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Supporting Information

Pt nanoparticles supported on $YCo_xFe_{1-x}O_3$ perovskite oxides: Highly efficient catalysts for liquid-phase hydrogenation of cinnamaldehyde

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Contents

Experimental

1. Preparation of Pt/$YCo_xFe_{1-x}O_3$ catalyst

SBA-15 was synthesized using the triblock copolymer Pluronic 123 and tetraethyl orthosilicate (TEOS) according to Ref. [1]. $YCo_{x5}Fe_{1-x}O_3$ perovskite-type composites were prepared by a modified sol-gel method [2]. The starting materials $Y(NO_3)_3 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in distilled water with a stoichiometric ratio of Y/Co/Fe=1/1/0, 1/0.7/0.3, 1/0.5/0.5, 1/0.3/0.7; 1/0/1, respectively. Citric acid was added to the above nitrate solution as a complexing agent to control the final citrate/transition metal ratio of 1/1. Then, SBA-15 (1.0 g) after sonicated in 10 mL deionized water was introduced to the above mixture. Subsequently, the solution was stirred for 3-4 h at room temperature. Next, the mixed solution was moved to a water bath at 90 ℃ until the sticky gel was formed. After that, the gel was dried at 140 ℃ overnight. After grinding, the precursor was calcined at 500 ℃ with a ramping rate of 5 ℃/min and kept at 500 ℃ for 4 h, followed by further calcination at 950 ℃ with a ramping rate of 3.5 ℃/min and remained at 950 ℃ for 5 h. Finally, the resultant powders were treated with sodium hydroxide solution (2 mol/L) to remove the SBA-15 template.

The nominal 5 wt% Pt catalysts were prepared via an impregnation method using an aqueous solution of H_2PtCl_6. The suspension was stirred for 4-6 h at room temperature and then evaporated to remove the excess solvent, followed by drying overnight at 100 ℃. Finally, catalyst precursors were reduced in an aqueous solution of sodium formate at 90 ℃ after calcined in air at 200 ℃ for 2 h.

References

[1] D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science*, 1998, 279, 548-552.

[2] Y. Wei, H. Gui, Z. Zhao, J. Li, Y. Liu, S. Xin, X. Li, W. Xie, *AIP Adv.*, 2014, **4**, ID: 127134.

2. Characterization

Powder X-ray diffraction (XRD) patterns of the samples were collected on a Bruker D8 ADVANCE instrument using Cu Kα radiation (λ=1.54178 Å) as X-ray source. The N_2-physisorption isotherms of samples were measured at 77 K on a Quantachrome Autosorb-3B system after the samples were evacuated at 300 ℃ for 4 h. The Brunauer-Emmett-Teller (BET) specific surface area was calculated using adsorption data in the relative pressure range from 0.05 to 0.35. Scanning electron microscopy (SEM) was performed using a Hitachi S-4800 microscope. The transmission electron microscopy (TEM) images were taken on an FEI Tecnai G2-TF30 microscope at an acceleration voltage of 300 kV. The actual Pt loading of samples was determined by Thermo Elemental IRIS Intrepid II XSP inductively coupled plasma-optical emission spectroscopy (ICP-OES). The thermogravimetric (TG) analysis of the samples was conducted from r.t. to 800 ℃ under an air atmosphere with Mettler Toledo TGA/SDTA851^e apparatus.

X-ray photoelectron spectrum (XPS) of the samples were measured with a Thermo Fisher Scientific ESCALAB 250Xi spectrometer with Al Kα radiation (1486.6 eV) as incident beam with a monochromator. The samples were directly measured only after pretreatment under vacuum. The binding energy (BE) was calibrated using C-C binding energy at 284.4 eV in order to compare the BEs with the data from the literature. The spectra shown in the figures have been corrected by subtraction of a Shirley background. Spectral fitting and peak integration was done using the XPSPEAK software.

Temperature-programmed reduction with hydrogen (H_2-TPR) was conducted to understand the interaction between Pt and support with a Micromeritics AutoChem II Chemisorption Analyzer. Prior to H_2-TPR experiments, the samples were pretreated in flowing Ar at 300 ℃ for 1 h and then cooled to room temperature in flowing Ar (99.999%, 50 mL/min).

After that, the sample was heated from room temperature to 800 ℃ with a heating rate of 10 ℃/min under a mixture of 10% H_2-Ar (50 mL/min). The rate of H_2 consumption was monitored by a gas chromatograph (GC) with a thermal conductivity detector (TCD).

3. Catalytic tests

A certain amount of catalyst was pretreated under hydrogen atmosphere (99.999%, 30 mL/min) at 200 ℃ for 2 h before use. The catalyst was then mixed with solvent and CAL without further exposure to air, which was subsequently transferred to a 100-mL autoclave. The hydrogenation reaction began with stirring (1000 rpm) at a designated temperature after hydrogen (2.0 MPa) was introduced into the autoclave. The reaction was stopped after a proper time, and then the products were analyzed by GC-FID (GC-2014, Shimadzu Co.) equipped with a capillary column (DM-WAX, 30 m × 0.25 mm × 0.25 μm).

