Electronic Supplementary Material (ESI) for EES Catalysis.

Boosting the catalytic performance of Pt/USY catalysts in hydrocracking of polyolefin plastics by optimizing nanoscale proximity

Supporting Information

Xinlei Han†, Xinru Zhou†, Tuo Ji†, Feng Zeng†, Weiping Deng‡, Zhenchen Tang†*, Rizhi Chen†

†State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 211816, Jiangsu, China

‡State Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, Fujian, China

*Corresponding author: z.tang@njtech.edu.cn

Table S1. Pt loading, textual properties, and Si/Al ratio of selected catalysts.

Catalyst	Pt loading [a] / wt%	Surface area [b] / $m^2 \cdot g^{-1}$	Pore volume [c] / $cm^3 \cdot g^{-1}$	Si/Al
0.05Pt/USY-CI	0.061	n.a.	n.a.	n.a.
0.5Pt/USY-CI	0.38	n.a.	n.a.	n.a.
1Pt/USY-CI	0.80	n.a.	n.a.	n.a.
MOR	n.a.	250	n.a.	50
Beta	n.a.	650	n.a.	72
ZSM-5	n.a.	340	n.a.	72
NaY	n.a.	650	0.3	10
HY	n.a.	503	0.086	20.5
0.1Pt/USY-CI - recycled	0.085	538	0.21	22

a, Pt loading was determined by ICP-OES.

b, surface area was determined by N_2-physisorption using BET method.

c, pore volume was determined by N_2-physisorption using BJH adsorption method.

