Electronic Supplementary Information

Hydrogenolysis of 5-hydroxymethylfurfural to 2,5-dimethylfuran over supported Pt-Co bimetallic catalysts under mild conditions

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Experimental details

1. Catalysts preparation

Platinum (Pt) atomic layer deposition (ALD) was carried out in a fluidized bed reactor at 300 °C, and the two precursors were (methylcyclopentadienyl)trimethyl platinum [(MeCp)$PtMe_3$] and oxygen (O_2), as described previously [1]. Briefly, in a typical run, certain amount of substrates (multi-walled carbon nanotubes, silica gel, or γ-Al_2O_3) were added into the reactor. The particle substrates were fully fluidized with a gas flow rate controlled by mass flow controllers. N_2 was used as flush gas to remove unreacted precursors and any byproducts during the reaction. A typical half coating cycle used the following sequence: precursor dose, N_2 purge, and evacuation. This sequence was repeated alternatively for both precursors.

Co nanoparticles (NPs) were deposited on substrates via ALD following the similar procedure as Pt ALD, but using cobaltocene ($CoCp_2$) and hydrogen (H_2) as precursors at 300 °C. The solid precursor $CoCp_2$ was loaded in a heated bubbler and carried by N_2. A typical Co deposition cycle used the following steps: $CoCp_2$ dose, N_2 purge, and evacuation; H_2 dose, N_2 purge, and evacuation.

Al_2O_3 ALD was performed following the similar procedure as mentioned above, but using trimethylaluminium (TMA) and deionized water (H_2O) as precursors at 177 ºC. A typical coating cycle contained the following steps: TMA dose, N_2 purge, and evacuation; H_2O dose, N_2 purge, and evacuation.

2. N_2 adsorption-desorption measurements

Nitrogen adsorption and desorption isotherms of substrates and catalysts were obtained at -196 ºC. The surface area and the total pore volume of the samples were calculated using the Brunauer–Emmett–Teller (BET) method in a relative pressure range of 0.05-0.25 and the adsorption quantity at a relative pressure of $P/P_0 = 0.99$, respectively. The pore size distributions were derived from the desorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) method.

3. TEM analysis

The supported Pt, Pt-Co, and Co NPs were visualized with a FEI Tecnai F20 field emission gun high-resolution TEM. At least 200 NPs on MWCNTs were measured to get an average particle size. The high-resolution TEM (HRTEM) images of 25c-Co/3c-Pt/MWCNTs catalyst were

obtained by a JEOL JEM-2100F TEM operated at 200 kV in Argonne National Laboratory.

4. TPR analysis

The reduction properties of the supported Pt, Pt-Co, Co, and Pt-Co/Al_2O_3-based catalysts were analyzed by H_2-TPR. The reaction temperature was programmed to rise at a heating rate of 10 ºC/min up to 1000 ºC and the flow rate was 20 mL/min of 10 mol% H_2/Ar gas. The consumption amount of H_2 during the H_2-TPR was analyzed and measured by a thermal conductivity detector (TCD, Micromeritics Autochem Ⅱ 2920).

5. CO-chemisorption

CO-chemisorption was performed using a Micromeritics Autochem Ⅱ 2920 to investigate the Pt particle size and dispersion of Pt monometallic catalysts. The catalysts were reduced at 350 ºC for 30 min and degassed at the same temperature in pure He for 90 min. The CO adsorption isotherms were obtained at 50 °C and the stoichiometry of Pt:CO was assumed to be 1:1.

6. XPS analysis

XPS spectra of Pt, Co, and Pt-Co based catalysts were recorded with a Kratos Axis 165 X-ray photoelectron spectrometer using a monochromatic Al Kα radiation (hν= 1486.6eV), at a take-off angle of 0°. The survey scan spectra, Pt 4f, and Co 2p core level spectra were recorded using a pass energy of 160 eV, 20 eV, and 20 eV, respectively. All binding energy values were corrected to C 1s signal (284.5 eV).

Reference

[1] Jiang, C. and X. Liang, Catalytic hydrogen transfer of ketones over atomic layer deposited highly-dispersed platinum nanoparticles supported on multi-walled carbon nanotubes. *Catalysis Communications*, 2014. **46**: p. 41-45.

