

Facile one-pot synthesis of Pt nanoparticles@SBA-15: A highly active and stable material for catalytic applications

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Supplementary information

Experimental

Synthesis of Pt@SBA-15: 0.5 g of P123 (triblock copolymer poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), (EO₂₀PO₇₀EO₂₀) was first dissolved in 7.5 mL of H₂O and 15 mL of 2M HCl solution, the mixture was stirred at room temperature for 24 hs. To this solution the desired amount of Pt colloid was added. The Pt colloid was freshly prepared by an immobilization method, where the H₂PtCl₆ (0.01522M) was first protected by 3 mL of 1 wt.% PVA, then reduced by the desired amount of 0.1M NaBH₄ solution. After the addition of the Pt colloid, 0.21 g of tetraethoxysilane (TEOS) was immediately added, and the solution was kept for stirring for another 24 hs. The resulting solution was then transferred to a 50 mL Teflon-lined autoclave and thermally hydrolyzed at 100 °C for 24 hs. Finally, the product was washed, dried and calcined in static air at 500 °C for 6 hs (heating rate of 1 °C/min).

Characterization of Pt@SBA-15: XRD patterns (WAXS and SAXS) were obtained on a Bruker D8 Advance X-ray diffractometer using Cu K α ₁ irradiation. Transmission electron microscopy (TEM) studies were performed on a FEI Tecnai G² 20 S-TWIN instrument (200 keV) equipped with a GATAN MS794 P CCD-Kamera, using carbon-coated copper grids (the specimens were loaded directly on the copper grids; no solvent dispersion was used). N₂ sorption isotherms were determined at liquid nitrogen temperature (-196 °C) with an Autosorb-1 apparatus. The sample was degassed at 150 °C overnight before the measurement. ICP analysis was carried out on a Perkin-Elmer 3300DV ICP.

Catalytic CO oxidation: The reaction was performed in a continuous-flow reactor. The catalyst (200 mg) was placed on a quartz (silica) wool bed in a silica tube, which was inserted into a vertical furnace equipped with a temperature controller. Reactant gas (5% CO, 10% O₂ in Helium) was passed through the catalytic bed at a total flow rate of 50 ml min⁻¹. Some tests carried out previously showed that the mass transport limitations could be neglected under the present conditions. The composition of the outgoing gas stream was determined at the exit of the tube using a GC equipped with a thermal conductivity detector (TCD). The conversion was calculated based on the change of CO concentration at the inlet and outlet.

Catalytic cyclooctadiene (COD) hydrogenation: the reaction was done in 100 mL five-neck flask with water jacket. Reaction conditions are: 1.0 g of catalyst, 1.13 mL COD and 60 mL heptane (used as solvent); H₂ pressure is 1.1 bars; reaction temperature is 70 °C and reaction time is 35 min. Recycle experiments was performed by first removing the used reactant, and then the catalyst was washed with heptane for 3 times (the removal of the used reactant and the washed heptane was done by a pump), after then, the reactor was refilled with fresh COD and the new reaction started. The compositions of the products were analyzed by GC. The activity was evaluated according to the initial and final cyclooctadiene concentration at each run.

Table S1: Physical properties of SBA-15 with or without the incorporation of Pt NPs

Sample	S_{BET} (m^2/g) ^a	Pore size (nm) ^b	Pore vol. (cm^3/g) ^c	S_{ext} (m^2/g) ^d	V_{micro} (cm^3/g) ^d	Pt loading (%) ^e	Pt loading (%) ^f
SBA-15	845	9.5	1.13	518	0.17	—	—
SBA-15-PVA	1132	9.5	1.41	585	0.29	—	—
0.2% Pt@SBA-15	1137	9.5	1.45	665	0.23	0.2	0.03
0.5% Pt@SBA-15	1311	9.5	1.60	737	0.26	0.5	0.10 (0.09) ^g
1.0% Pt@SBA-15	1197	9.5	1.63	685	0.241	1.0	0.25
2.0% Pt@SBA-15	1206	9.5	1.67	733	0.22	2.0	0.35

