Supplementary Information

Study on Carbon Cycle of Hydrogen Supply System over Supported Pt Catalyst: Methylcyclohexane-Toluene-Hydrogen Cycle

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Table S1 Chemical compositions of catalysts from ICP analysis

	Pt content wt%	Cu content wt%
Pt/S-1	0.34	0
Cu/S-1	0	0.38
Cu-Pt/S-1	0.44	0.37
Cu-Pt/SiO_2	1.41	1.41

Table S2 Comparison on MCH dehydrogenation over Cu-Pt/S-1 with other Pt supported catalysts from literatures. [23-30]

No.	Catalyst	Reaction conditions	Conversion/H_2 evolution rate	Ref.
23	Pt/SBA-15 (Pt 3.1 wt%)	T=300 ℃,catalyst weight=0.05 g, WHSV =27.1 h^{-1} Hydrogen was used as carrier gas	65.0%/96.4 mmol/g_{Pt}/min	Chen AB, Zhang WP, Li XY, Tan DL, Han XW, Bao XH. One-pot encapsulation of Pt nanoparticles into the mesochannels of SBA-15 and their catalytic dehydrogenation of methylcyclohexane. Catal Lett. 2007;119(1-2):159-64.[1]
24	Pt/activated carbon (Pt 1wt%)	T=300 ℃, catalyst weight = 0.03 g, MCH rate = 0.03 mL/min	42%/121.9 mmol/g_{Pt}/min	Li XY, Ma D, Bao XH. Dispersion of Pt catalysts supported on activated carbon and their catalytic performance in methylcyclohexane dehydrogenation. Chinese J Catal. 2008;29(3):259-63.[2]
25	Pt/$La_{0.7}Y_{0.3}NiO_3$ (Pt 1 wt%)	T=350 ℃,catalyst weight=0.3 g, pulse injection of MCH	14%/45.3 mmol/g_{Pt}/min	Shukla AA, Gosavi PV, Pande JV, Kumar VP, Chary KVR, Biniwale RB. Efficient hydrogen supply through catalytic dehydrogenation of methylcyclohexane over Pt/metal oxide catalysts. Int J Hydrog Energy. 2010;35(9):4020-6.[3]
26	Pt/pyrolytic waste tire char (Pt 0.4 wt%)	T=300 ℃, catalyst weight =0.554 g, MCH rate =1.8 mL/h, WHSV=2.5 h^{-1}	95%/300 mmol/g_{Pt}/min	Zhang C, Liang XQ, Liu SX. Hydrogen production by catalytic dehydrogenation of methylcyclohexane over Pt catalysts supported on pyrolytic waste tire char. Int J

				Hydrog Energy. 2011;36(15):8902-7.[4]
27	Pt/Mo_{10}-SiO_2 (Pt 5 wt%)	T=400 ℃, catalyst weight =0.10 g, WHSV=92.4 h^{-1} H_2 pressure 2.2 MPa	10%/30 mmol/g_{Pt}/min	Boufaden N, Akkari R, Pawelec B, Fierro JLG, Zina MS, Ghorbel A. Dehydrogenation of methylcyclohexane to toluene over partially reduced silica-supported Pt-Mo catalysts. J Mol Catal a-Chem. 2016;420:96-106.[5]
28	Pt/ACC (Pt 5wt%)	T=350 ℃ spray pulse reactor	26.8%/ 373.1 mmol/g_{Pt}/min	Patil SP, Bindwal AB, Pakade YB, Biniwale RB. On H_2 supply through liquid organic hydrides - Effect of functional groups. Int J Hydrog Energy. 2017;42(25):16214-24.[6]
29	PtSn-5/Mg-Al-O-350 (Pt 2wt%)	T=300 ℃, catalyst weight =0.5 g, MCH rate =0.1 mL/min , WHSV=9.2 h^{-1}	90.5%/262.1 mmol/g_{met}/min	Yan J, Wang WY, Miao L, Wu K, Chen GL, Huang YP, et al. Dehydrogenation of methylcyclohexane over Pt-Sn supported on Mg-Al mixed metal oxides derived from layered double hydroxides. Int J Hydrog Energy. 2018;43(19):9343-52.[7]
30	Pt/Ce-Mg-Al-O (Pt 0.4wt%)	T=350 ℃, catalyst weight =0.5 g, MCH rate =0.1 mL/min, WHSV=9.2 h^{-1}	98.5%/1358.6 mmol/g_{Pt}/min	Wang W, Miao L, Wu K, Chen G, Huang Y, Yang Y. Hydrogen evolution in the dehydrogenation of methylcyclohexane over Pt/Ce-Mg-Al-O catalysts derived from their layered double hydroxides. Int J Hydrog Energy. 2019;44(5):2918-25.[8]
this work	Cu-Pt/S-1 (Pt 0.4wt%)	T=400 ℃, catalyst weight=1.0 g, MCH rate =0.1 mL/min, WHSV= 4.6 h^{-1}	92%/430 mmol/g_{Pt}/min	This work

