

Supporting information for

Selective 5-hydroxymethylfurfural hydrogenolysis to 2,5-dimethylfuran over bimetallic Pt-FeO_x/AC catalysts

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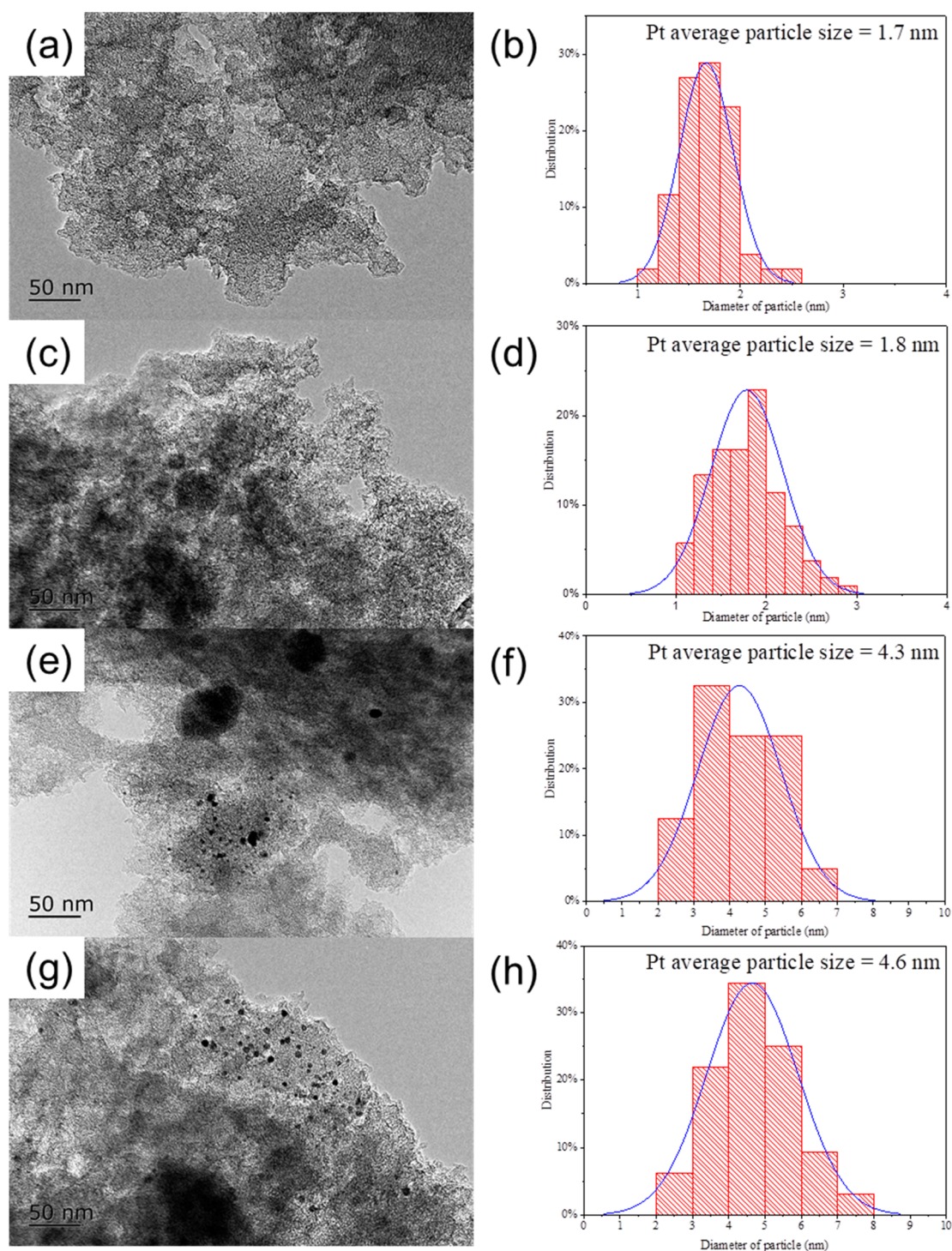


Figure S1. TEM images and particle size distribution histogram of 0.1% Pt-2% FeO_x/AC (a, b), 0.3% Pt-2% FeO_x/AC (c, d), 0.5% Pt-1% FeO_x/AC (e, f), 0.5% Pt-5.83% FeO_x/AC (g, h).