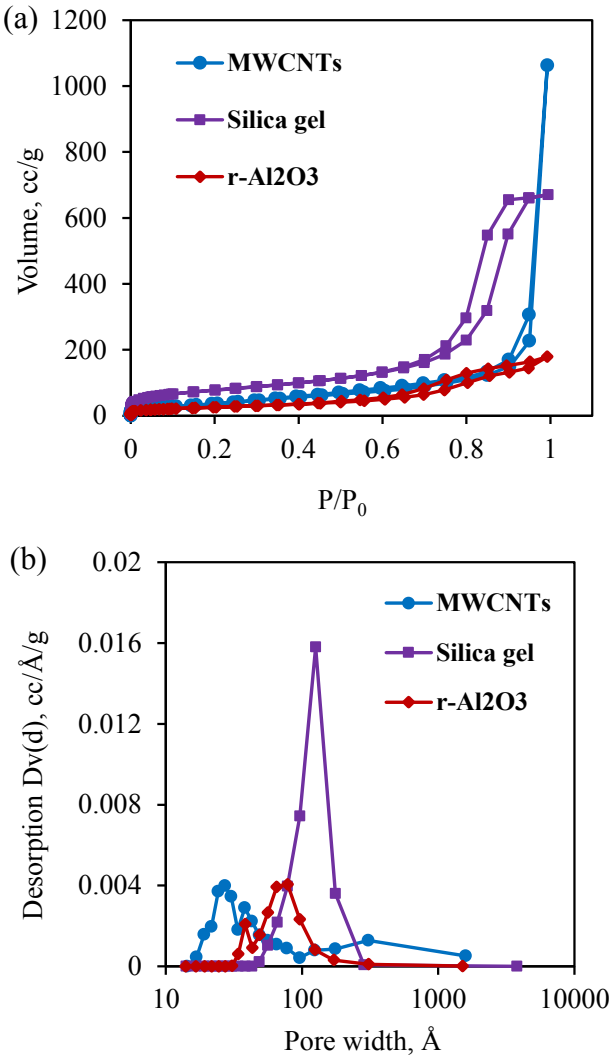

Figure S1. (a) Nitrogen adsorption and desorption isotherms, and (b) pore size distributions of MWCNTs, silica gel, and γ-Al_2O_3.

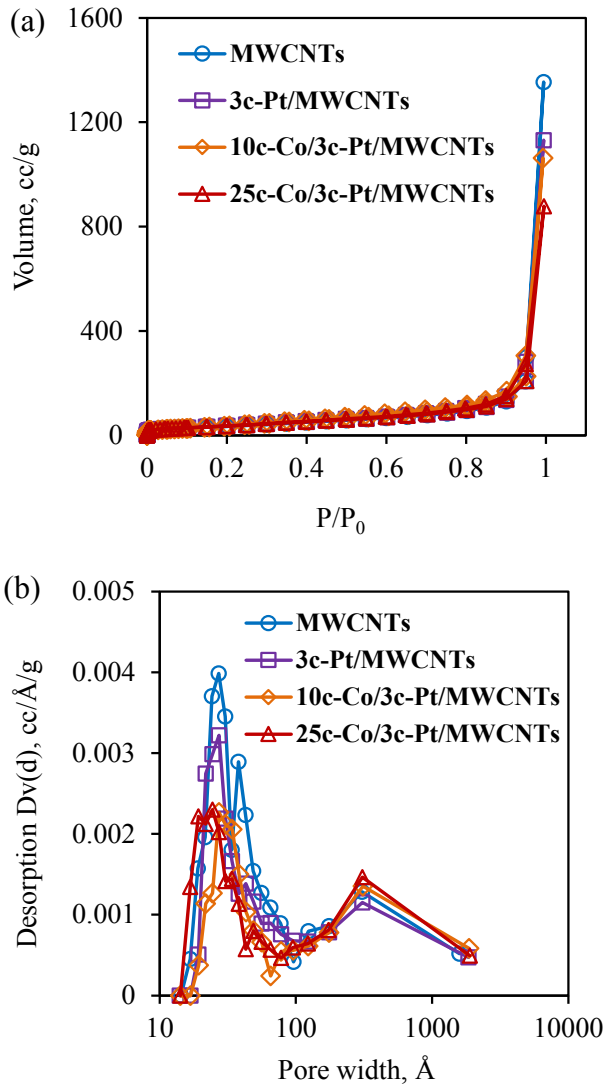

Figure S2. (a) Nitrogen adsorption and desorption isotherms, and (b) pore size distributions of MWCNTs and MWCNTs-supported catalysts.

