Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Information

Stability of monometallic Pt and Ru supported on hierarchical HZSM-5 nanosheets for hydrodeoxygenation of lignin-derived compounds in aqueous-phase

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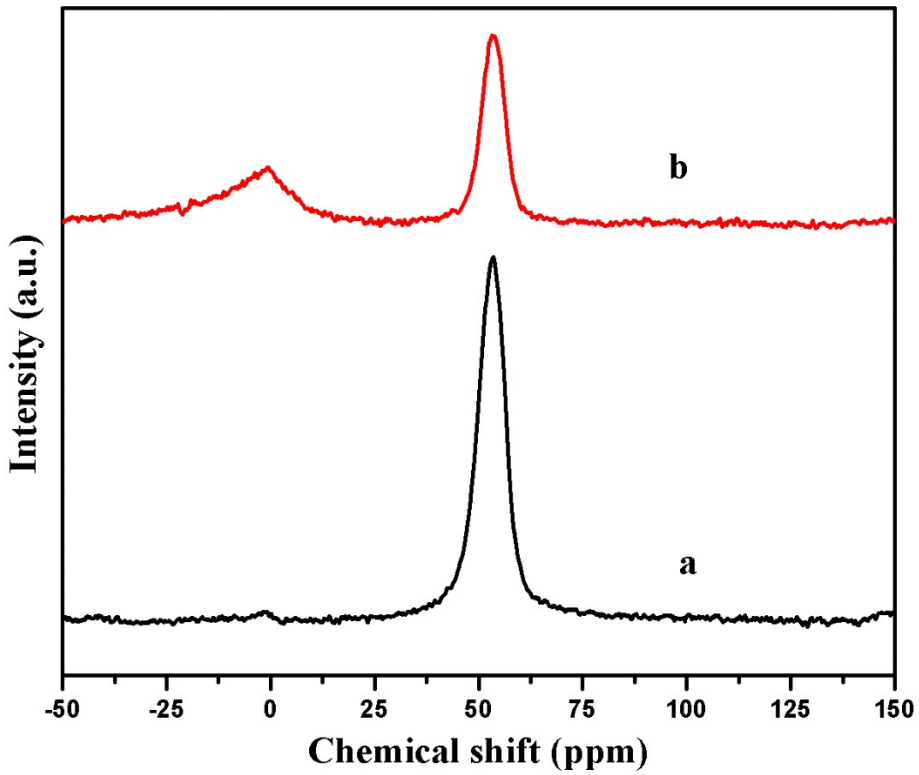

Figure S1. ^{27}Al NMR spectra of (a) HZSM-5-CON, and (b) HZSM-5-NS.