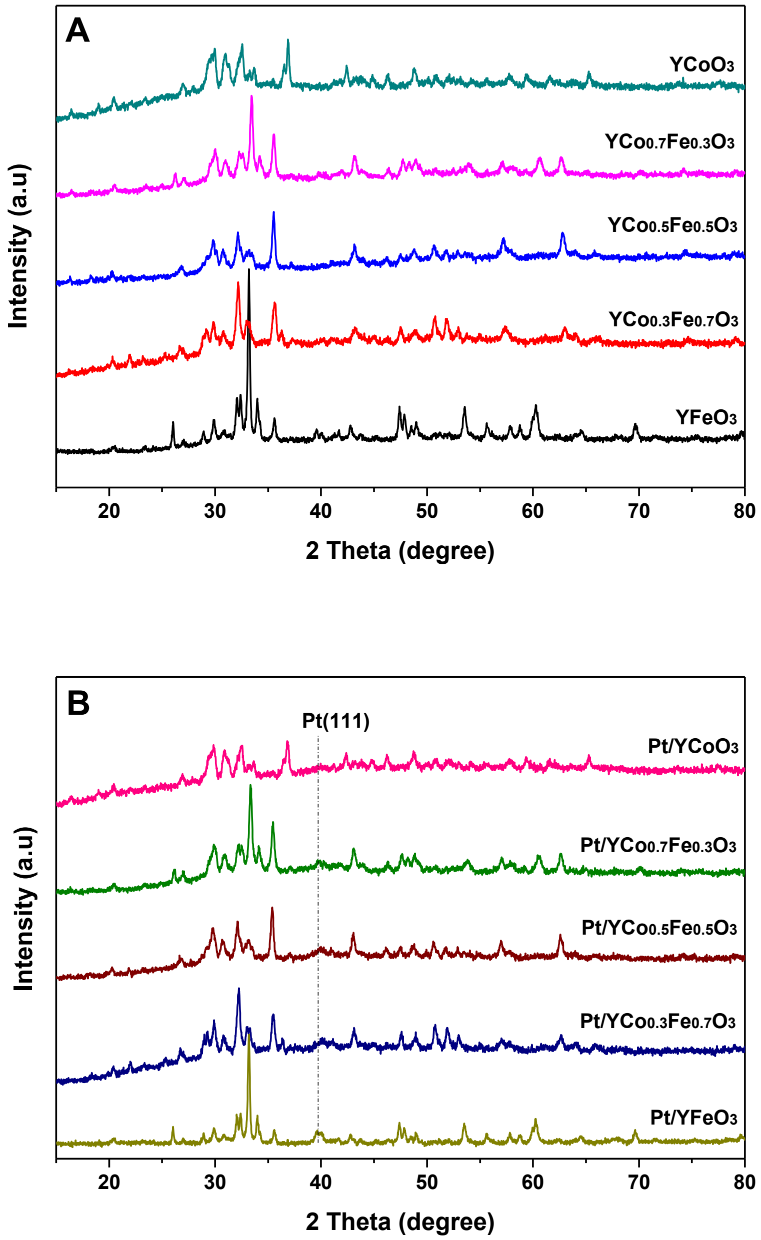


Fig. S1. Wide-angle XRD patterns of the Pt-based catalysts and $YCo_xFe_{1-x}O_3$ supports.