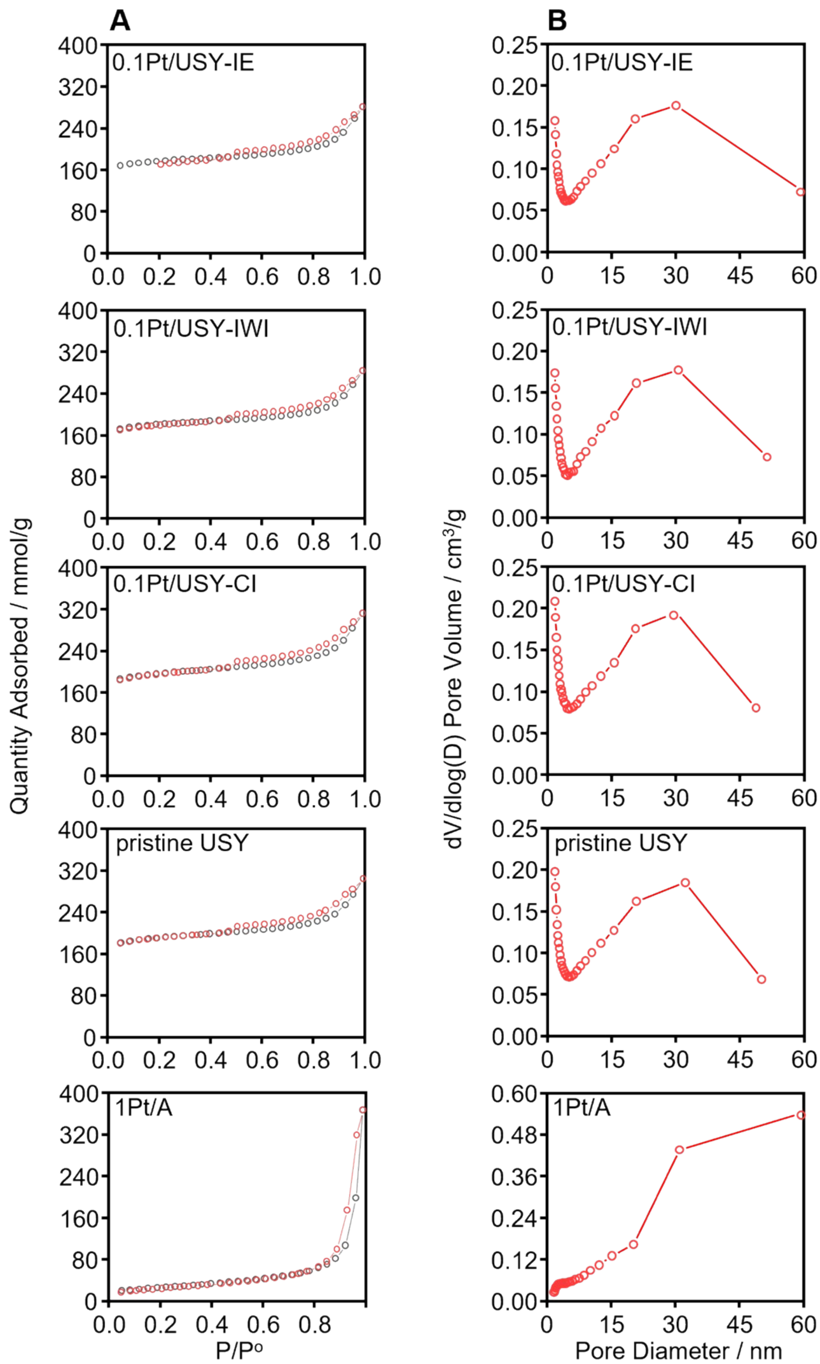

Figure S1. N_2-physisorption A) isotherms and B) pore size distribution of pristine USY, 0.1Pt/USY by different loading methods and 1Pt/A.

Table S2. NH_3-TPD results of total, strong and weak acidity of different catalysts.

Catalyst	Total acidity / mmol·g^{-1}	Strong acidity / mmol·g^{-1} [a]	Weak acidity / mmol·g^{-1} [b]
0.1Pt/USY-IE	0.41	0.27 (65%)	0.14 (35%)
0.1Pt/USY-IWI	0.35	0.23 (65%)	0.12 (35%)
1Pt/USY-CI	0.37	0.23 (62%)	0.14 (38%)
pristine USY	0.38	0.26 (68%)	0.12 (32%)
γ- Al_2O_3	0.003	0.002(67%)	0.001(33%)
0.1Pt/USY-CI -recycled	0.23	0.16 (68%)	0.07 (32%)

a. Acidity corresponding to the high temperature desorption peak.

b. Acidity corresponding to the low temperature desorption peak.

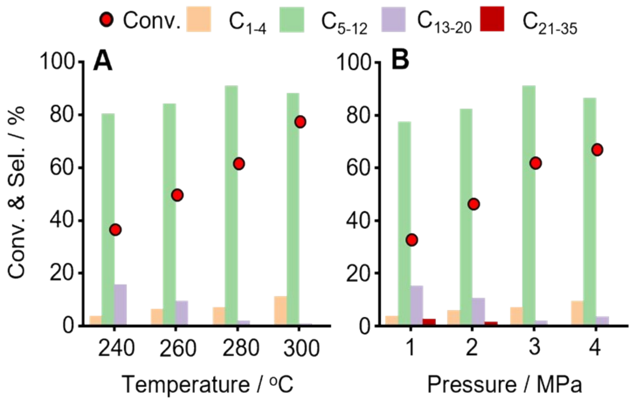

Figure S2. Hydrocracking of PE at different temperature and H_2 pressure over 0.1Pt/USY-CI. Reaction conditions: A) PE, 4.0 g, catalyst, 0.2 g, 3 MPa H_2, 3 h; B) PE, 4.0 g, catalyst, 0.2 g, 280 ^{o}C, 3 h.

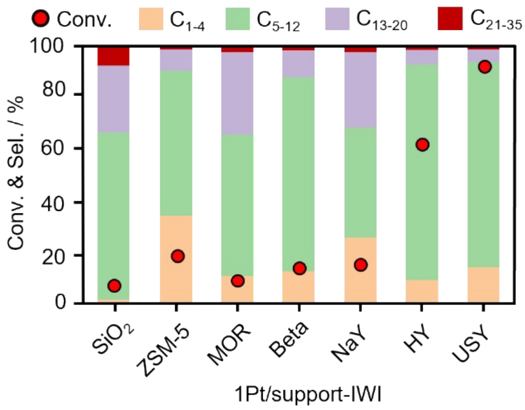

Figure S3. Hydrocracking of PE over 1wt% Pt on different supports. Reaction conditions: PE, 4.0 g, catalyst, 0.2 g, 280 ^{o}C, 3 MPa H_2, 3 h.