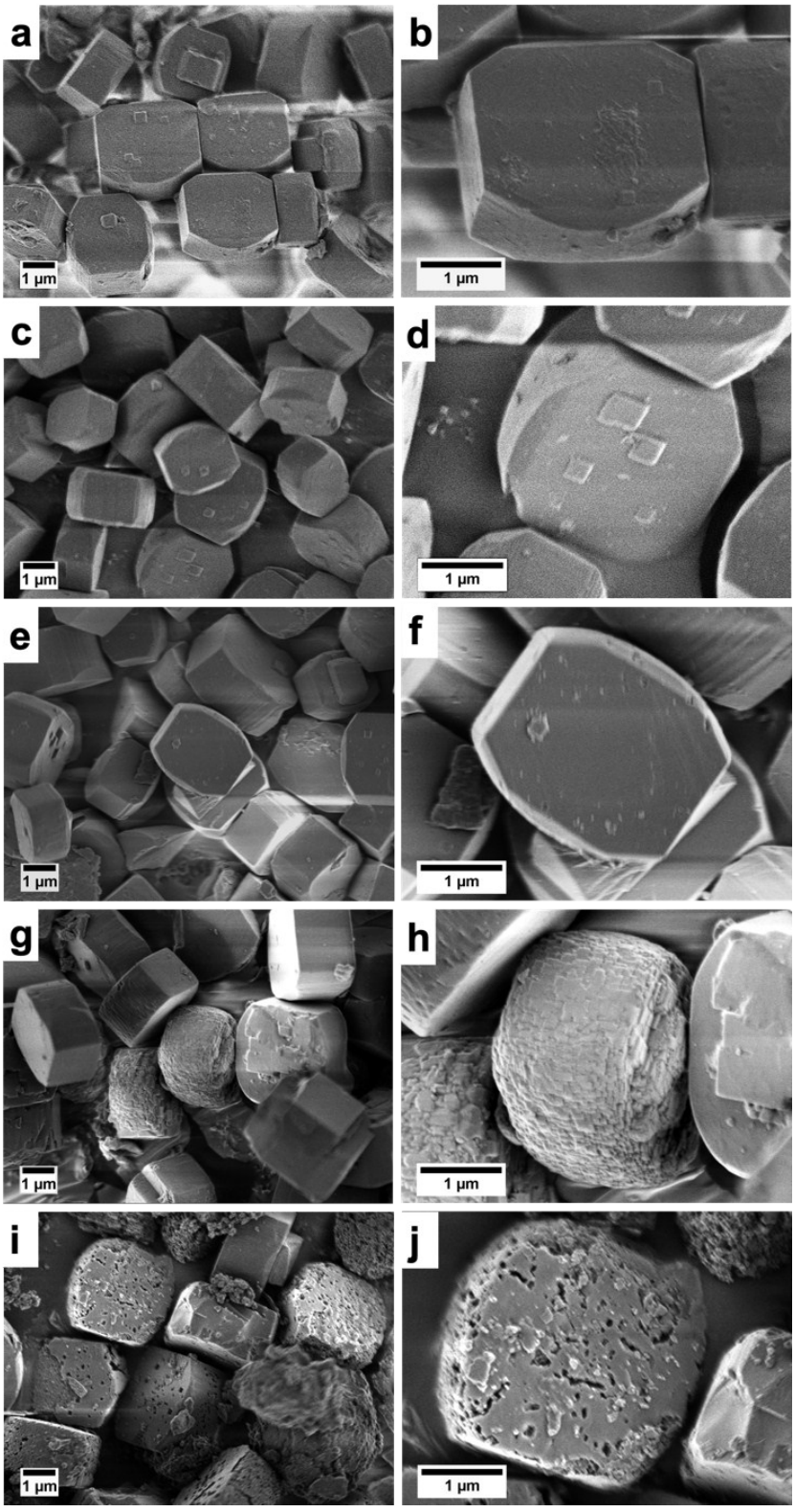

Figure S2. SEM images of Pt/HZSM5-CON of (a-b) fresh Pt/HZSM5-CON, (c-d) treated at 50 °C, (e-f) treated at 100 °C, (g-h) treated at 150 °C, and (i-j) treated at 200 °C in hot liquid water.