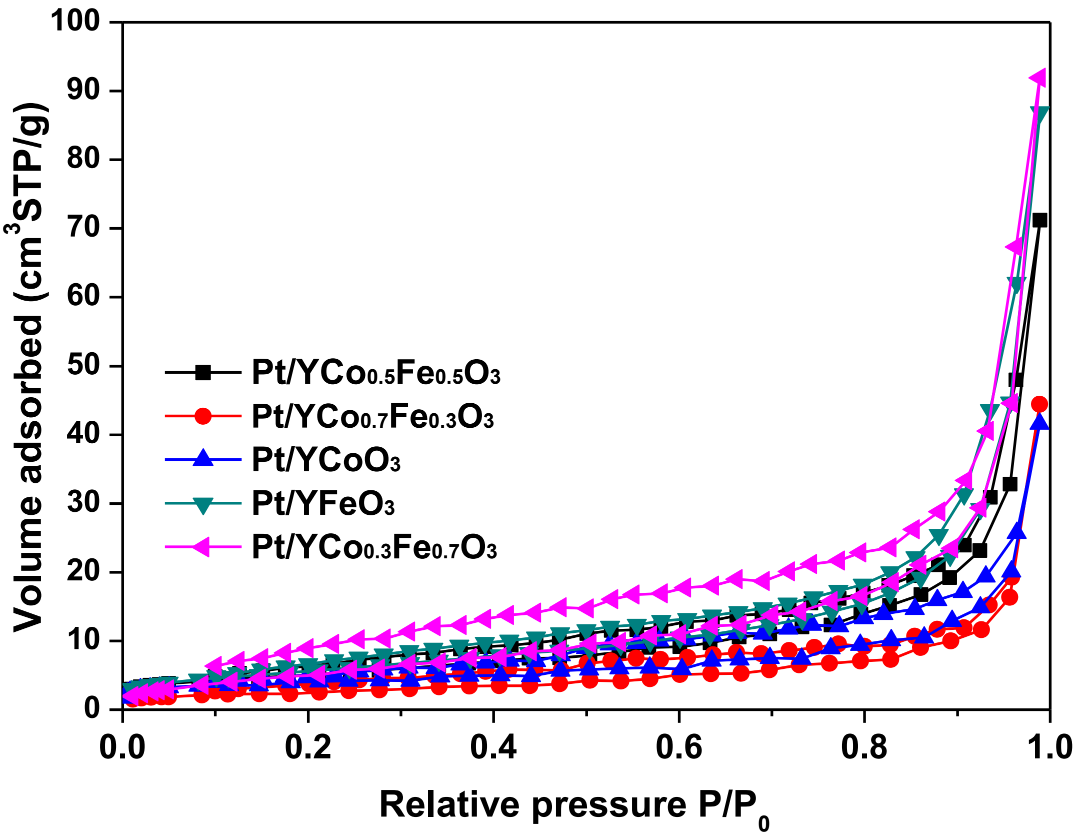


Fig. S2. N_2-physisorption isotherms of Pt/$YCo_xFe_{1-x}O_3$ catalysts.

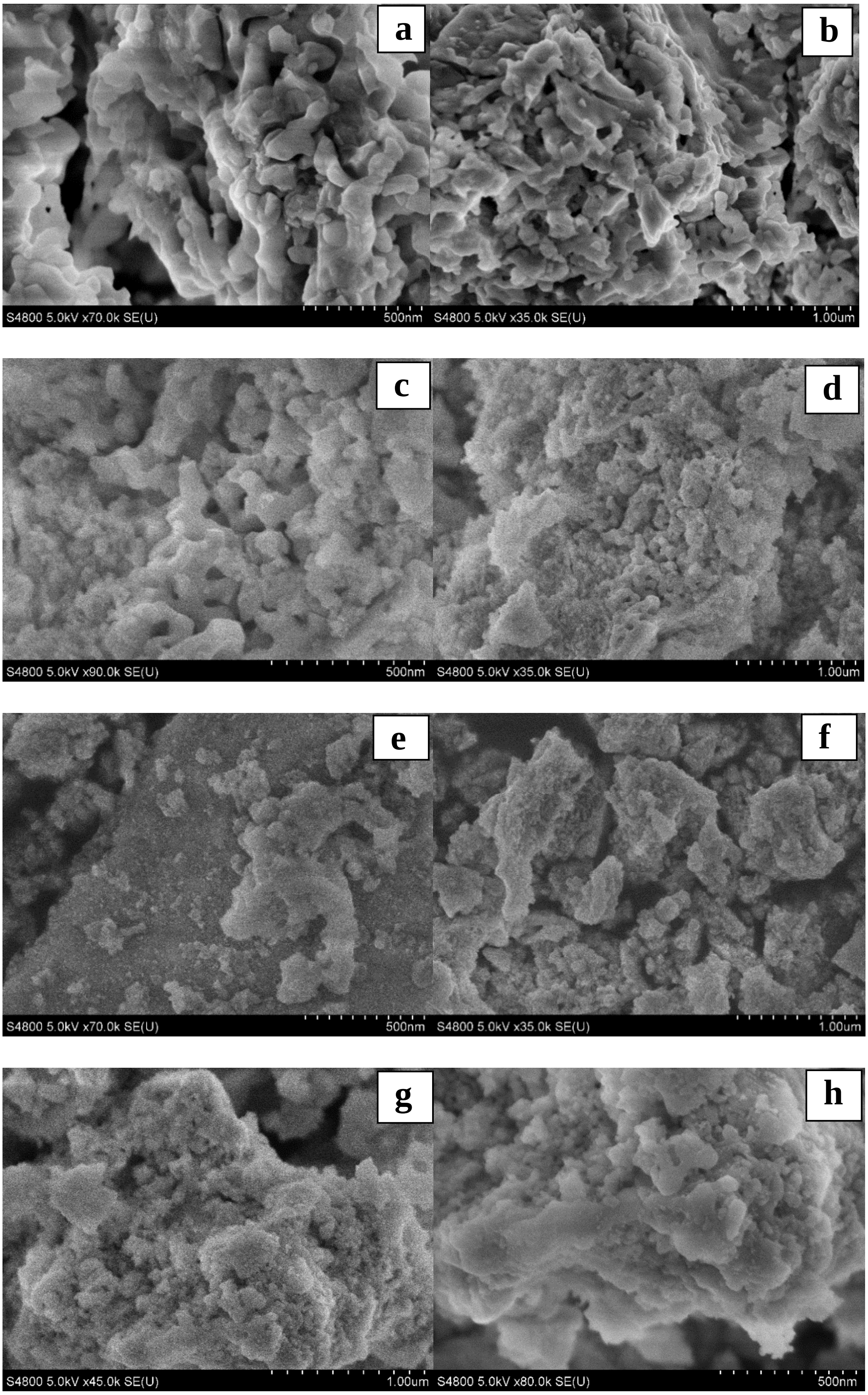


Fig. S3. SEM images of (a, b) $YCoO_3$; (c, d) $YCo_{0.3}Fe_{0.7}O_3$; (e, f) Pt/$YCo_{0.3}Fe_{0.7}O_3$-fresh and (g, h) Pt/$YCo_{0.3}Fe_{0.7}O_3$-used.