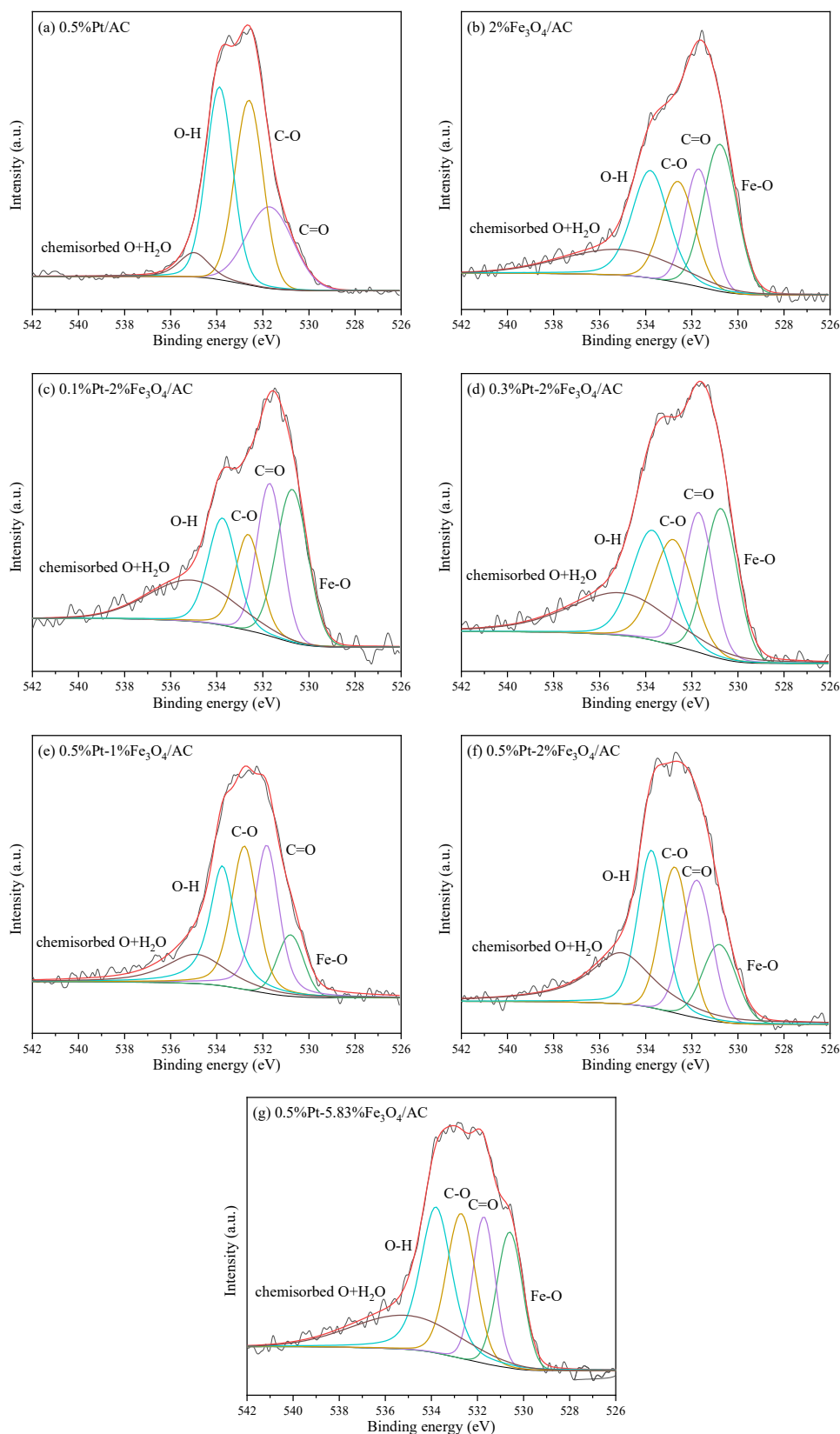


Figure S2. The O 1s XPS spectra of different catalysts.