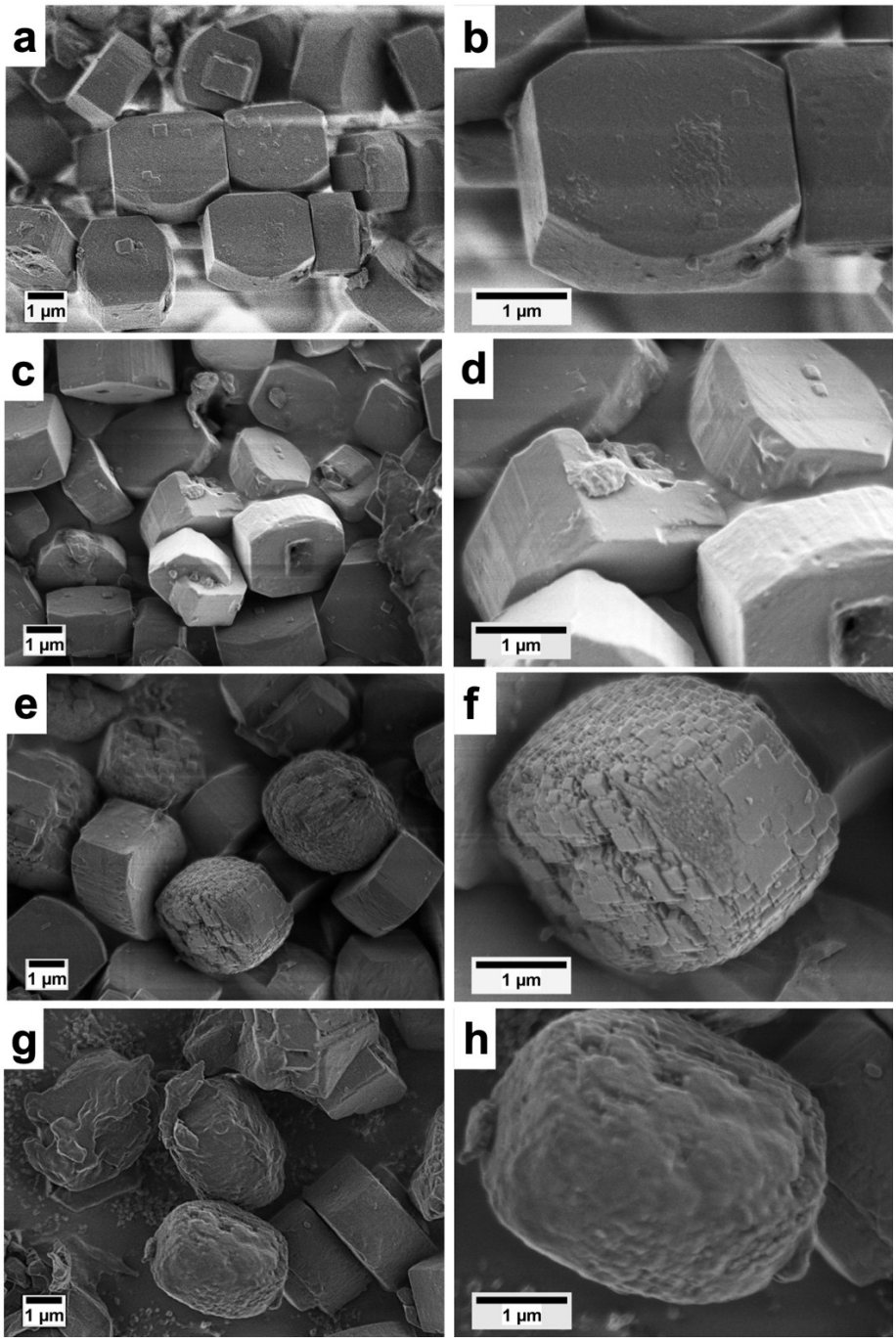

Figure S3. SEM images of Pt/HZSM5-CON of (a-b) fresh Pt/HZSM5-CON, (c-d) treated at 0.5 MPa, (e-f) treated at 1 MPa, (g-h) treated at 2 MPa with N_2 pressurized gas in water.