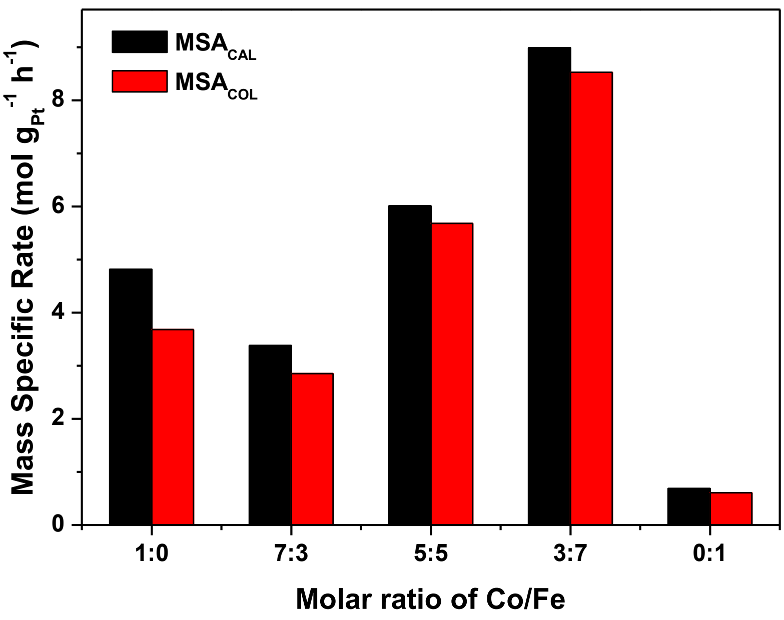
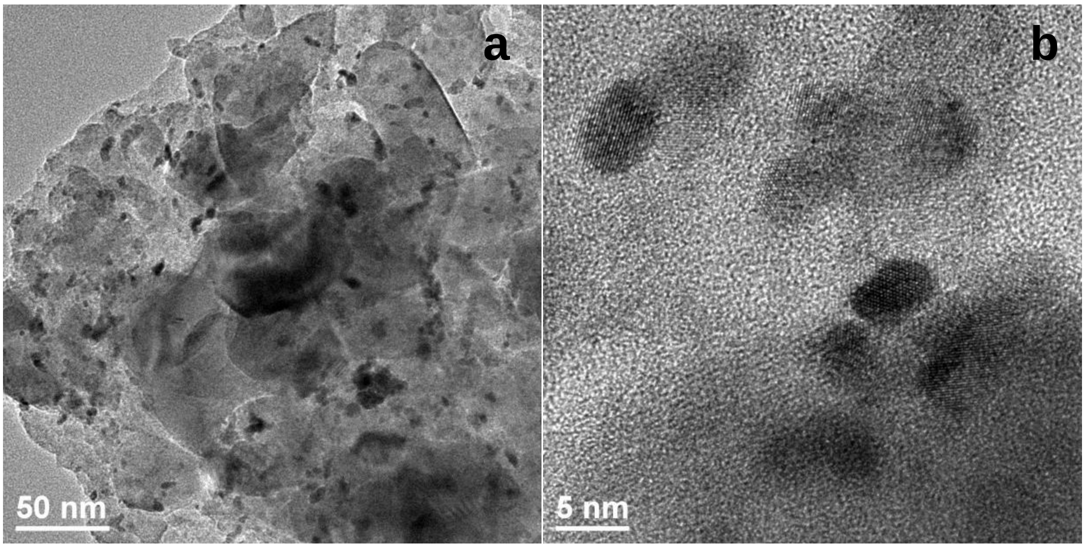


Fig. S4. The correlation of Mass Specific Rate versus the molar ratio of Co/Fe.



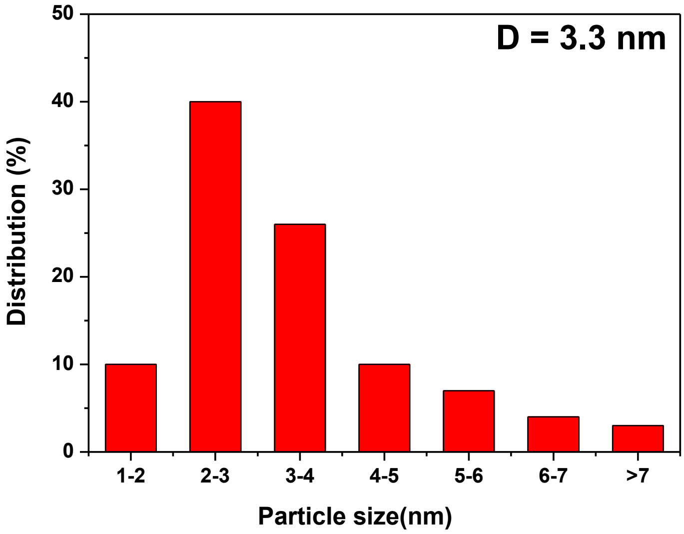


Fig. S5. TEM images and Pt particle size distribution of the used $Pt/YCo_{0.3}Fe_{0.7}O_3$ catalyst.