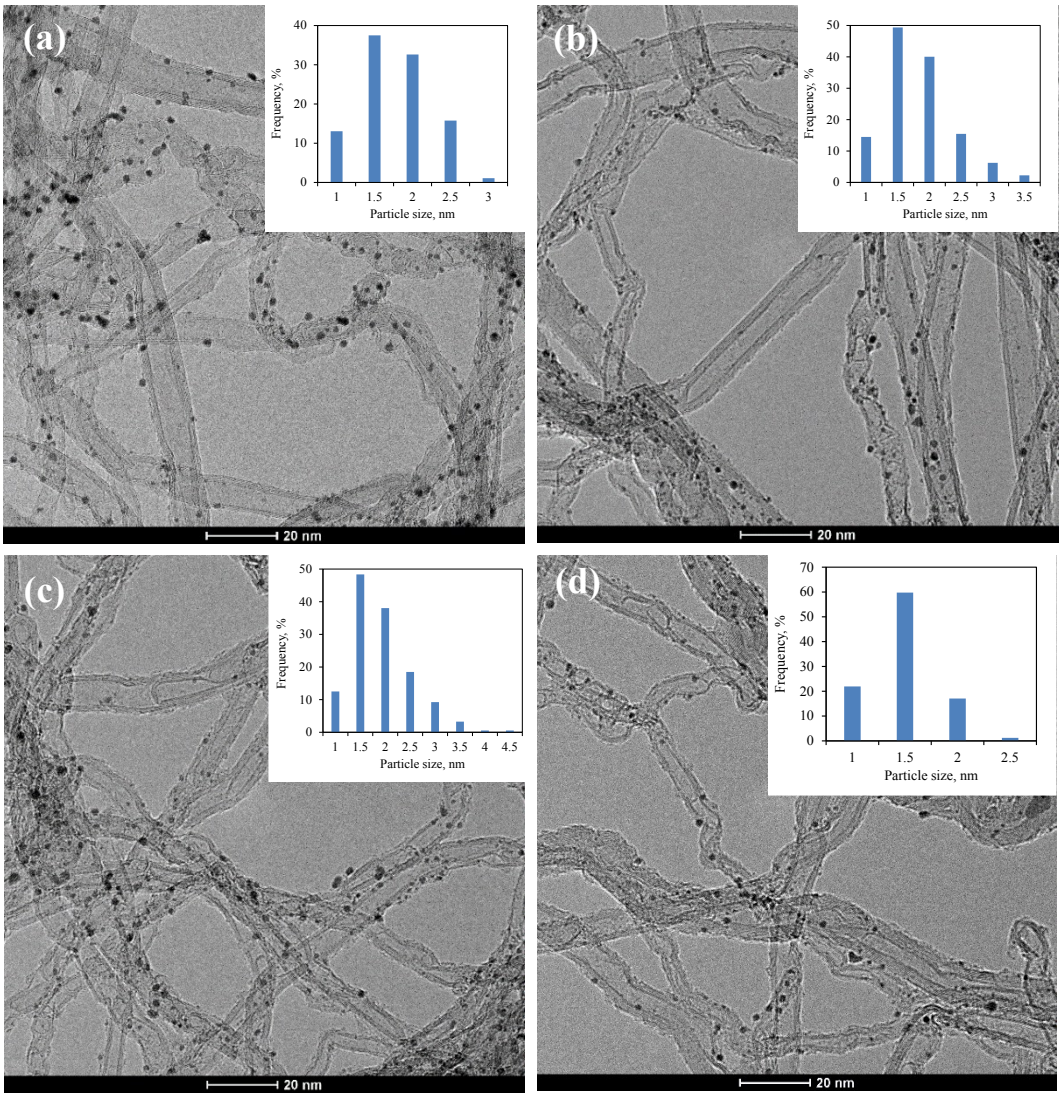

Figure S3. TEM images of (a) 3c-Pt/MWCNTs, (b) 10c-Co/3c-Pt/MWCNTs, (c) 25c-Co/3c-Pt/MWCNTs, and (d) 15c-Co/MWCNTs. The *inset* figures show the size distributions of Pt, Pt-Co, or Co nanoparticles.

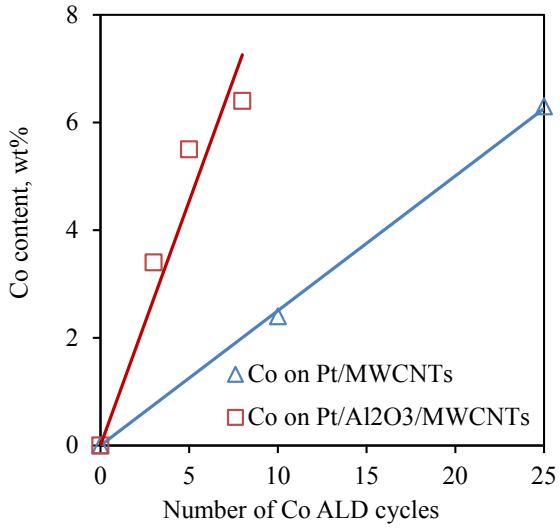

Figure S4. Co content (based on ICP-AES) of Pt-Co bimetallic catalysts versus the number of Co ALD cycles.