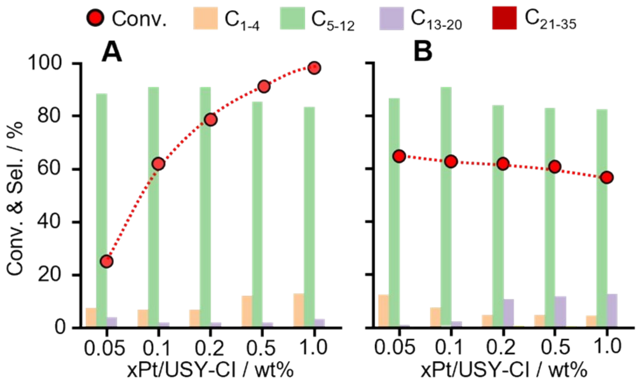

Figure S4. Hydrocracking of PE over Pt/USY catalysts with different Pt loading. Reaction conditions: A) PE, 4.0 g, catalyst, 0.2 g, 280 ºC, 3 MPa H_2, 3 h; B) PE, 4.0 g, catalyst, from 0.4 g to 0.02 g to keep Pt usage at 0.2 mg, 280 ºC, 3 MPa H_2, 3 h.

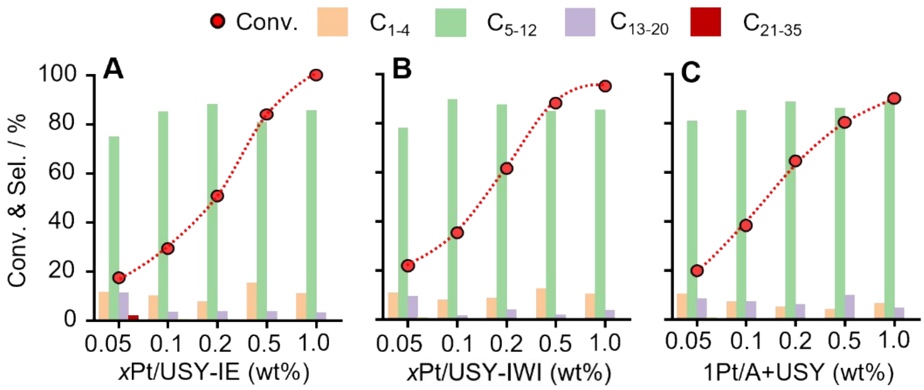

Figure S5. Hydrocracking of PE over Pt/USY and 1Pt/A + USY catalysts with different Pt loading. A) *x*Pt/USY-IE, B) *x*Pt/USY-IWI, C) 1Pt/A + USY. Reaction conditions: PE, 4.0 g, catalyst, 0.2 g (for A and B) or 1Pt/A + USY, 0.02 + 0.2g (for C), 280 ^{o}C, 3 MPa H_2, 3 h.

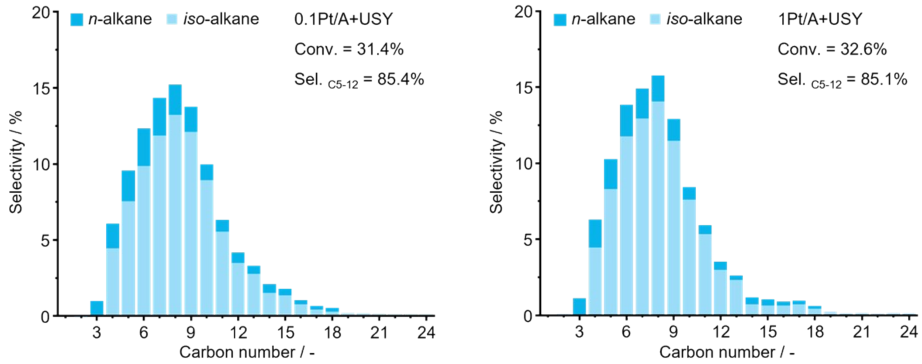

Figure S6. Hydrocracking of PE over Pt on γ-Al_2O_3 with different loading. Reaction conditions: PE, 4.0 g, 280 ^oC, 3 MPa H_2, 3 h, for 0.1Pt/A + USY the catalyst weight is 0.2 g + 0.2 g, for 1Pt/A + USY the catalyst weight is 0.02 g + 0.2 g.

Reactant	Conversion rate / $g_{reactant} \cdot g_{Pt}^{-1} \cdot h^{-1}$			
	0.1Pt/USY-IE	0.1Pt/USY-IWI	0.1Pt/USY-CI	1Pt/A+USY
C_6	1033	905	854	843
C_8	3353	2098	2069	2313
C_{12}	3820	3242	3840	3486
C_{16}	4160	4000	5542	5254
C_{24}	3687	3774	6646	6196
PE	1953	1859	4333	2487

Table S3. Conversion rate of various alkanes and PE over different Pt-USY catalysts

Reaction conditions: *n*-alkane or PE, 4.0 g, catalyst, 0.2 g (for 0.1Pt/USY-IE, 0.1Pt/USY-IWI, 0.1Pt/USY-CI) or 1Pt/A + USY, 0.02 + 0.2 g, 240 ^{o}C for *n*-alkane, 280 ^{o}C for PE, 3 MPa H_2, 3 h.