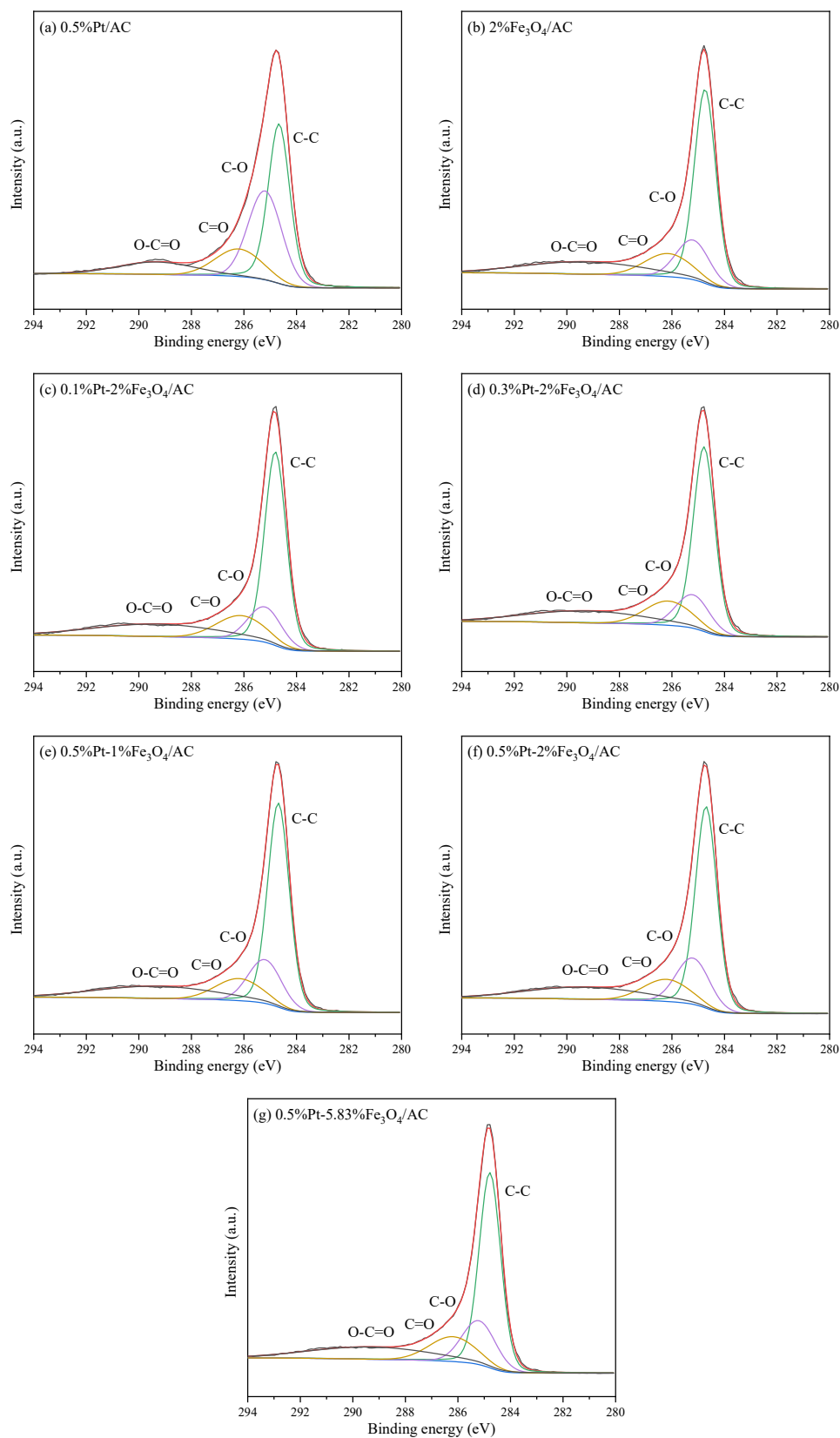


Figure S3. The C 1s XPS spectra of different catalysts.

Table S1. The O 1s and C 1s XPS peak fitting data of different catalysts.

catalysts	O 1s					C 1s			
	Fe-O	C=O	C-O	O-H	chemisorbed O+H ₂ O	C-C	C-O	C=O	O-C=O
0.5%Pt/AC	-	24.5%	34.4%	35.4%	5.7%	42.2%	32.5%	14.7%	10.6%
2%FeO _x /AC	27.3%	17.0%	18.0%	21.9%	15.8%	53.0%	16.3%	12.8%	17.9%
0.1%Pt-2%FeO _x /AC	26.1%	21.7%	14.8%	18.0%	19.4%	52.6%	15.3%	13.7%	18.4%
0.3%Pt-2%FeO _x /AC	20.8%	18.2%	18.5%	20.3%	22.2%	53.1%	14.5%	14.2%	18.2%
0.5%Pt-1%FeO _x /AC	10.8%	27.5%	24.2%	20.3%	17.1%	54.2%	16.6%	12.2%	17.1%
0.5%Pt-2%FeO _x /AC	12.8%	20.2%	20.3%	23.4%	23.3%	53.7%	18.2%	11.6%	16.5%
Used-1st 0.5%Pt-2%FeO _x /AC	6.9%	21.0%	37.9%	28.5%	5.7%	52.3%	17.5%	18.4%	11.8%
Used-4th 0.5%Pt-2%FeO _x /AC	1.7%	13.9%	35.2%	34.9%	14.3%	41.9%	24.7%	23.3%	10.1%
0.5%Pt-5.83%FeO _x /AC	17.2%	16.5%	21.4%	26.8%	18.1%	51.8%	16.4%	14.0%	17.7%

Table S2. Reports on the hydrogenation of HMF to DMF over Pt based catalysts.