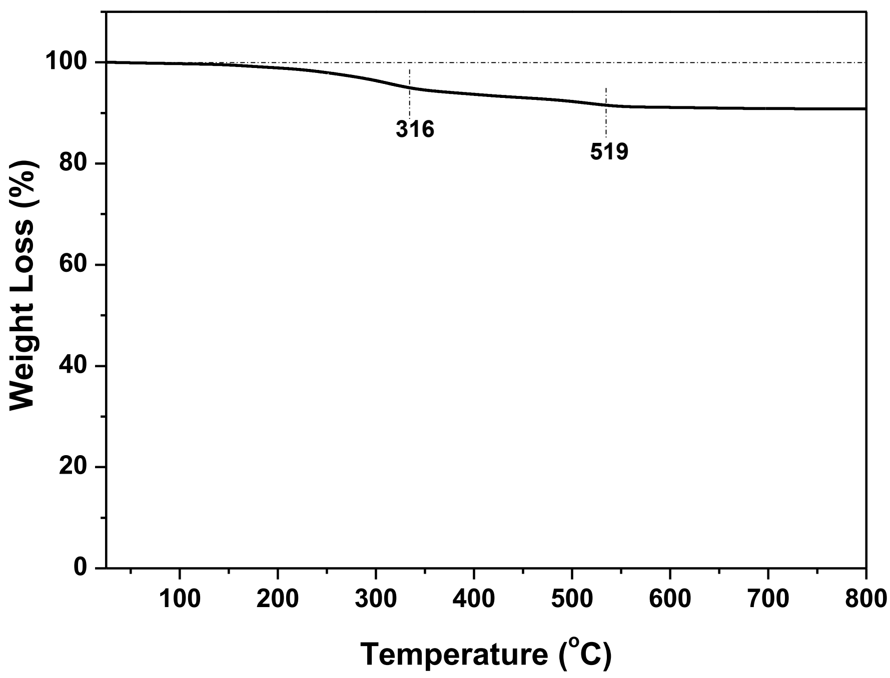


Fig. S6. TG curve of the used Pt/$YCo_{0.3}Fe_{0.7}O_3$ catalyst.

Table S1. Comparison of the Pt-based catalysts for the selective hydrogenation of CAL to yield COL.

Catalyst	T (℃)	P_{H2} (MPa)	t (h)	Conv. (%)	COL Sel. (%)	TOF (h^{-1})	MSR [a] (mol/(g·h))	Ref.
Pt-1a/n-Al_2O_3	30	1.0	3	99.0	91.0	3746	-	3
$PtFe_{0.25}$/15AS	90	2.0	1	77.4	76.9	5544	13.9	5
$PtFe_{0.25}$/15TS	90	2.0	0.5	68.0	86.4	11016	12.2	6
Pt/SiC-C	25	2.0	1	84.9	80.0	2446	-	7
Pt/TiO_2-SiO_2	80	4.0	0.5	98.8	91.0	-	3.9×10^{-2}	8
Pt/$CeZrO_2$-1.5	60	1.0	0.5	95.0	94.0	10423	-	9
Pt/3DHPC	70	2.0	1	92.7	91.1	1554	-	10
Pt-Mo_2N/SBA-15	80	1.0	2	70.8	76.9	521	-	13
PtFe NWs	70	0.1	2.5	95.7	95.5	100	-	14
Pt_3Fe/CNT	60	2.0	0.5	62.1	97.2	1200	-	15
MIL-101@Pt@FeP-CMP^{sponge}	RT	3.0	0.25	97.6	97.3	1516	-	19
Pt/FeFe-LDH	110	1.0	2	90.0	92.0	1026	-	21
Co-Pt/C-0.6	80	2.0	2	100	99.0	15084	-	24
Pt/$YCo_{0.3}Fe_{0.7}O_3$	90	2.0	0.5	98.9	94.9	15163	31.1	This study

[a]: MSR means mass-specific rate, defined as the converted CAL or formed COL per gram of Pt per hour

References:

[3] H. Liu, Q. Mei, S. Li, Y. Yang, Y. Wang, H. Liu, L. Zheng, P. An, J. Zhang, B. Han, Chem. Commun., 2018, 54, 908.

[5] H. Pan, J. Li, J. Lu, G. Wang, W. Xie, P. Wu, X. Li, J. Catal., 2017, 354, 24-36.

[6] Y. Xue, R. Yao, J. Li, G. Wang, P. Wu, X. Li, Catal. Sci. Technol., 2017, 7, 6112-6123.

[7] R. Yao, RSC Adv., 2016, 6,

[8] Q. Wu, C. Zhang, B. Zhang, X. Li, Z. Ying, T. Liu, W. Lin, Y. Yu, H. Cheng, F. Zhao, J. Colloid Interf. Sci., 2016, 463, 75-82.

[9] S. Wei, Y. Zhao, G. Fan, L. Yang, Li, F. Li, Chem. Eng. J., 2017, 322, 234-245.

[10]. D. Hu, W. Fan, Z. Liu, L. Li, ChemCatChem, 2018, 10, 779-788.

[13] D. Wang, Y. Zhu, C. Tian, L. Wang, W. Zhou, Y. Dong, Q. Han, Y. Liu, F. Yuan, H. Fu, Catal. Sci. Techol., 2016, 6, 2403-2412.