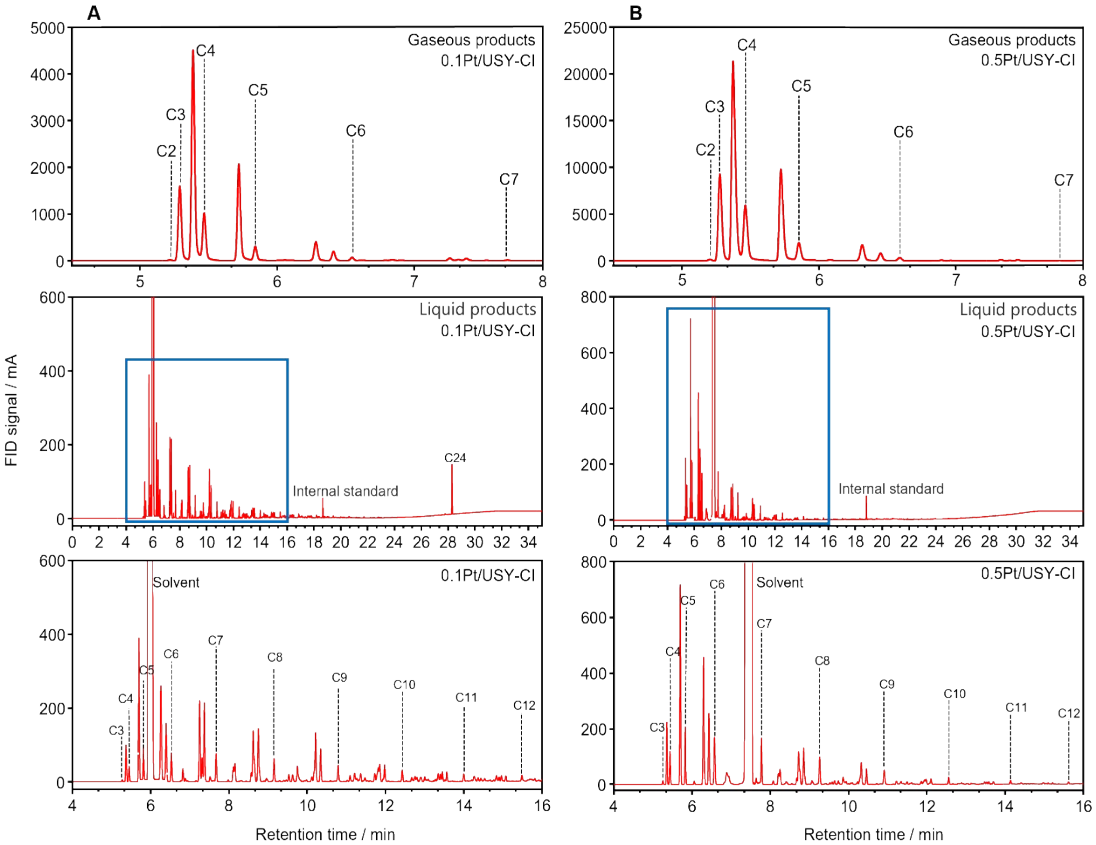

Figure S7. Typical gas and liquid products analyzed by GC-FID. A) Hydrocracking of C_{24} over 0.1Pt/USY-CI; B) hydrocracking of PE over 0.5Pt/USY-CI. Reaction conditions: C_{24} or PE, 4.0 g, catalyst, 0.2 g, 240 °C for C_{24} and 280 °C for PE, 3 MPa H_2, 3 h. Cyclohexane or dichloromethane was used as solvent and 1,3,5-Tri-tert-butylbenzene was used as internal standard.

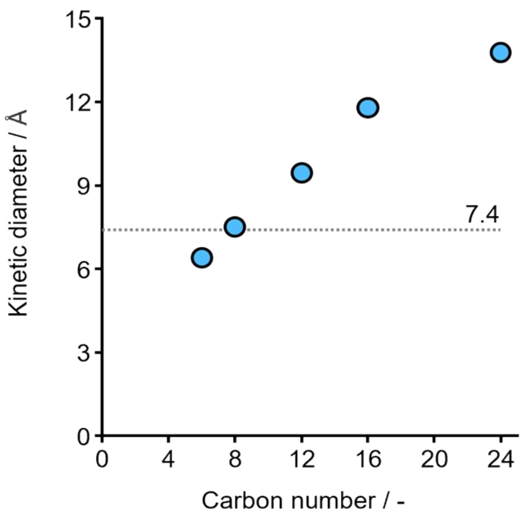

Figure S8. Molecular dynamics diameters of different *n*-alkanes based on calculation.