Catalyst	Catalyst/metal amount	HMF concentration	Reaction conditions	Solvent	Conv. (%)	DMF yield (%)	Average reaction rate (mmol·g ⁻¹ ·h ⁻¹)	Ref.
Pt/C	50mg, 10wt%Pt	W/F=50 g*min/g	180°C, 3.3MPa H ₂	ethanol	100%	70.0%	-	[1]
Pt/rGO	0.02mmol Pt, 5wt%Pt	2mmol/12ml	120°C, 2h, 3MPa H ₂	n-butanol	100%	73.2%	187.6	[2]
Pt@MOF-T3	0.02mmol Pt, 10wt%Pt	2mmol/12ml	140°C, 8h, 3MPa H ₂ ,	n-butanol	99.6%	96.1%	61.6	[3]
Pt ₃ Co ₂ /C	50mg, 10wt%	W/F=1.0 g*min/mL	160°C, 3.3MPa H ₂ ,	1-propanol	100%	98.0%	46.4	[4]
PtCo/GC	50mg, 10wt%Pt, 10wt%Co	2mmol/45ml	180°C, 2h, 1MPa H ₂ .	commercial gasoline	100%	95.0%	95.0	[5]
PtCo/MWCNTs	4.35 mg Pt, 8.2wt%Pt, 6.3wt%Co	0.4mmol/30 mL	160°C, 8h, 1MPa H ₂	n-butanol	100%	92.3%	6.0	[6]
PtCo@HCS	50mg, 12.0wt%Pt, 12.2wt%Co	2mmol/6ml	180°C, 2h, 1MPa H ₂	n-butanol	100%	98.0%	81.0	[7]
Pt ₁ /Co SAA	80mg, 0.001mmol Pt	0.5mmol/10ml	180°C, 2h, 1MPa H ₂	tetrahydrofuran	100%	92.9%	2.90	[8]
Pt ₃ Co BNN	1.3 mg	0.25mmol/2ml	160°C, 24h, 1MPa H ₂	ethanol	100%	78.0%	6.25	[9]
Pt ₃ Ni/C	50mg, 10wt%	W/F=1.0 g*min/mL	200°C, 3.3MPa H ₂ ,	1-propanol	100%	98.0%	46.4	[10]
PtIr-CMK-3	150mg, 0.5wt%Pt, 0.5wt%Ir	1.2mmol/50mL	120°C, 4h, 1.5MPa H ₂	tetrahydrofuran	98%	86.0%	172	[11]
Pt-FeO _x /AC	100mg, 0.5wt%Pt, 2wt%Fe	2mmol/20ml	180°C, 6h, 1.5MPa H ₂	n-butanol	100%	91.1%	121.5	This work

Average reaction rate = DMF yield × mmol of HMF / metal mass / reaction time.