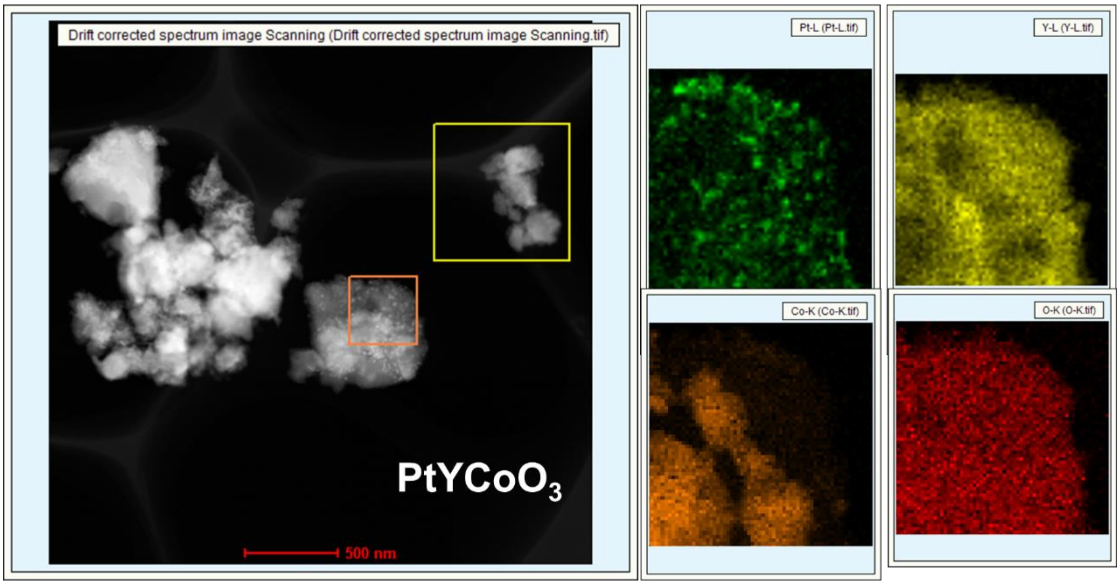
[14] S. Bai, L. Bu, Q. Shao, X. Zhu, X. Huang, J. Am. Chem. Soc., 2018, 140, 8384-8387.

[15] Y. Dai, X. Gao, X. Chu, C. Jiang, Y. Yao, Z. Guo, C. Zhou, C. Wang, H. Wang, Y. Yang, J. Catal., 2018, 364, 192-203.

[19] K. Yuan, T. Song, D. Wang, X. Zhang, X. Gao, Y. Zou, H. Dong, Z. Tang, W. Hu, Angew. Chem. Int. Ed., 2018, 57, 5708-5713.

[21] Y. Zhang, S. Wei, Y. Lin, G. Fan, F. Li, ACS Omega, 2018, 3, 12778-12787.