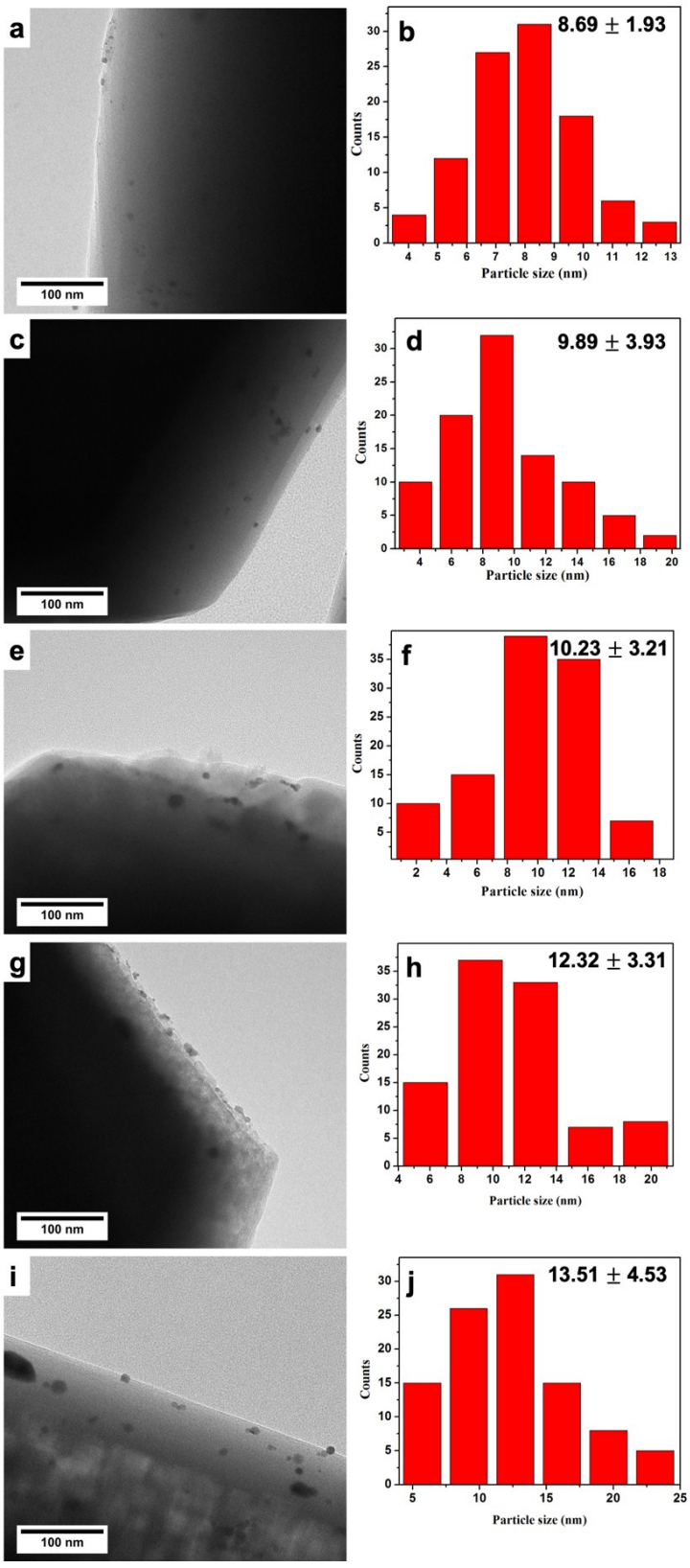

Figure S4. TEM images and particle size distribution of Pt/HZSM5-CON of (a-b) fresh Pt/HZSM5-CON, (c-d) treated at 50 °C, (e-f) treated at 100 °C, (g-h) treated at 150 °C, and (i-j) 200 °C.