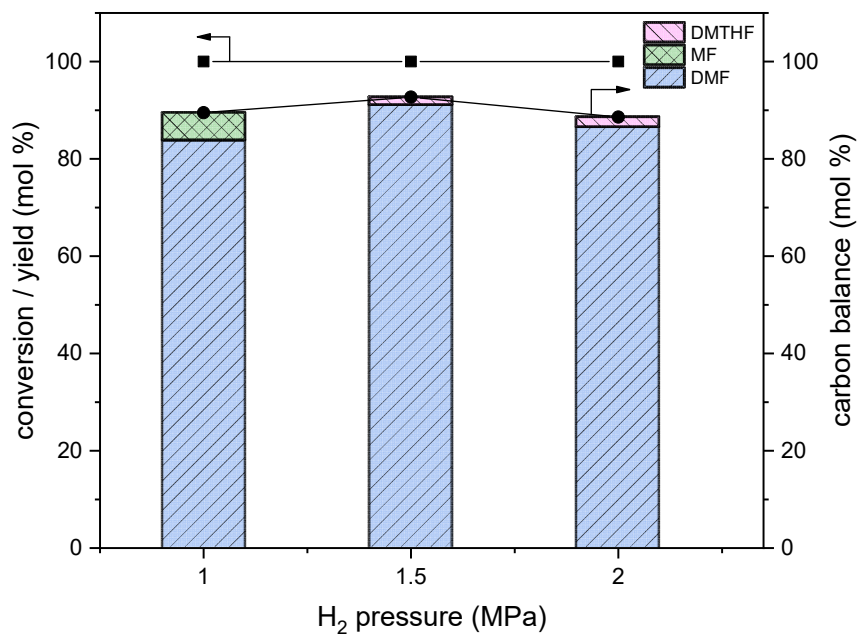


Figure S4. Effect of H₂ pressure on HMF hydrogenolysis over 0.5% Pt-2% FeO_x/AC. [Reaction conditions: $T = 180\text{ }^{\circ}\text{C}$, $t = 6\text{ h}$, stirring speed = 600 rpm, $m_{\text{HMF}} = 250\text{ mg}$, $m_{\text{catalyst}} = 100\text{ mg}$, $V_{\text{n-butanol}} = 20\text{ mL}$.]