[24] C. Li, C. Ke, R. Han, G. Fan, L. Yang, F. Li, Mol. Catal., 2018, 455, 78-87.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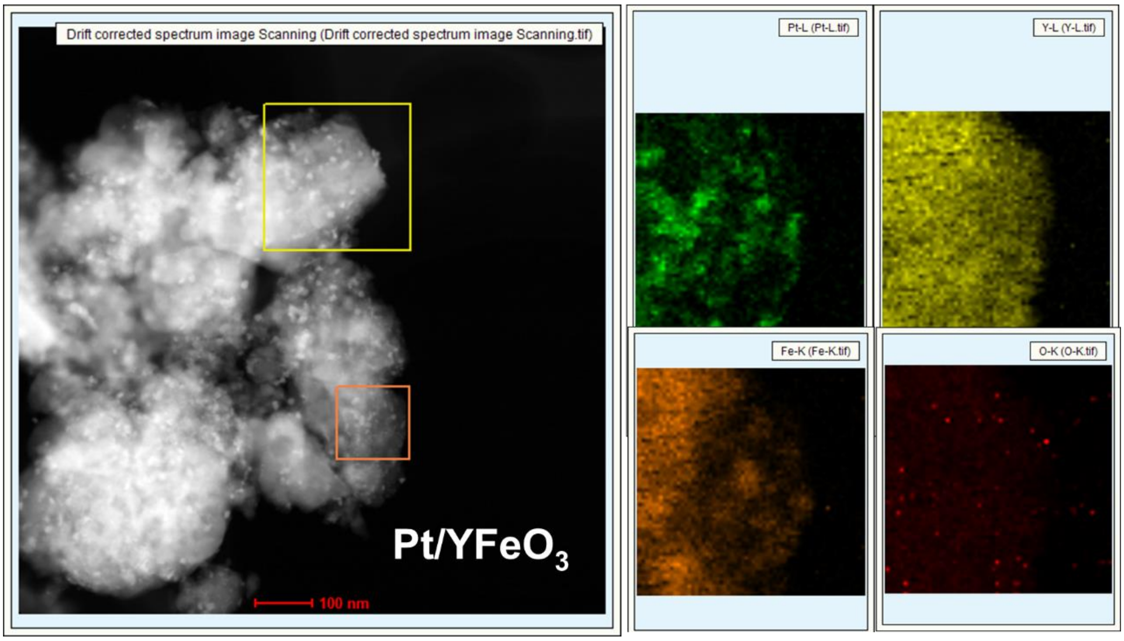
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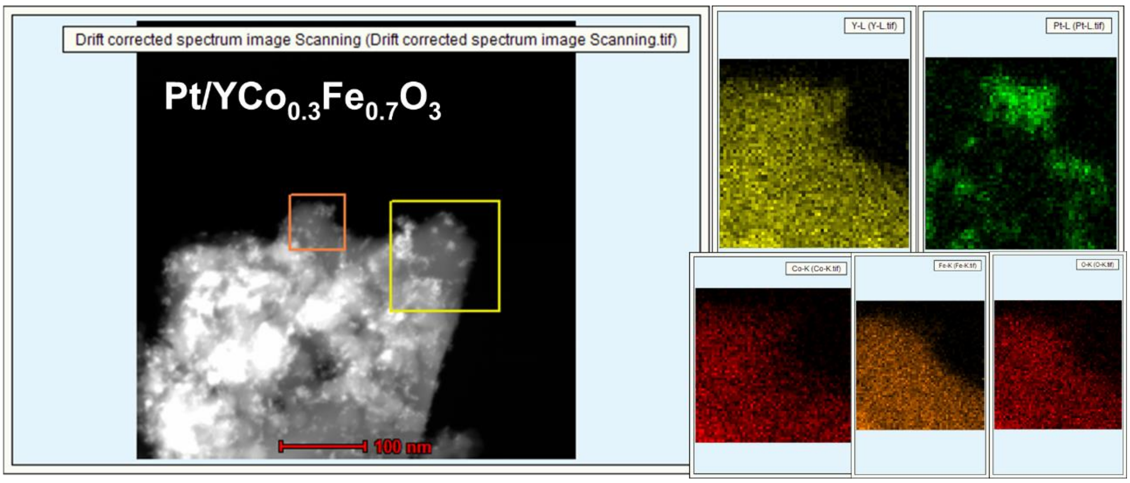
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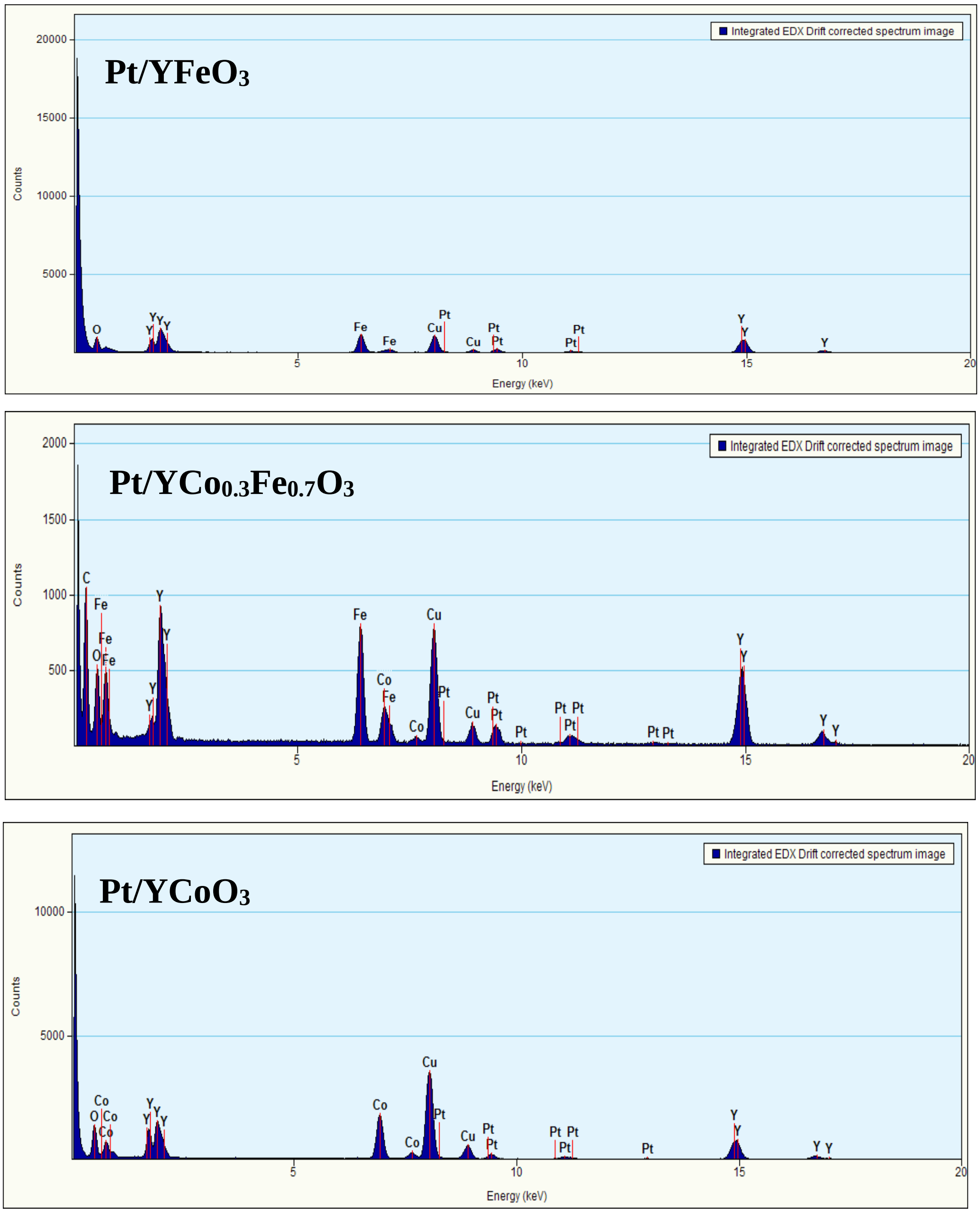

Fig. S7. HAADF-STEM images and STEM-EDS elemental mapping images for the area enclosed by the orange square for Pt/$YCoO_3$; Pt/$YFeO_3$ and Pt/$YCo_{0.3}Fe_{0.7}O_3$.