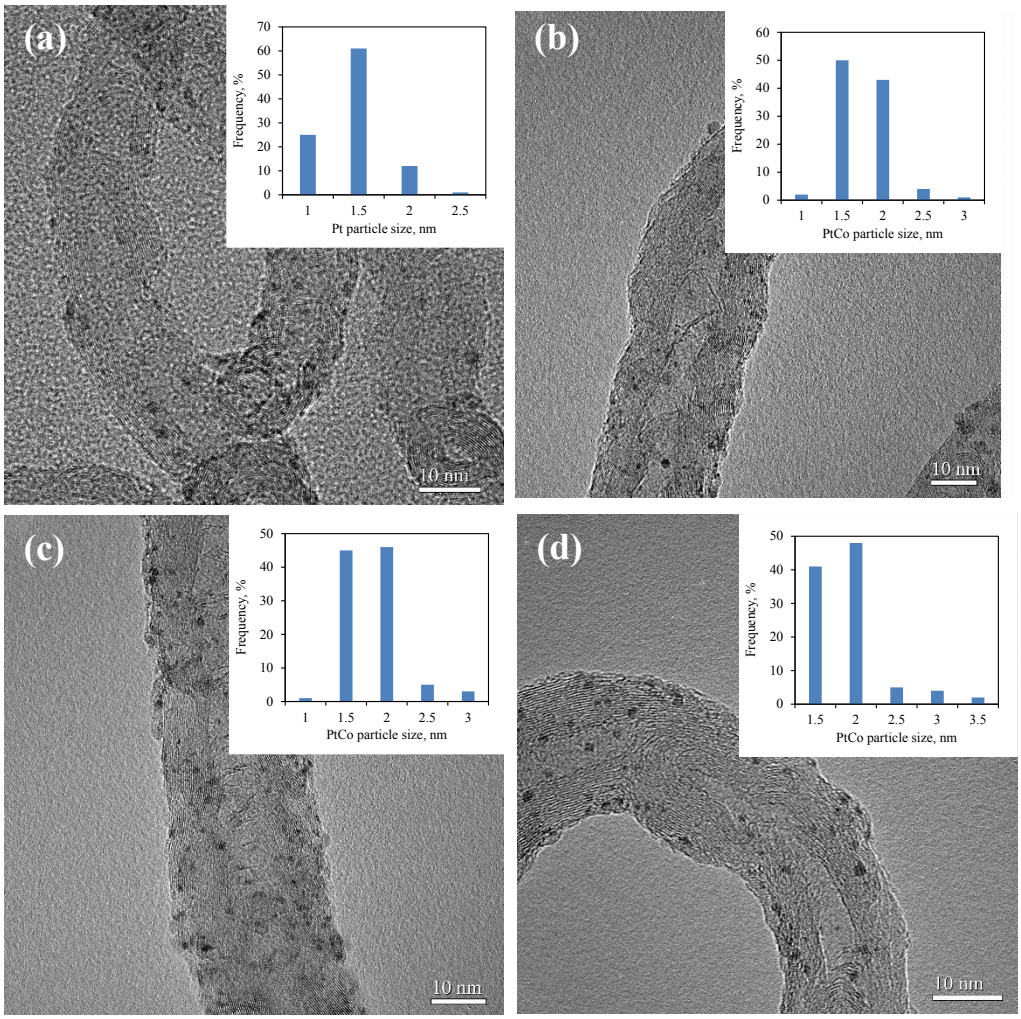

Figure S5. TEM images of (a) 2c-Pt/5c-Al_2O_3/MWCNTs, (b) 3c-Co/2c-Pt/5c-Al_2O_3/MWCNTs, (c) 5c-Co/2c-Pt/5c-Al_2O_3/MWCNTs, and (d) 8c-Co/2c-Pt/5c-Al_2O_3/MWCNTs. The *inset* figures show the size distributions of Pt or Pt-Co nanoparticles.