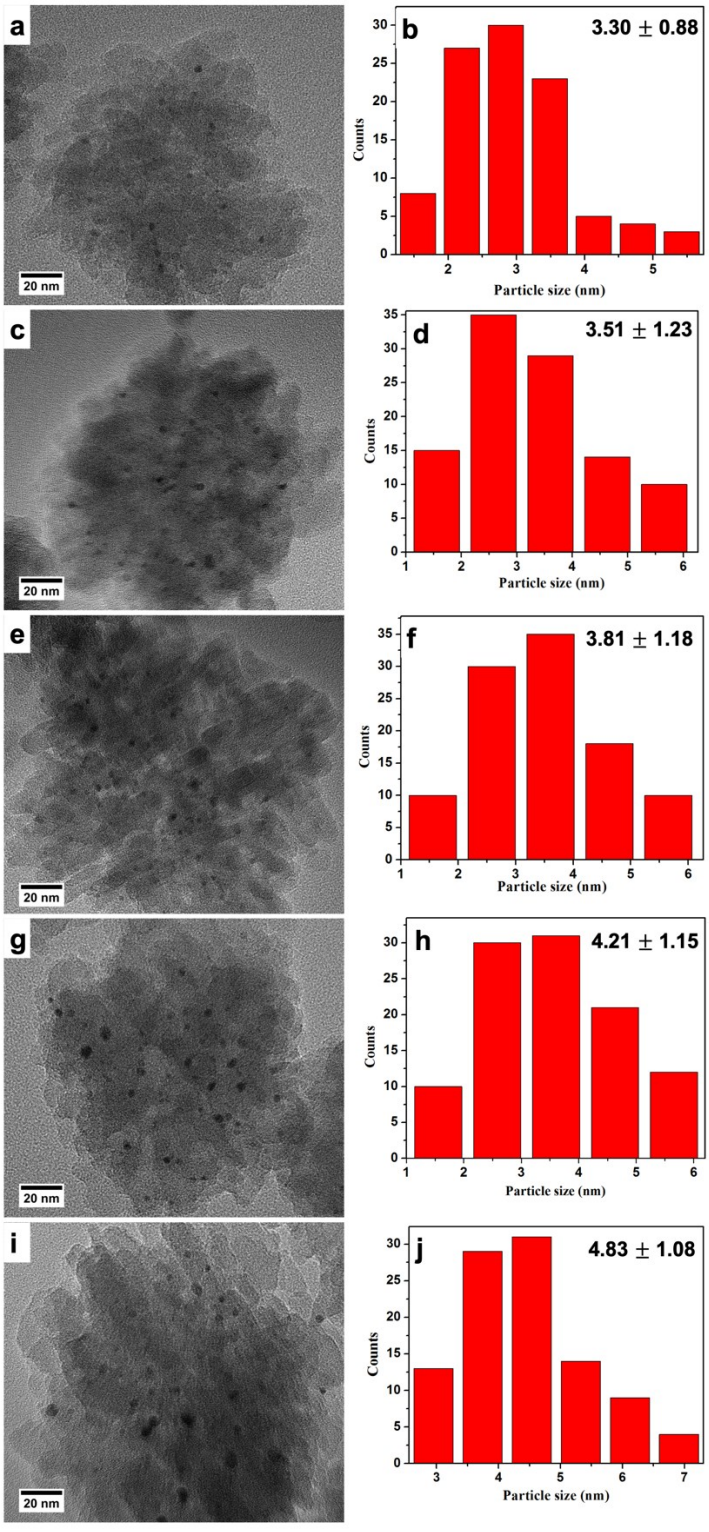

Figure S5. TEM images and particle size distribution of Pt/HZSM5-NS of (a-b) fresh Pt/HZSM5-NS, (c-d) treated at 50 °C, (e-f) treated at 100 °C, (g-h) treated at 150 °C, and (i-j) 200 °C.

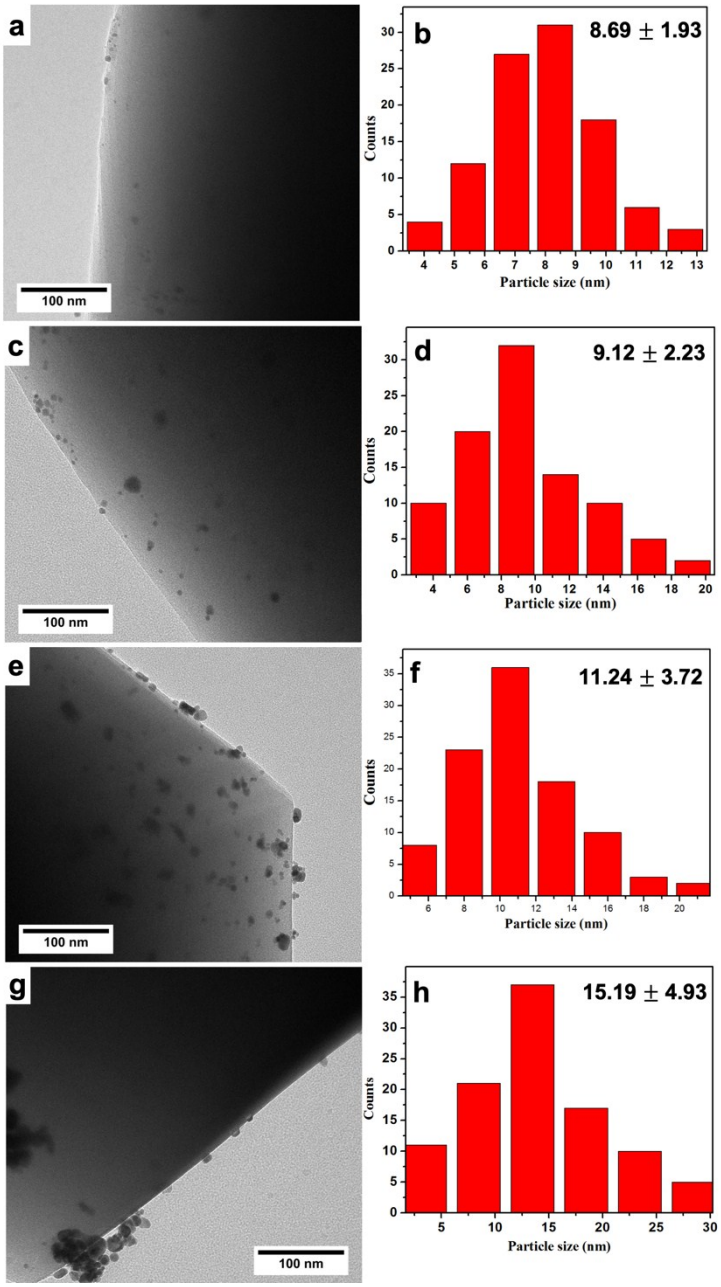

Figure S6. TEM images and particle size distribution of Pt/HZSM5-CON of (a-b) fresh Pt/HZSM5-CON, (c-d) treated at 0.5 MPa, (e-f) treated at 1 MPa, (g-h) treated at 2 MPa.