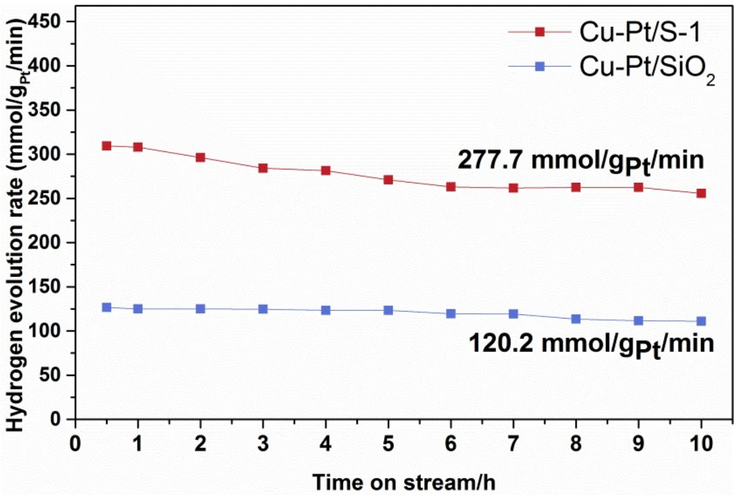

Fig. S1 H_2 evolution rate over 10 hours on Cu-Pt/S-1 and Cu-Pt/SiO_2 (T=350 ℃, P=101 KPa, WHSV=4.6 h^{-1}).

Table S3 Physicochemical properties of Cu-Pt/S-1 and Cu-Pt/SiO_2.

Samples	S_{BET}[§] (m^2/g)	S_{micro}[§§] (m^2/g)	S_{exter}[§§§] (m^2/g)
Cu-Pt/S-1	415.1	267.6	**147.5**
Cu-Pt/SiO_2	**190.1**	19.5	170.5

[§] The total surface area was calculated from BET method.

[§§] The microspore and external surface area were obtained from the t-plot method.

Table S4. Comparison on toluene hydrogenation over Pt/S-1 with other Pt supported catalysts from literatures based on toluene conversion and H_2 storage rate.[13, 32-38]

Ref No.	Catalyst	Reaction conditions	Conversion/ hydrogen storage rate	Ref.
32	Pt/CBV-780 (Pt 0.3 wt%)	T=120 ℃, toluene flow rate=0.3 ml/h catalyst weight=0.03g,	~100%/1574 mmol/g_{Pt}/min	Thomas K, Binet C, Chevreau T, Cornet D, Gilson JP. Hydrogenation of toluene over supported Pt and Pd catalysts: Influence of structural factors on the sulfur tolerance. J Catal. 2002;212(1):63-75.