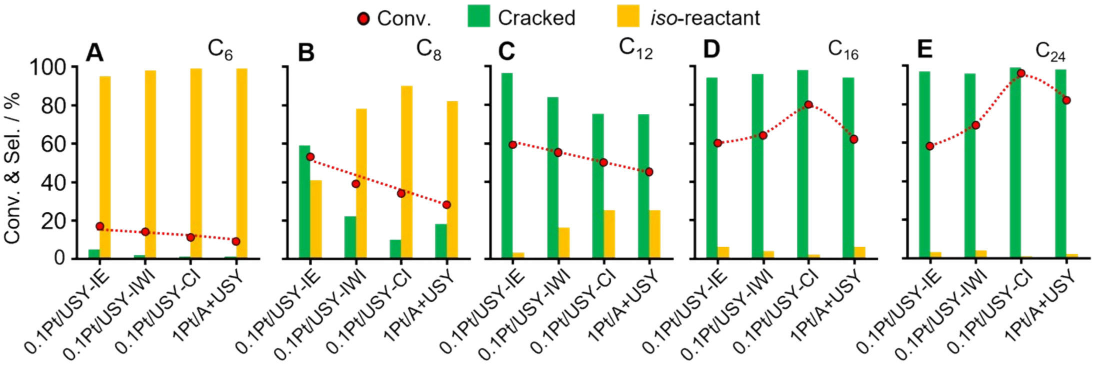

Figure S9. Hydrocracking different *n*-alkanes over Pt-USY catalysts with various metal-acid proximity. Reaction conditions: *n*-alkanes, 4.0 g, catalyst, 0.2 g (for 0.1Pt/USY-IE, 0.1Pt/USY-IWI, 0.1Pt/USY-CI) or 1Pt/A + USY, 0.02 + 0.2 g, 240 ^{o}C, 3 MPa H_2, 3 h.

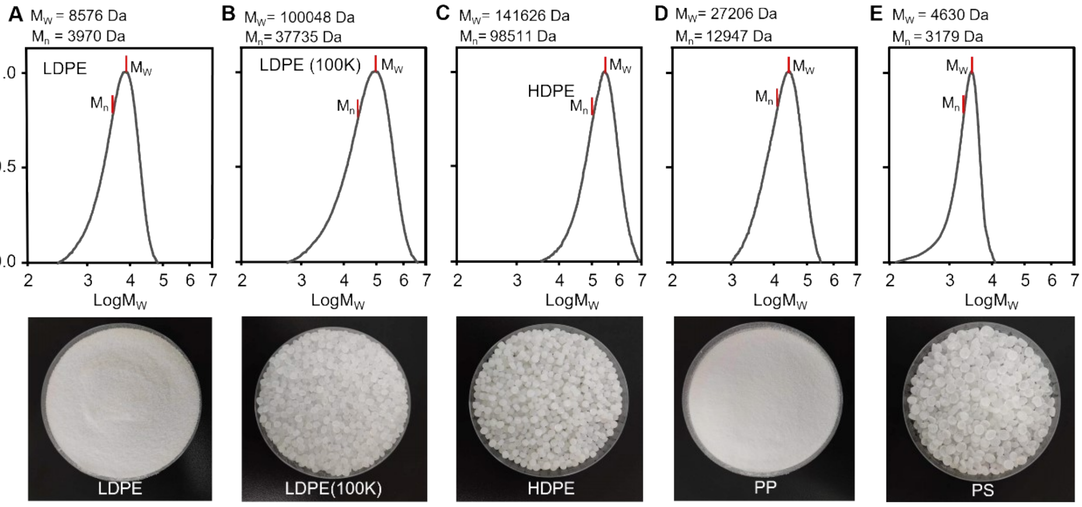

Figure S10. Molecular weight distributions of different polyolefins determined by HT-GPC.