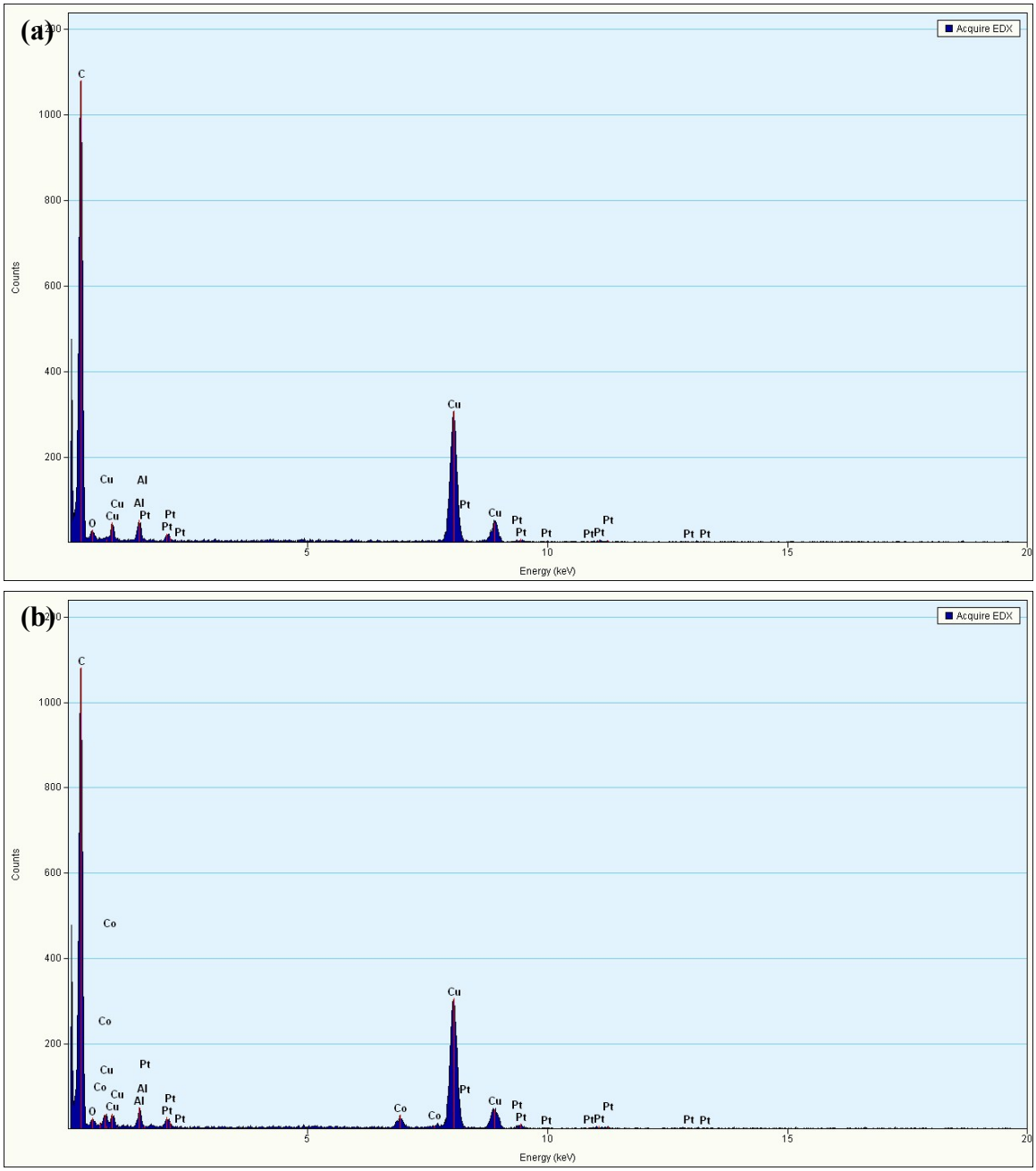

Figure S6. EDS spectra of (a) 2c-Pt/5c-Al_2O_3/MWCNTs catalyst in Figure S5a, and (b) 5c-Co/2c-Pt/5c-Al_2O_3/MWCNTs catalyst in Figure S5c.

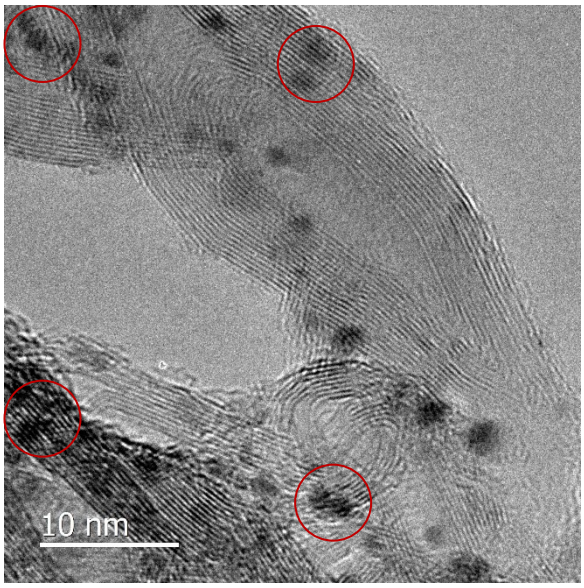

Figure S7. HRTEM image of 5c-Co/2c-Pt/5c-Al_2O_3/MWCNTs catalyst.