		total pressure=3 MPa fixed bed		
13	3Pt3Pd/HBEA(Pt 3wt%)	T=150 ℃, catalyst weight=0.07g, H_2/toluene=28, fixed bed	~100%/102 mmol/g_{Pt}/min	Loiha S, Foettinger K, Zorn K, Klysubun W, Rupprechter G, Wittayakun J. Catalytic enhancement of platinum supported on zeolite beta for toluene hydrogenation by addition of palladium. Journal of Industrial and Engineering Chemistry. 2009;15(6):819-23.
33	Pt/H-Y (Pt 0.8wt%)	T=110 ℃, P(H_2)/P(toluene) = 4, fixed bed	75%/363 mmol/g_{Pt}/min	Mediavilla M, Melo L, Brito JL, Moronta D, Solano R, Gonzalez I, et al. Synthesis of Pt and Pt-Sn catalysts supported on H-Y zeolite induced by microwave radiation. Micropor Mesopor Mat. 2013; 170: 189-93.
34	Pt-Pd/ Zr-HMS (Pt 0.15wt%)	T=225 ℃, catalyst weight=5 g, hydrogen pressure =2 MPa, fixed bed	~100%/360 mmol/g_{met}/min	Roy S, Datta S. Hydrogenation of Toluene on Zirconium-Modified Hexagonal Molecular Sieve Supported Platinum and Palladium Catalysts. Ind Eng Chem Res. 2013; 52 (49): 17360-8.
35	Pt1Ru1.5 (Pt 1.6wt%)	Room temperature, catalyst weight=0.2 g, hydrogen pressure=0.1 MPa, in ethanol	85%/2.6 mmol/g_{met}/min	Stanley JNG, Heinroth F, Weber CC, Masters AF, Maschmeyer T. Robust bimetallic Pt-Ru catalysts for the rapid hydrogenation of toluene and tetralin at ambient temperature and pressure. Appl Catal a-Gen. 2013;454:46-52.

36	Pt/TiO_2-SiO_2 (Pt 5.0wt%)	T=200 ℃, catalyst weight=0.5 g, hydrogen pressure =1 MPa, 100 mL stainless-steel autoclave	Small/0.6 mmol/g_{Pt}/min	Gonda M, Ohshima M-a, Kurokawa H, Miura H. Toluene hydrogenation over Pd and Pt catalysts as a model hydrogen storage process using low grade hydrogen containing catalyst inhibitors. Int J Hydrog Energy. 2014; 39(29): 16339-46.
37	Pt-Pd/SiO_2-Al_2O_3 (Pt 0.2wt%)	T=150 ℃, catalyst weight=5 g, hydrogen pressure =2 MPa, fixed bed	88%/407mmol/g_{Pt}/min	Kumar SAK, John M, Pai SM, Niwate Y, Newalkar BL. Low temperature hydrogenation of aromatics over Pt-Pd/SiO_2-Al_2O_3 catalyst. Fuel Processing Technology. 2014; 128:303-9.
38	Pt/Al_2O_3-HUSY (Pt 0.37wt%)	T=110 ℃, H_2/toluene=45, P=0.1MPa	<15%/144 mmol/g_{Pt}/min	Mendes PSF, Gregorio AFC, Daudin A, Bouchy C, Silva JM, Ribeiro MF. Elucidation of the zeolite role on the hydrogenating activity of Pt-catalysts. Catal Commun. 2017; 89:152-5.
this work	Pt/S-1 (Pt 0.3 wt%)	T=150 ℃, n(H_2)/n(toluene) ≈3.1, P（H_2）=1.5MPa, 70 mL stainless-steel autoclave	~100%/1271 mmol/g_{Pt}/min	This work