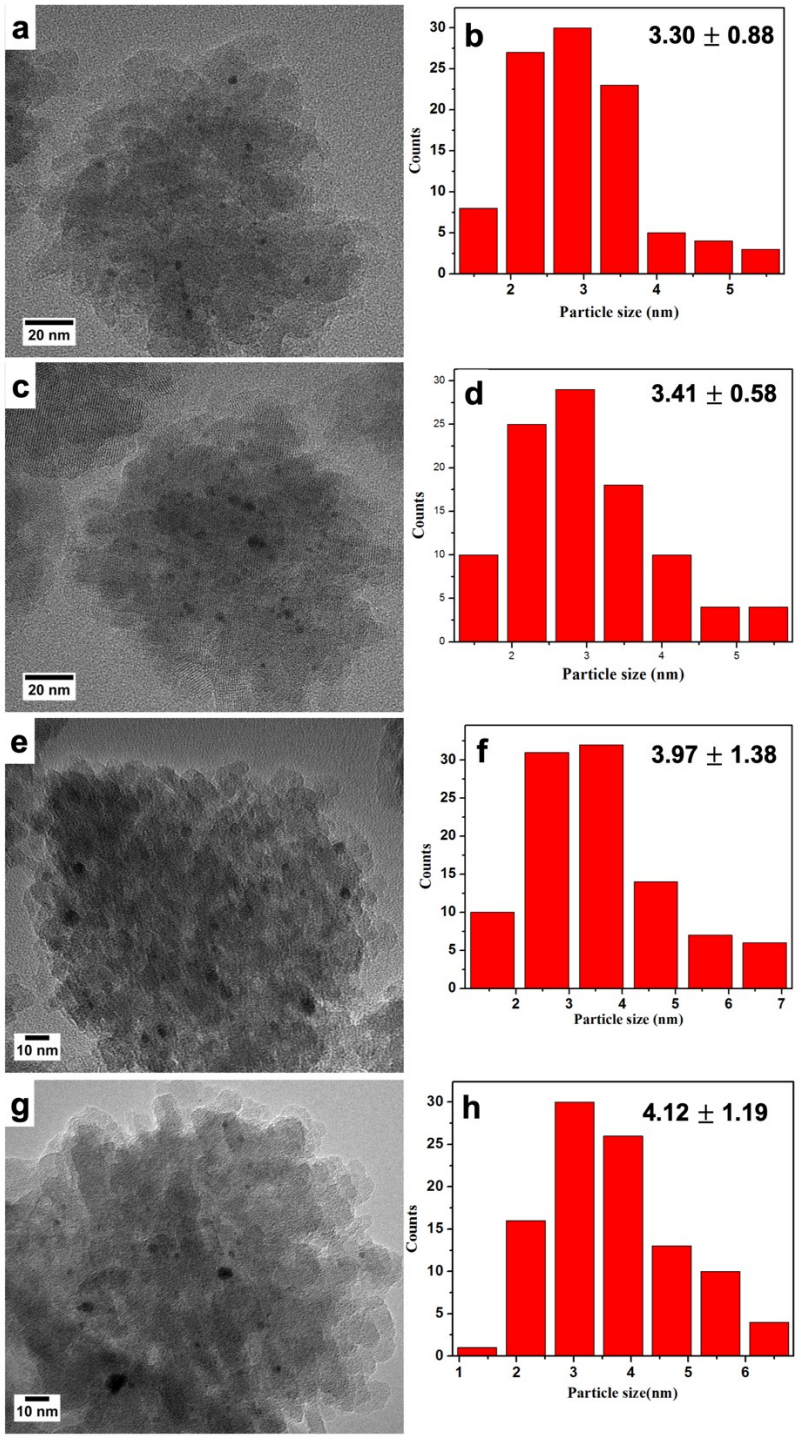

Figure S7. TEM images and particle size distribution of Pt/HZSM5-NS of (a-b) fresh Pt/HZSM5-NS, (c-d) treated at 0.5 MPa, (e-f) treated at 1 MPa, (g-h) treated at 2 MPa.