^a Surface area determined by the BET equation; ^b Pore size determined from the adsorption branch; ^c Pore volume determined at $p/p_0 = 0.99$; ^d External (mesopore) surface area and pore volume calculated by the t-plot method; ^e Pt amount calculated from the initial precursor loading; ^f Pt loading calculated by ICP analysis; ^g The value in brackets was measured on the used catalyst (“U2”, see below)

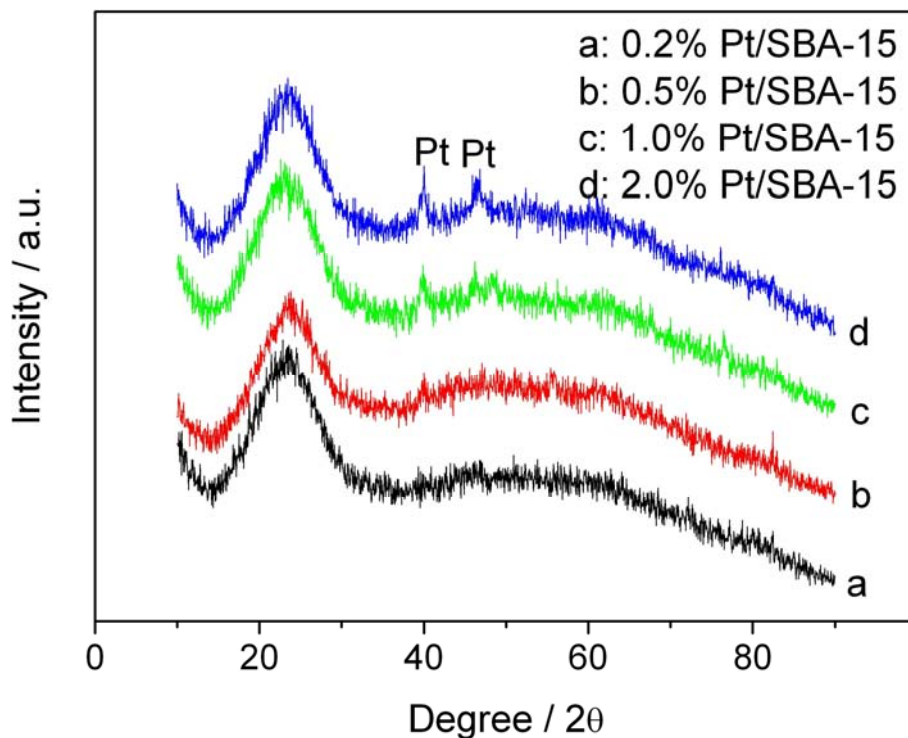


Figure S1: WAXS profiles of the Pt@SBA-15 material with different Pt loadings

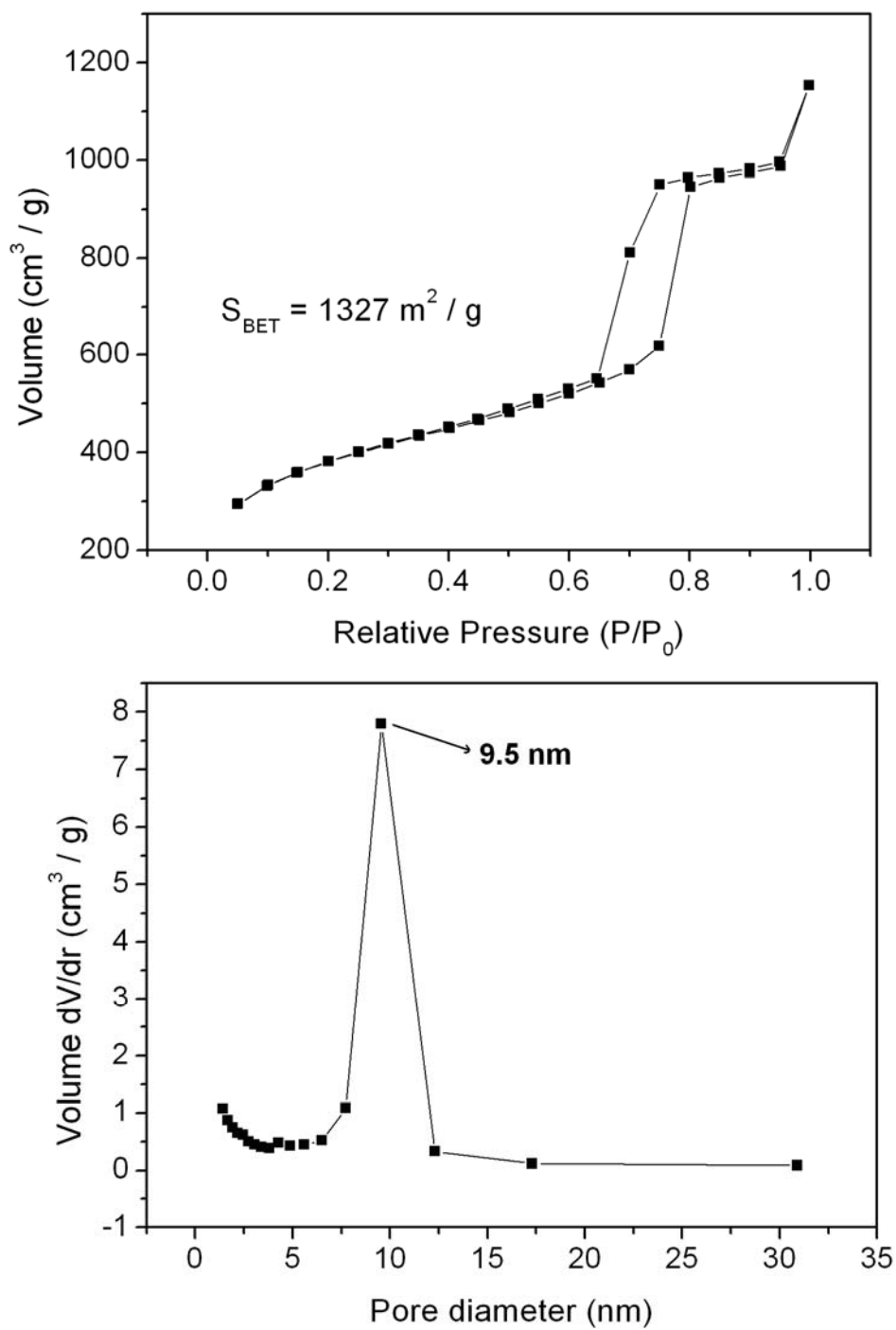


Figure S2: N₂ sorption isotherm (above) and pore size distribution (bottom) of [1.0%Au@SBA-15](#).