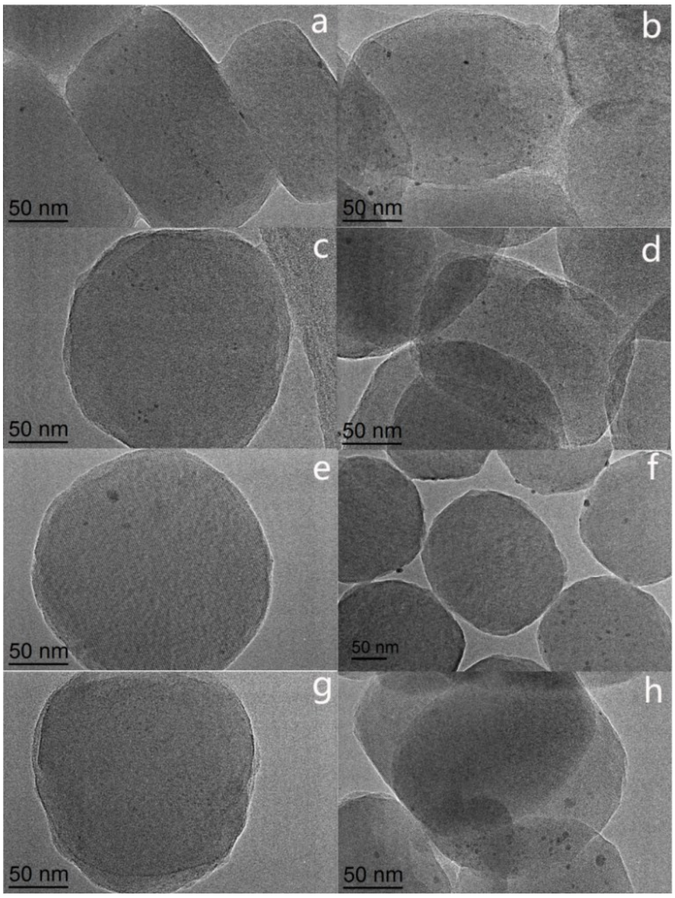

Fig. S2 TEM images of fresh and spent catalysts: Pt/S-1(a, b), Cu-Pt/S-1 (c, d), spent Pt/S-1 (e, f) (after reaction 10 hours at 350 ℃) and spent Cu-Pt/S-1 (g, h) (after reaction 10 hours at 350 ℃).

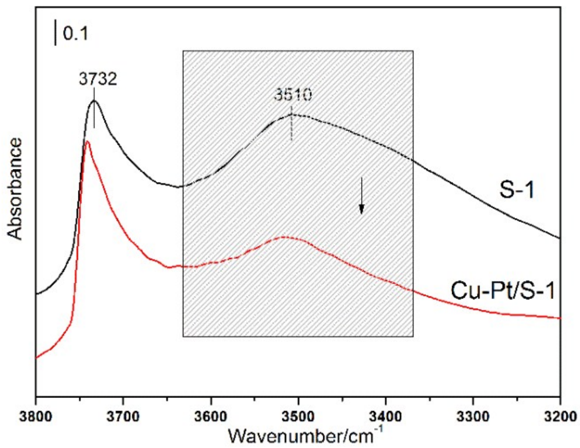

Fig. S3 Hydroxyl IR spectrums of S-1 and reduced Cu-Pt/S-1.

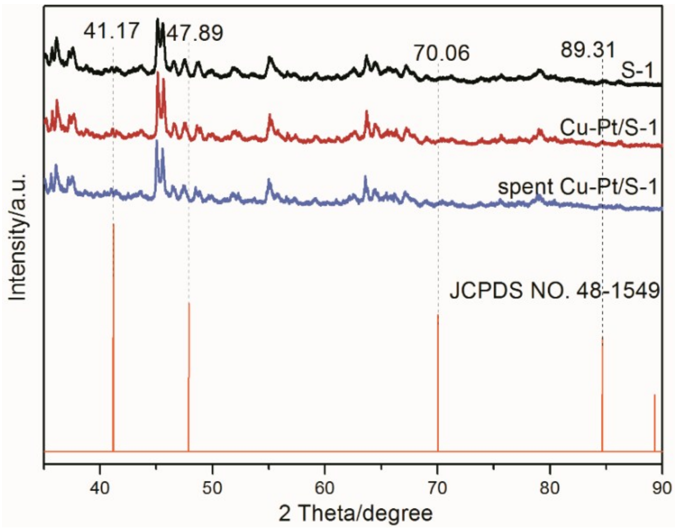

Fig. S4 X-ray diffraction patterns of Cu-Pt/S-1, spent Cu-Pt/S-1, S-1 and CuPt alloy (JCPDS NO.48-1549).