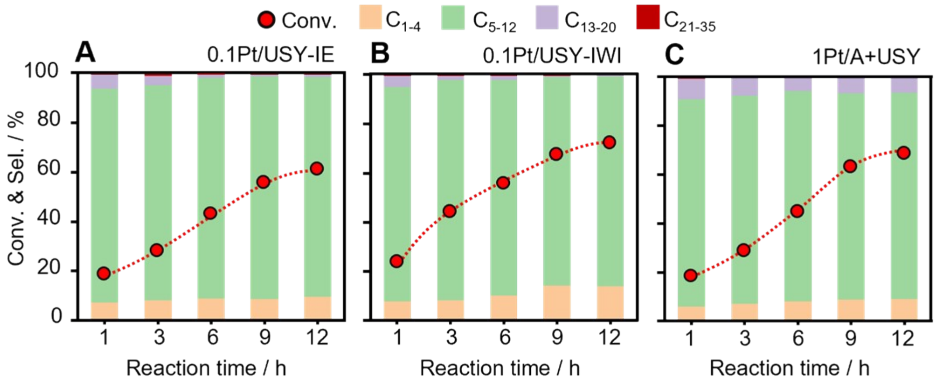

Figure S11. Time course of the PE conversion over Pt-USY catalysts with different metal-acid proximity. Reaction conditions: PE, 4.0 g, catalyst, 0.2 g (for A, B) or 1Pt/A + USY, 0.02 + 0.2 g (for C), 280 ^{o}C, 3 MPa H_2.

Table S4. Comparison of the formation rate of soluble liquid products of various catalysts for hydrocracking and hydrogenolysis of polyolefins.

Entry	Catalyst	Substrate	Temp. / °C	P. of H_2 / MPa	Time / h	Conv. / %	Sel.[a] / %	rate / $g_{liquid} \cdot g_{metal}^{-1} \cdot h^{-1}$	Ref.
1	0.1Pt/USY-CI	PE	280	3	1	31.7	92.7	6122	This work
2	0.1Pt/USY-CI	PE	280	3	3	62.4	92.4	4004	This work
3	0.1Pt/USY-CI	PE	280	3	6	80.2	89.8	2500	This work
4	0.1Pt/USY-CI	PE	260	3	3	50.8	93.4	3294	This work
5	0.1Pt/USY-CI	PE	240	3	3	36.3	96.0	2420	This work
6	0.1Pt/USY-CI	PP	280	3	3	79.8	91.1	5048	This work
7	Pt/2D-WO_3	HDPE	250	3	1	88.0	83.4	3884	[1]
8	Pt/WO_3/ZrO_2+ HY	LDPE	250	3	2	94.0	93.0	1748	[2]
9	Pt/AC	PP	300	1.5	24	100.0	100.0	8.3	[3]
10	Pt/$SrTiO_3$	PE	300	1.17	24	100.0	91.0	1.9	[4]
11	Pt-WZr	LDPE	250	3	3	55.0	100.0	366.7	[5]
12	Pt/Al_2O_3	PE	280	0[c]	6	72.0	90.2	4.3	[6]
13	Pt@S-1 + Beta	LDPE	250	3	2	99.5	89.9	2983	[7]
14	Pt@S-1 + Beta	LDPE	250	3	0.5	84.5	64.3	7245	[7]
15	Ru/FAU	PP	215	3	16	100.0	91.0	15.9	[8]
16	Ru/C	PE	200	3	16	100.0	50.0	17.5	[9]
17	Ru/TiO_2	PP	250	3	6	70.0	71.0	33.3	[10]
18	Ru/ZrO_2	LDPE	240	6	2	64.0	84.0	182.8	[11]
19	Ru-WZr	LDPE	250	5	2	73.0	82.6	241.2	[12]
20	Ru/CeO_2	LDPE	240	6	5	76.0	90.0	93.0	[13]
21	Ru/HZSM-5	HDPE	280	2[d]	2	55.0	41.4	15.4	[14]
22	Ni/SiO_2	LDPE	280	3	4	93.0	81.0	18.8	[15]

[a] Selectivity to soluble liquid products (C_5-C_{45}).

[b] Formation rate of liquid fuels = m (polyolefins) * liquid yield * conversion / (m (metal loading) * t).

[c] The reaction was conducted under Ar.

[d] The reaction was conducted under He with 5 vol% N_2 as internal standard.

