA	TPA	BHET
5 wt.% Pd/C	100	84.5	10.5	--	1.2	--	3.7	0.1	--
5 wt.% Pd/CeO_2	98.7	84.7	6.2	--	1.1	--	5.3	2.5	--
5 wt.% Pd/ZrO_2	100	73.8	17.3	--	0.6	--	4.3	0.1	--
5 wt.% Pd/SiO_2	100	37.9	25.4	0.1	0.6	2.8	7.1	2.7	0.9
0.5 wt.% Pd/C	97.0	47.2	11.2	0.3	0.9	0.8	5.0	29.1	0.5
0.5 wt.% Pd/SiO_2	100	4.6	--	0.6	--	0.3	--	77.7	0.1
0.5 wt.% Pd/Al_2O_3	100	75.6	17.9	--	2.1	--	3.5	0.2	--
0.5 wt.% Pd/CeO_2	89.3	5.9	--	0.1	7.3	0.6	2.7	54.8	0.9
0.5 wt.% Pd/ZrO_2	91.7	70.0	12.4	--	2.3	--	4.3	3.7	--
1 wt.% Pd (IE)/H-ZSM-5 (Si/Al 25)	93.0	69.2	4.7	--	2.4	0.4	2.0	12.0	9.7
1 wt.% Pd (Imp)/H-ZSM-5 (Si/Al 25)	87.4	33.8	8.9	2.9	3.1	0.3	2.9	31.1	4.2
1 wt.% Pd (IE)/H-Beta (Si/Al 12.5)	95.1	86.4	8.5	--	1.3	--	4.4	0.1	--
1 wt.% Pd (IE)/H-Beta (Si/Al 20)	93.2	55.1	22.1	--	1.07	1.3	4.1	16.1	0.4

* Reaction conditions: 300 mg PET, 50 mg catalyst, 25 ml H_2O, 200 ^oC, 3 MPa H_2, 5 h.

Table S3 Reactions of PET on Pd/C catalyst with different mass ratios of PET to Pd/C. *

Mass ratio of PET to Pd/C	Reaction time (h)	PET Conversion (%)	Selectivity (%)							
			CHDA	HMCA	BA	CCA	MPA	MHA	TPA	BHET
	5	100	75.2	19.3	--	1.2	--	3.2	0.7	--
3	7	100	76.5	18.0	--	1.6	--	3.9	--	--
	10	100	76.1	17.4	--	2.0	--	4.1	--	--
	5	100	84.5	10.5	--	1.2	--	3.7	0.08	--
6	7	100	84.7	10.1	--	1.3	--	4.0	0.05	--
	10	100	83.6	8.7	--	1.8	--	4.7	--	--
	5	98.0	76.5	11.2	--	0.6	0.03	4.1	0.8	--
9	7	100	84.6	10.1	--	0.8	--	4.6	0.2	--
	10	100	86.1	8.1	--	1.0	--	5.3	--	--
	5	96.9	69.4	9.5	0.02	0.5	0.4	5.0	1.7	0.01
12	7	100	83.2	7.2	--	0.4	--	5.3	0.2	--
	10	100	88.0	6.5	--	0.7	--	5.6	--	--
	5	95.8	68.8	11.3	0.02	0.4	0.35	3.3	2.2	0.02
15	7	100	77.1	7.1	--	0.4	--	5.1	1.4	--
	10	100	89.4	5.4	--	0.8	--	6.3	0.7	--
	5	88.9	68.6	6.5	0.1	0.3	0.8	3.4	3.6	0.1
18	7	100	83.7	4.8	0.02	0.7	0.11	5.8	2.7	0.01
	10	100	91.1	1.2	--	0.9	0.04	6.9	0.8	--

* Reaction conditions: 50 mg Pd/C, 25 ml H_2O, 200 ^oC, 3 MPa H_2.

Table S4 Reactions of CHDA on Ru-Sn/C catalyst with different mass ratios of CHDA to Ru-Sn/C. *

Mass ratio of CHDA to Ru-Sn/C	CHDA Conversion (%)	CHDM Yield (%)	HMCA Yield (%)
2	100	85.7	1.2
4	100	88.9	5.4
6	88.3	65.7	16.8

* Reaction Conduction: 50 mg Ru-Sn/C, 25 ml H_2O, 5 MPa H_2, 250 ^oC, 10h.

Table S5 ICP-OES results of catalysts after every cycle.

Catalyst	Metal	Fresh	1	2	3	4
Pd/C	Pd (wt.%)	5.1	4.7	3.8	3.0	1.8
Ru-Sn/C	Ru (wt.%)	4.2	3.4	2.1	1.5	1.6
	Sn (wt.%)	5.3	4.4	3.0	2.4	1.6

Note to Table S5. The metal loading of the catalysts after each cycle was measured by ICP-OES. The results show that the Pd contents in Pd/C decreased from 5.13% to 1.77% after four cycles. This is likely due to the detachment of Pd particles from the carbon support. For Ru-Sn/C, the results showed that the Ru and Sn contents in the catalyst decreased from 4.19% to 1.59% and from 5.31% to 1.56% after four cycles, respectively. Ru and Sn dissolved into the reaction solution during the hydrogenation might be responsible for the decrease in activity.