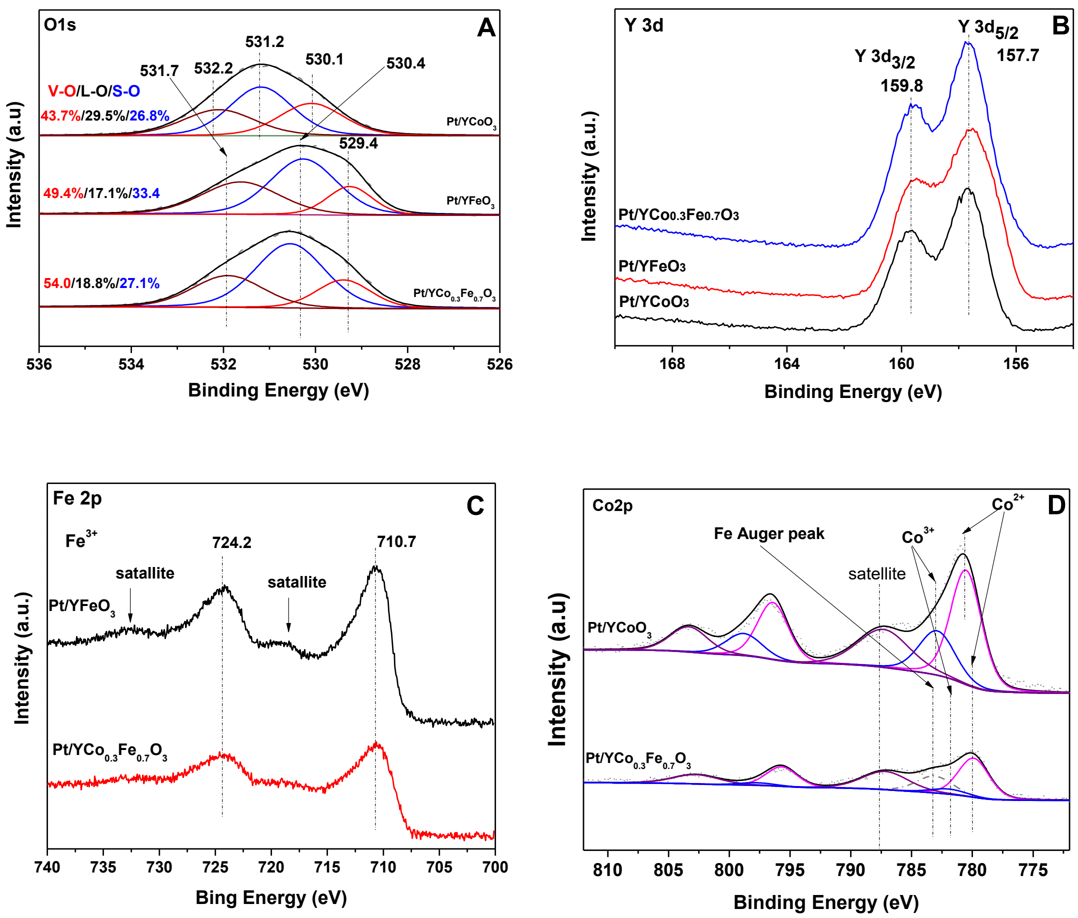

Fig. S8. XPS spectra of the Pt/$YCo_xFe_{1-x}O_3$ catalyst

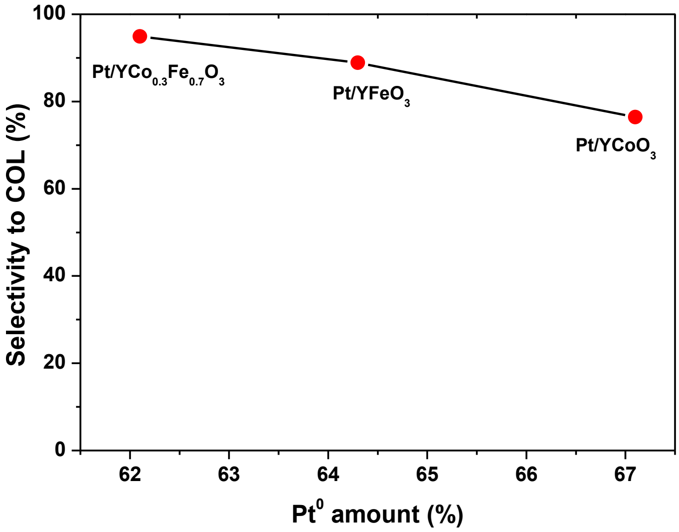

Fig. S9. The correlation of COL selectivity versus Pt^0 amount on the $Pt/YCo_xFe_{1-x}O_3$ catalyst according to XPS results.