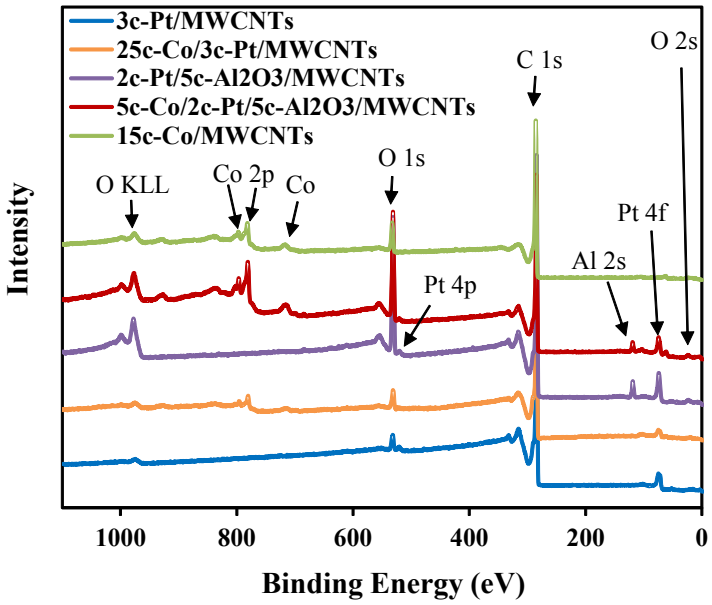

Figure S8. XPS spectra of survey scan for different catalysts.

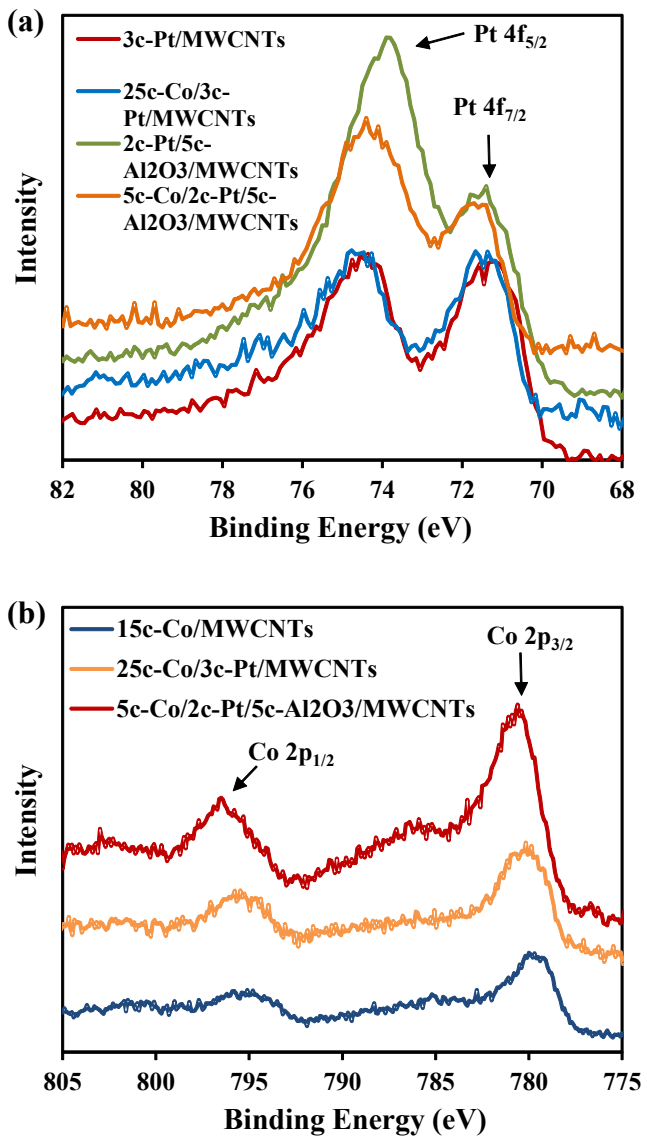

Figure S9. High resolution XPS spectra of (a) Pt 4f and (b) Co 2p of different catalysts.