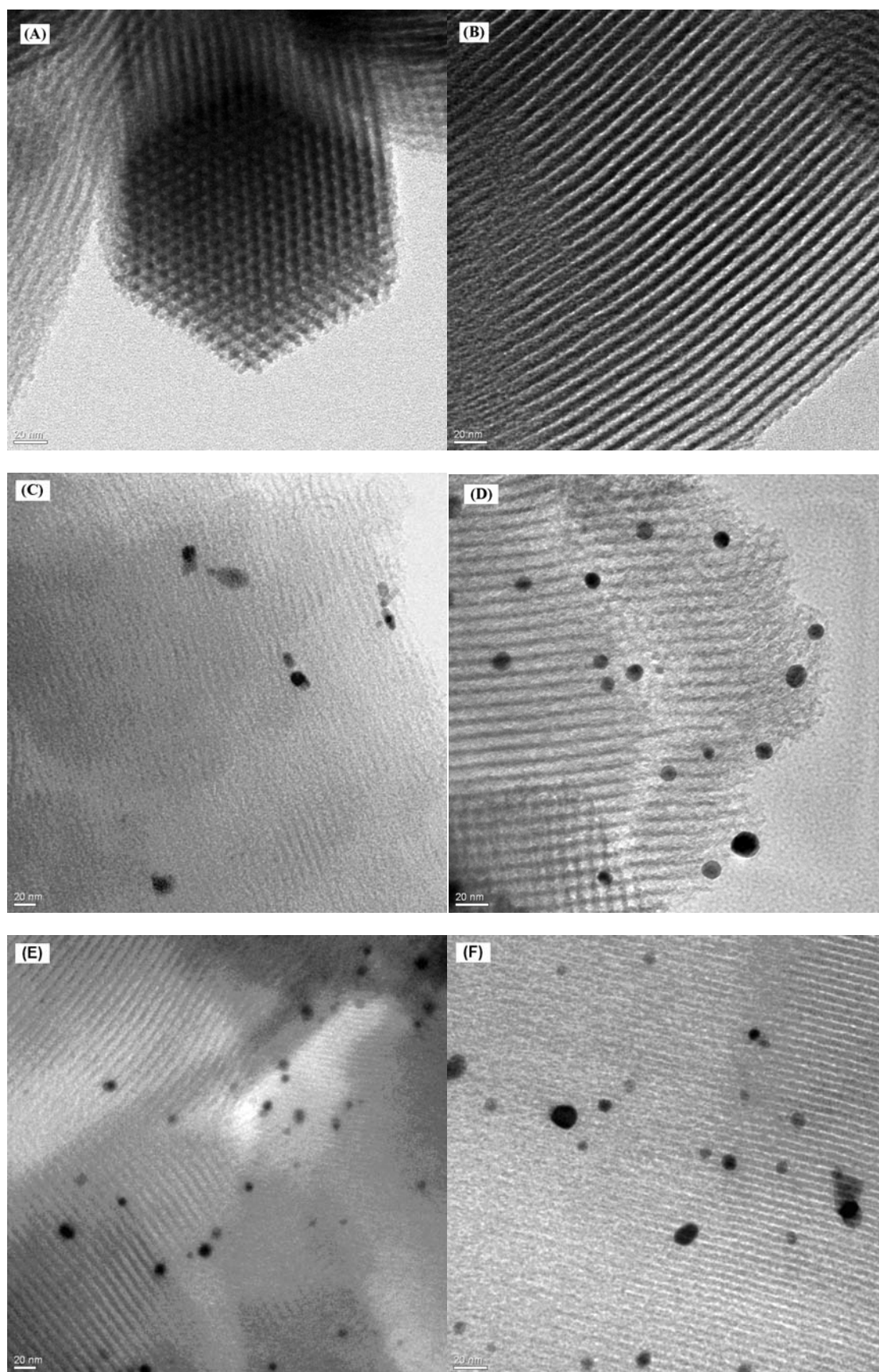


Figure S3: TEM images of (A): SBA-15; (B): SBA-15-PVA; (C): 0.2% Pt@SBA-15; (D): 0.5% Pt@SBA-15; (E): 1.0% Pt@SBA-15 and (F): 2.0% Pt@SBA-15