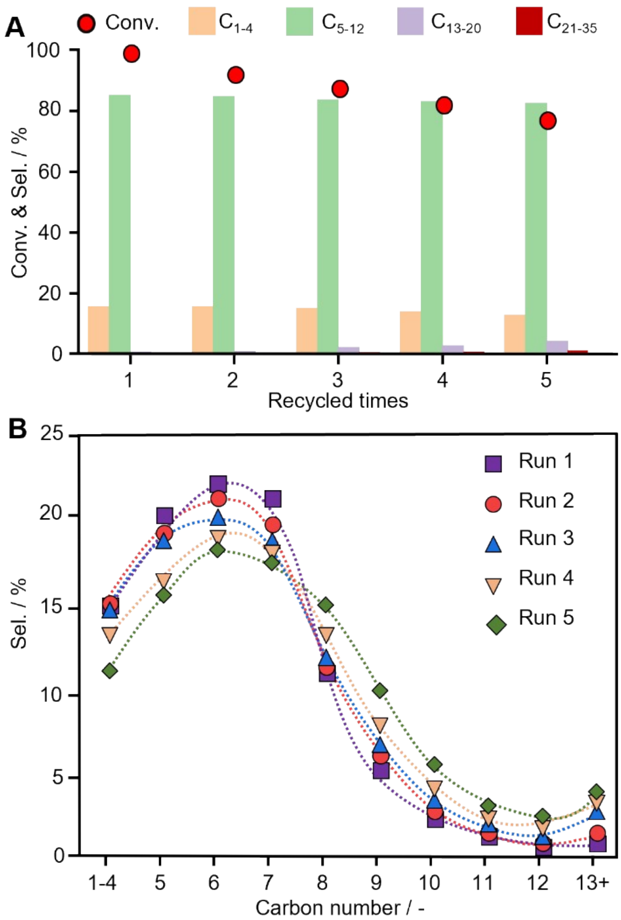

Figure S12. Reusability test of 0.1Pt/USY-CI catalyst. A) Catalytic performance and B) product distribution over run times. Reaction conditions: PE, 4.0 g, catalyst (1Pt/USY-CI), 0.4 g, 280 °C, 3 MPa H_2, 6 h.

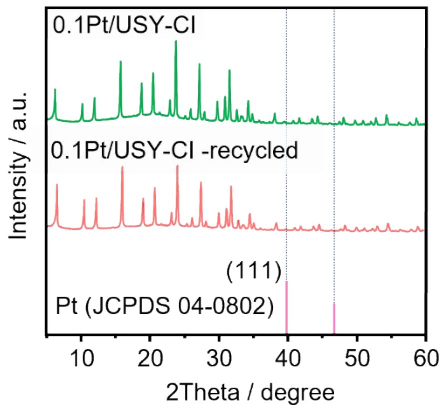

Figure S13. X-Ray diffraction patterns of fresh 0.1Pt/USY-CI and 0.1Pt/USY-CI-recycled.

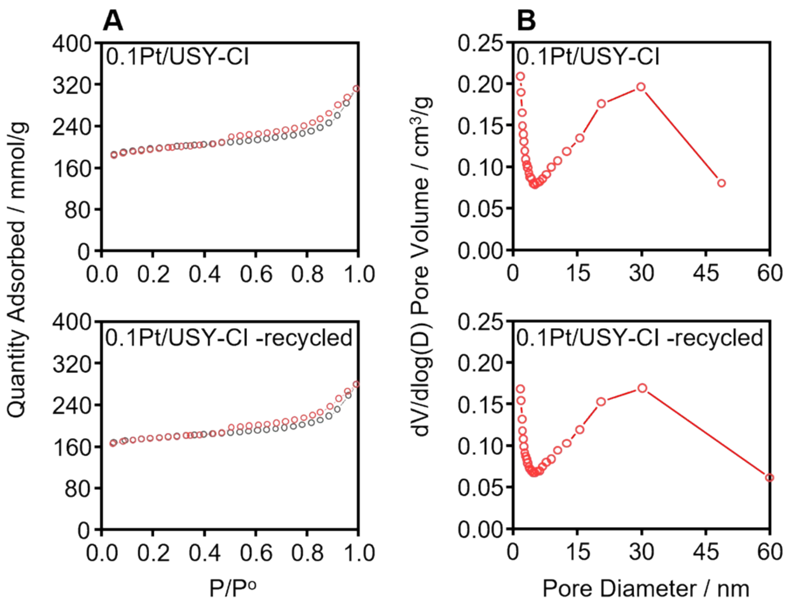

Figure S14. N_2-physisorption A) isotherms and B) pore size distribution of 0.1Pt/USY-CI and 0.1Pt/USY-CI-recycled.