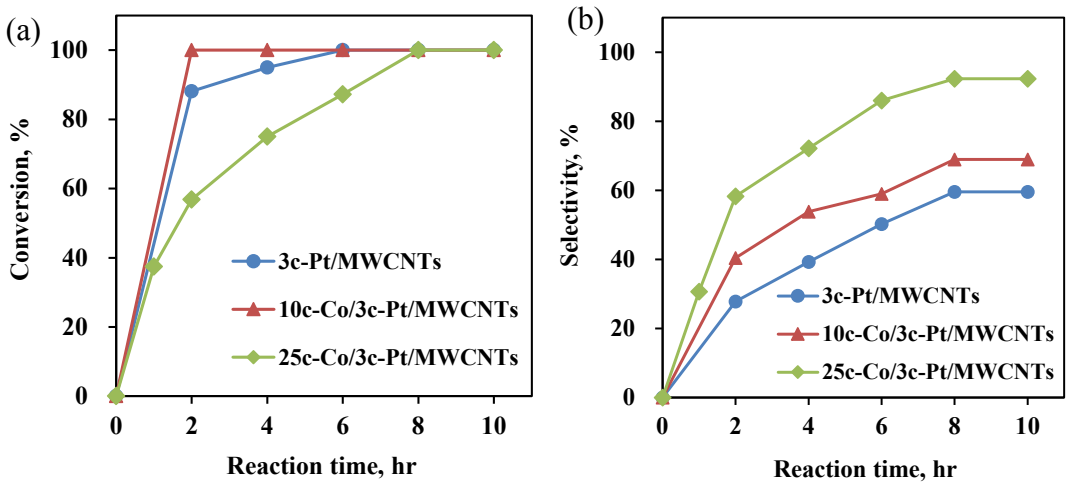

Figure S10. (a) Conversion of HMF and (b) selectivity to DMF versus reaction time for Pt and Pt-Co catalysts at 180 ºC.

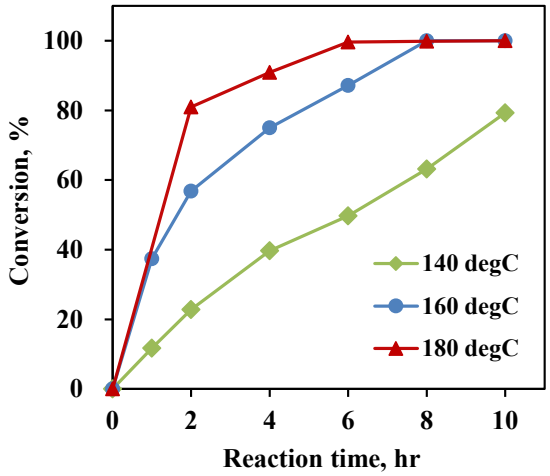

Figure S11. Conversion of HMF versus reaction time for 25c-Co/3c-Pt/MWCNTs catalyst at different reaction temperatures.