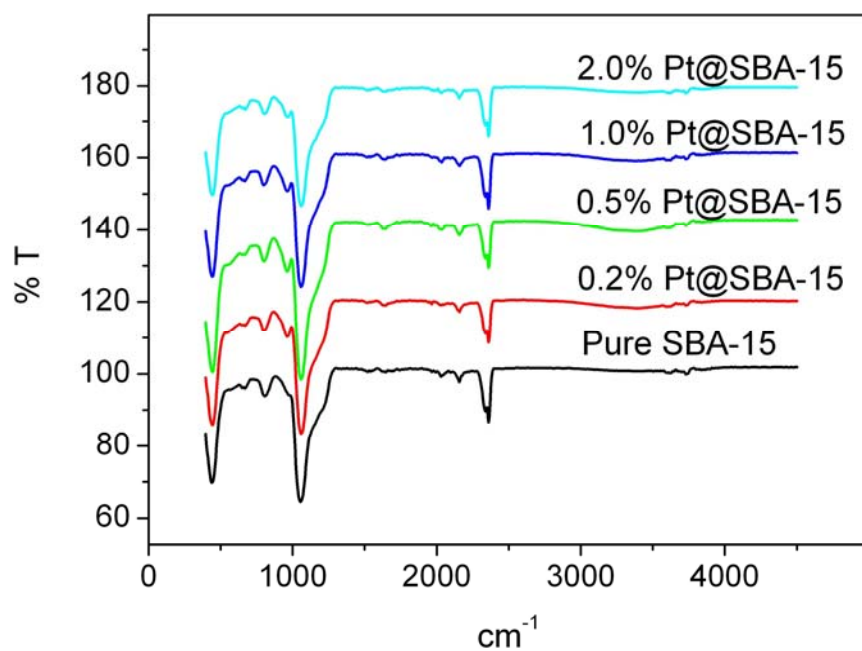


Figure S4: FTIR spectra of the pure SBA-15 and that incorporated with different amounts of Pt.

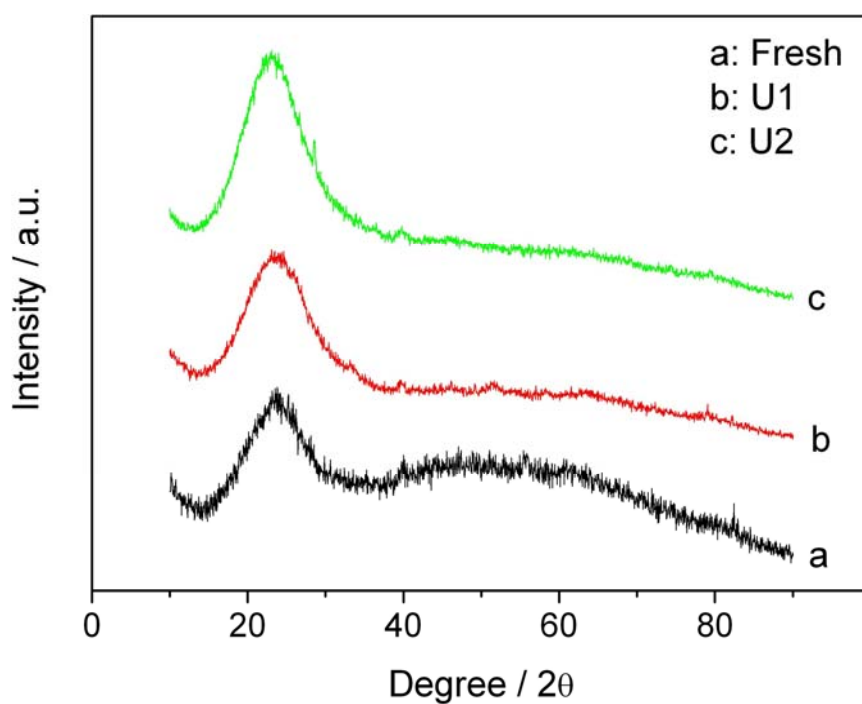


Figure S5: WAXS profiles of sample 0.5% Pt@SBA-15 before and after reaction. U1: after CO oxidation reaction; U2: after cyclooctadiene hydrogenation reaction