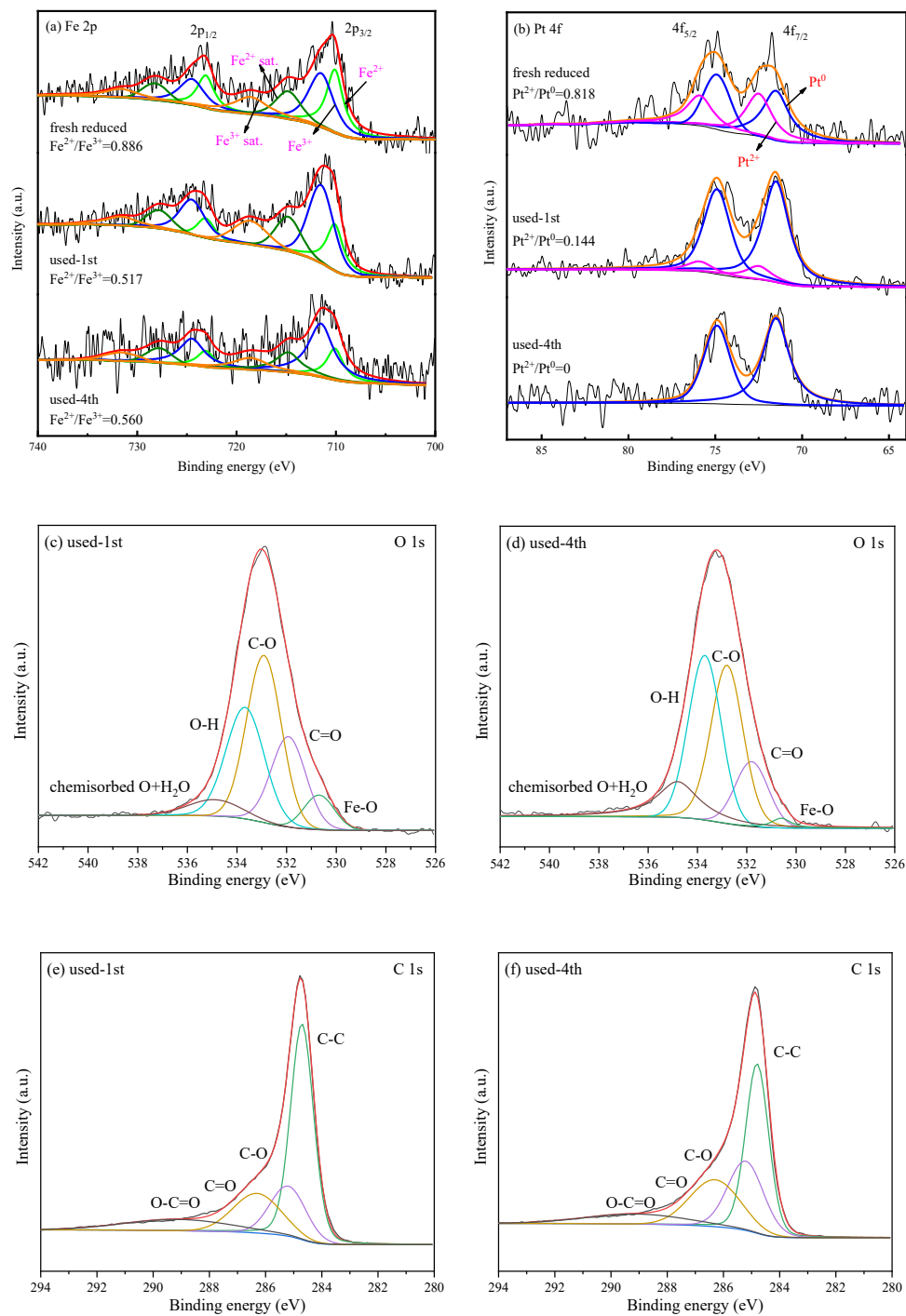


Figure S5. The Fe 2p (a), Pt 4f (b), O 1s (c) and C 1s (d-f) XPS spectra of fresh reduced, used-1st and used-4th 0.5% Pt-2% FeO_x/AC catalyst.

References

1. Luo, J.; Arroyo-Ramírez, L.; Gorte, R. J.; Tzoulaki, D. and Vlachos, D. G. Hydrodeoxygenation of HMF over Pt/C in a continuous flow reactor. *AIChE J.* **2015**, 61, 590-597.
2. Shi, J.; Wang, Y.; Yu, X.; Du, W. and Hou, Z. Production of 2,5-dimethylfuran from 5-hydroxymethylfurfural over reduced graphene oxides supported Pt catalyst under mild conditions. *Fuel* **2016**, 163, 74-79.
3. Wang, K.; Zhao, W.; Zhang, Q.; Li, H. and Zhang, F. In Situ One-Step Synthesis of Platinum Nanoparticles Supported on Metal–Organic Frameworks as an Effective and Stable Catalyst for Selective Hydrogenation of 5-Hydroxymethylfurfural. *ACS Omega* **2020**, 5, 16183-16188.
4. Luo, J.; Yun, H.; Mironenko, A. V.; Goulas, K.; Lee, J. D.; Monai, M.; Wang, C.; Vorotnikov, V.; Murray, C. B.; Vlachos, D. G.; Fornasiero, P. and Gorte, R. J. Mechanisms for High Selectivity in the Hydrodeoxygenation of 5-Hydroxymethylfurfural over PtCo Nanocrystals. *ACS Catal.* **2016**, 6, 4095-4104.
5. Nürenberg, E.; Schulze, P.; Kohler, F.; Zubel, M.; Pischinger, S. and Schüth, F. Blending Real World Gasoline with Biofuel in a Direct Conversion Process. *ACS Sustain. Chem. Eng.* **2018**, 7, 249-257.
6. Wang, X.; Liu, Y. and Liang, X. Hydrogenolysis of 5-hydroxymethylfurfural to 2,5-dimethylfuran over supported Pt–Co bimetallic catalysts under mild conditions. *Green Chem.* **2018**, 20, 2894-2902.
7. Wang, G.; Hilgert, J.; Richter, F. H.; Wang, F.; Bongard, H. J.; Spliethoff, B.; Weidenthaler, C. and Schüth, F. Platinum–cobalt bimetallic nanoparticles in hollow carbon nanospheres for hydrogenolysis of 5-hydroxymethylfurfural. *Nat. Mater.* **2014**, 13, 293-300.
8. Gan, T.; Liu, Y.; He, Q.; Zhang, H.; He, X. and Ji, H. Facile Synthesis of Kilogram-Scale Co-Alloyed Pt Single-Atom Catalysts via Ball Milling for Hydrodeoxygenation of 5-Hydroxymethylfurfural. *ACS Sustain. Chem. Eng.* **2020**, 8, 8692-8699.
9. Carmiel-Kostan, M.; Nijem, S.; Dery, S.; Horesh, G. and Gross, E. Composition–Reactivity Correlations in Platinum–Cobalt Nanoporous Network as Catalyst for Hydrodeoxygenation of 5-Hydroxymethylfurfural. *J. Phys. Chem. C* **2019**, 123, 30274-30282.
10. Luo, J.; Lee, J. D.; Yun, H.; Wang, C.; Monai, M.; Murray, C. B.; Fornasiero, P. and Gorte, R. J. Base metal-Pt alloys: A general route to high selectivity and stability in the production of biofuels from HMF. *Appl. Catal. B* **2016**, 199, 439-446.
11. Ledesma, B.; Juárez, J.; Mazarío, J.; Domine, M. and Beltramone, A. Bimetallic platinum/iridium modified mesoporous catalysts applied in the hydrogenation of HMF. *Catal. Today* **2019**, 360, 147-156.