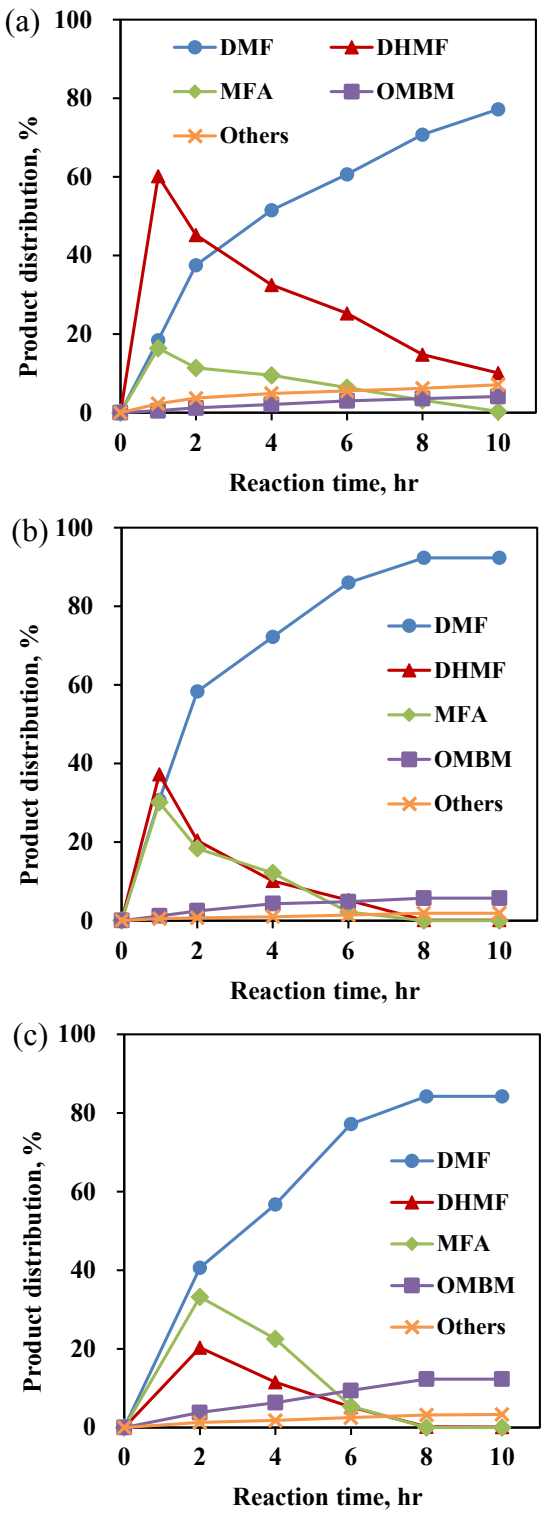

Figure S12. Product distribution versus reaction time for 25c-Co/3c-Pt/MWCNTs catalyst at reaction temperature of (a) 140 ºC, (b) 160 ºC, (c) 180 ºC.

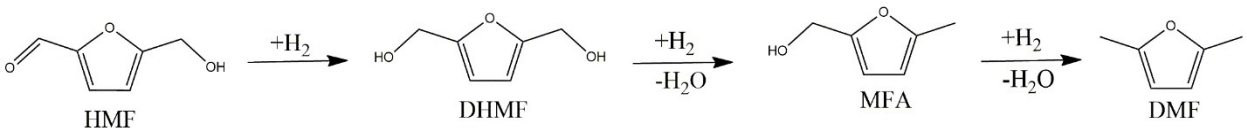

Figure S13. The main reaction pathway of HMF hydrogenolysis reaction.

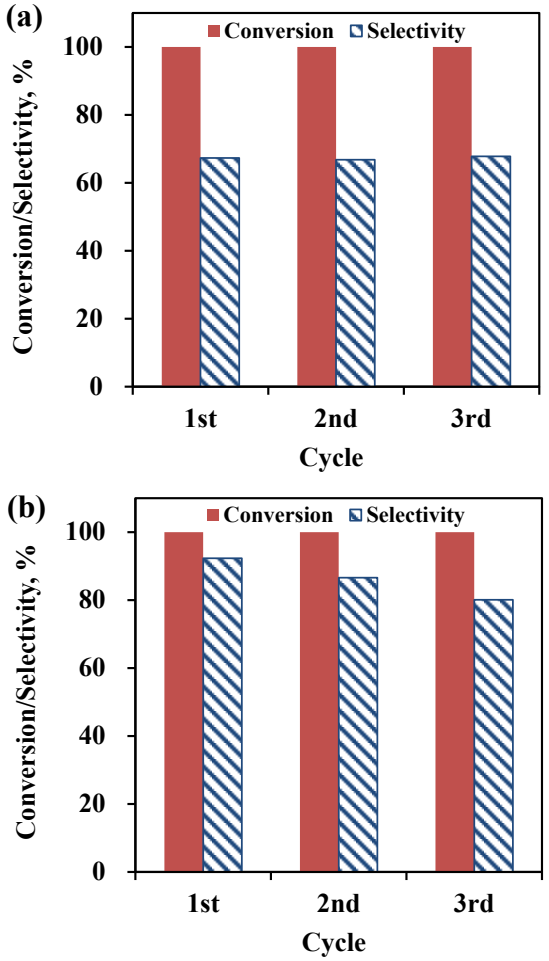

Figure S14. The conversion of HMF and the selectivity to DMF in the cycling tests of HMF hydrogenolysis over (a) 3c-Pt/MWCNTs, and (b) 25c-Co/3c-Pt/MWCNTs catalysts. Reaction conditions: 4.35 mg Pt, 0.5 g HMF, 30 mL 1-butanol, P_{H2} = 10 bar, 160 ºC, 500 rpm, and 8 hr.

Table S1. Properties of silica gel and γ-Al_2O_3 supported catalysts.

Sample	BET surface area, m^2/g	Pore volume, cm^3/g	Pt, wt.%	Pt average particle size, nm[a]	Pt dispersion, %
Silica gel	272	0.9	4.0	1.8	62
γ-Al_2O_3	91	0.3	2.4	1.3	83

[a] The Pt particle size was obtained according to CO-chemisorption results.