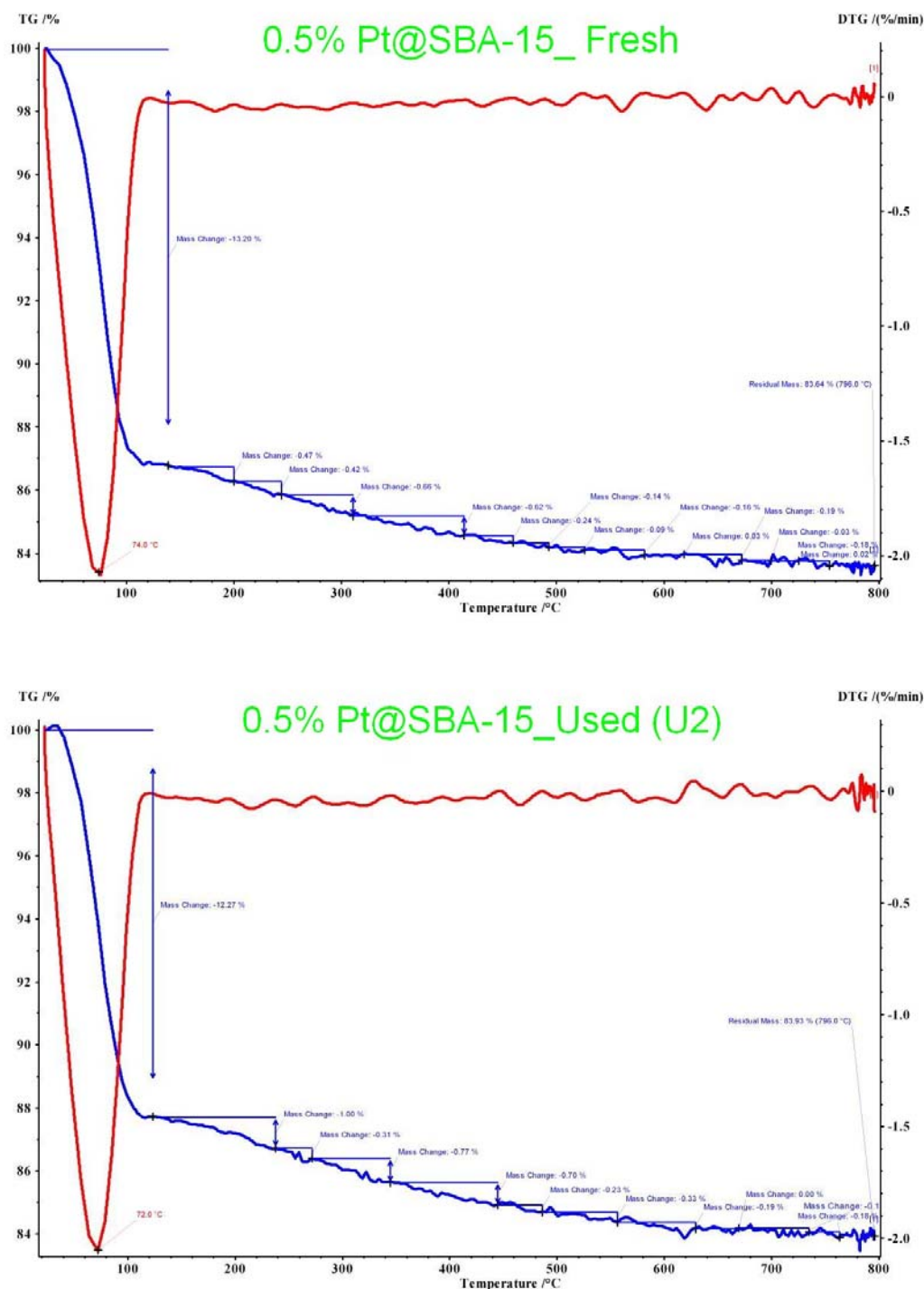


Figure S6: TGA and DTG profiles of 0.5% Pt@SB-15 before and after reaction (for liquid-phase catalytic cyclooctadiene (COD) hydrogenation reaction. Namely, catalyst U2 defined in the text)