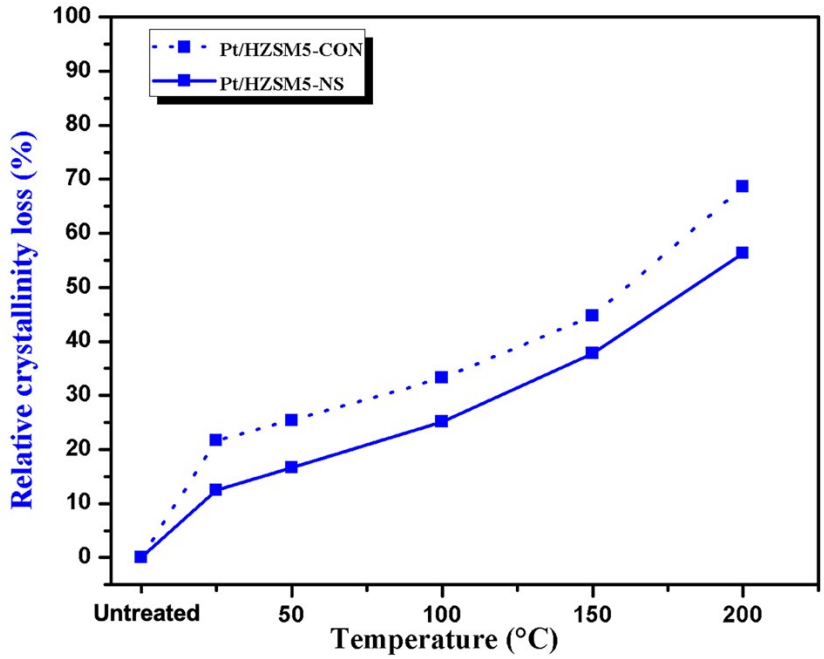

Figure S8. The effect of treated temperature on the relative crystallinity-loss obtained at the same total pressure of 1.5 MPa (including autogenous pressure) over Pt/HZSM5-CON and Pt/HZSM5-NS. Testing condition: a 0.15 g of dried catalyst, and a 10 ml of DI water at 1.5 MPa for 12 h.

Table S1. Textural data obtained from N_2 adsorption measurement of all as-synthesized samples.

Samples	Si/Al[a]	Pt or Ru[b]	S_{BET}[c]	S_{micro}[d]	S_{ext}[e]	V_{total}[f]	V_{micro}[g]	V_{ext}[h]
0.5Pt/HZSM5-CON	68	0.50	372.5	350.0	22.5	0.21	0.13	0.09
0.5Ru/HZSM5-CON	68	0.49	374.3	354.2	20.1	0.22	0.13	0.09
0.5Pt/HZSM5-NS	70	0.50	391.5	278.5	112.5	0.67	0.12	0.55
0.5Ru/HZSM5-NS	70	0.50	389.2	289.1	100.1	0.64	0.12	0.52

[a]Si/Al obtained by WDXRF; [b]Pt content reported in % weight obtained by WDXRF. [c]$S_{BET:}$ BET specific surface area; [d]$S_{micro:}$ micropore surface area; [e]$S_{ext;}$ external surface area; [f]V_{total}: total pore volume obtained at P/P_0=0.99; [g]V_{micro}: micropore volume; [h]V_{ext}: external pore volume; All surface areas and pore volumes are in the units of m^2/g and cm^3/g, respectively.