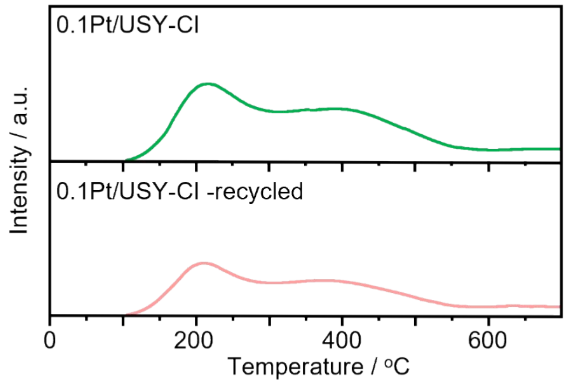

Figure S15. NH_3-TPD profile of 0.1Pt/USY-CI and 0.1Pt/USY-CI-recycled.

References

1. Q. Zhou, D. Wang, Q. Wang, K. He, K. H. Lim, X. Yang, W.-J. Wang, B.-G. Li and P. Liu, *Angew. Chem. Int. Ed.*, 2023, **n/a**, e202305644.
2. S. Liu, P. A. Kots, B. C. Vance, A. Danielson and D. G. Vlachos, *Sci. Adv.*, 2021, **7**, eabf8283.
3. S. D. Jaydev, A. J. Martín and J. Pérez-Ramírez, *ChemSusChem*, 2021, **14**, 5179-5185.
4. G. Celik, R. M. Kennedy, R. A. Hackler, M. Ferrandon, A. Tennakoon, S. Patnaik, A. M. LaPointe, S. C. Ammal, A. Heyden, F. A. Perras, M. Pruski, S. L. Scott, K. R. Poeppelmeier, A. D. Sadow and M. Delferro, *ACS Cent. Sci.*, 2019, **5**, 1795-1803.
5. B. C. Vance, P. A. Kots, C. Wang, Z. R. Hinton, C. M. Quinn, T. H. Epps, L. T. J. Korley and D. G. Vlachos, *Appl. Catal., B*, 2021, **299**, 120483.
6. F. Zhang, M. Zeng, R. D. Yappert, J. Sun, Y.-H. Lee, A. M. LaPointe, B. Peters, M. M. Abu-Omar and S. L. Scott, *Science*, 2020, **370**, 437-441.
7. L. Li, H. Luo, Z. Shao, H. Zhou, J. Lu, J. Chen, C. Huang, S. Zhang, X. Liu, L. Xia, J. Li, H. Wang and Y. Sun, *J. Am. Chem. Soc.*, 2023, **145**, 1847-1854.
8. J. E. Rorrer, A. M. Ebrahim, Y. Questell-Santiago, J. Zhu, C. Troyano-Valls, A. S. Asundi, A. E. Brenner, S. R. Bare, C. J. Tassone, G. T. Beckham and Y. Román-Leshkov, *ACS Catal.*, 2022, **12**, 13969-13979.
9. J. E. Rorrer, G. T. Beckham and Y. Román-Leshkov, *JACS Au*, 2021, **1**, 8-12.
10. P. A. Kots, S. Liu, B. C. Vance, C. Wang, J. D. Sheehan and D. G. Vlachos, *ACS Catal.*, 2021, **11**, 8104-8115.
11. M. Tamura, S. Miyaoka, Y. Nakaji, M. Tanji, S. Kumagai, Y. Nakagawa, T. Yoshioka and K. Tomishige, *Appl. Catal., B*, 2022, **318**, 121870.
12. C. Wang, T. Xie, P. A. Kots, B. C. Vance, K. Yu, P. Kumar, J. Fu, S. Liu, G. Tsilomelekis, E. A. Stach, W. Zheng and D. G. Vlachos, *JACS Au*, 2021, **1**, 1422-1434.
13. Y. Nakaji, M. Tamura, S. Miyaoka, S. Kumagai, M. Tanji, Y. Nakagawa, T. Yoshioka and K. Tomishige, *Appl. Catal., B*, 2021, **285**, 119805.
14. J. Du, L. Zeng, T. Yan, C. Wang, M. Wang, L. Luo, W. Wu, Z. Peng, H. Li and J. Zeng, *Nat. Nanotechnol.*, 2023, DOI: 10.1038/s41565-023-01429-9.
15. Z. Zhao, Z. Li, X. Zhang, T. Li, Y. Li, X. Chen and K. Wang, *Environ. Pollut.*, 2022, **313**, 120154.