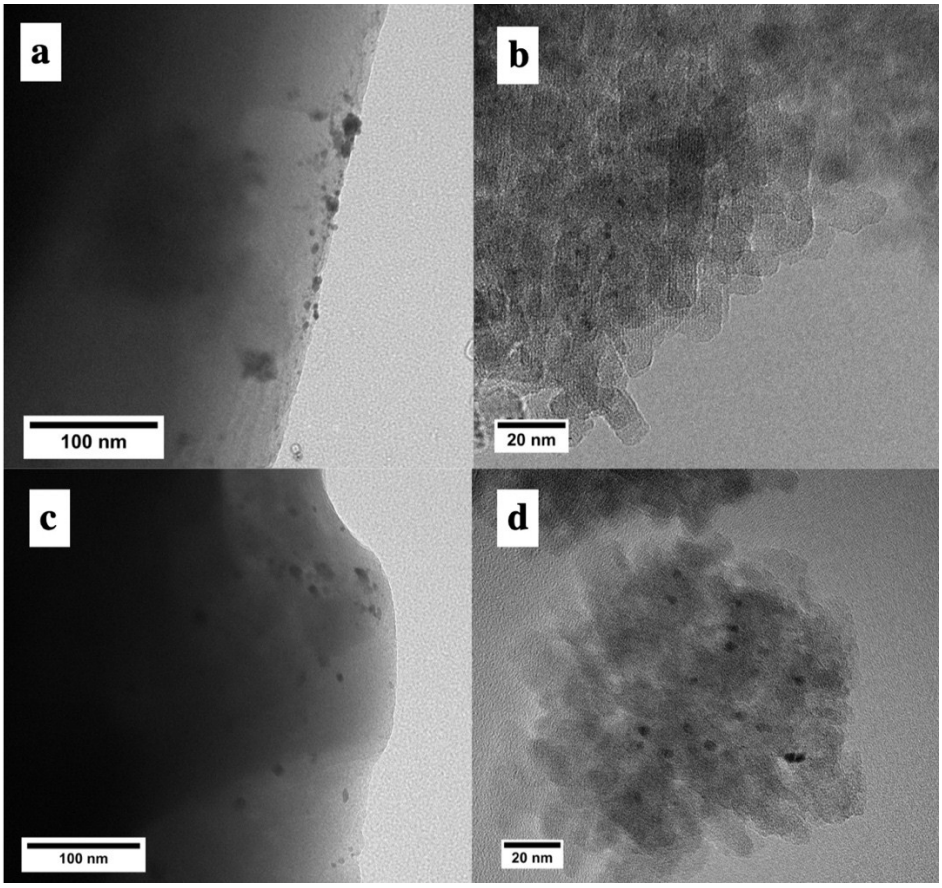

Figure S9. TEM images of (a) fresh Pt/HZSM5-CON, (b) fresh Pt/HZSM5-NS, (c) Pt/HZSM5-CON after reaction, and (d) Pt/HZSM5-NS after reaction.

Table S2. Catalytic performance in the HDO of 4-propylphenol over Pt supported on hierarchical HZSM-5 nanosheets and the recyclability test.

No. of runs	Conversion (%)	Selectivity (%)				
		Propyl cyclohexane	Propyl cyclohexene	Propyl benzene	Propyl cyclohexanol	Propyl cyclohexanone
1	99.11	32.16	0	4.40	63.44	0
2	82.12	28.29	0	3.54	56.05	12.12

Reaction conditions: 0.5 g of unreduced catalyst, 5 ml of water, and 0.5 mmol of *4*-propylphenol at 110 °C, and 1 MPa of H_2 for 10 h.

$$4-propylcyclohexanol\ conversion\ (\%) = \left(\frac{moles\ of\ 4-propylcyclohexanol_{initial}\ -\ moles\ of\ 4-propylcyclohexanol_{final}}{moles\ of\ 4-propylcyclohexanol_{initial}}\right) \times 100$$

$$Product\ selectivity_i(\%) = \left(\frac{mole\ of\ desired\ product_i}{total\ number\ of\ moles\ of\ all\ the\ quantified\ products}\right) \times 100$$

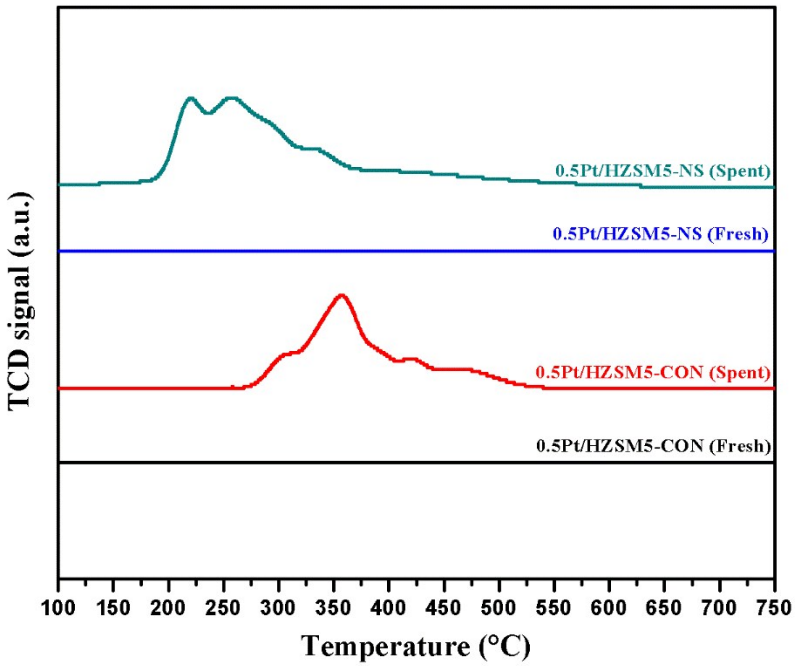

Figure S10. O_2-TPO profiles of fresh and spent catalysts of 0.5wt% Pt supported on conventional and hierarchical HZSM-5 zeolites.

Table S3. Coke amount of spent 0.5Pt/HZSM5-CON and 0.5Pt/HZSM5-NS obtained from integrating the peak area of O_2-TPO profiles

Samples	Coke amount (mmol.g^{-1})
0.5Pt/HZSM5-CON	0.197
0.5Pt/HZSM5-NS	0.238