

Supporting Information

Highly Selective Aromatization and Isomerization of n-Alkanes from Bimetallic Pt-Zn Nanoparticles Supported on a Uniform Aluminosilicate

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Materials and Methods

Synthesis of U-ZSM-5

U-ZSM-5 was synthesized by the hydrothermal technique. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 98% from Alfa Aesar was added to 1.0 M Tetrapropylammonium hydroxide (TPAOH) from Sigma Aldrich and stirred at room temperature (RT) until a clear solution was obtained. Tetraethyl orthosilicate (TEOS) from Merck KGaA was then added dropwise to the above solution whilst maintaining stirring at RT. Upon completion of TEOS addition, the solution was left to stir at RT until supersaturation after approximately 1 hour. The resulting supersaturated gel was applied to an autoclave and treated in a furnace at 170 °C for 72 hours. Amounts were calculated to obtain a molar ratio of $\text{Al}_2\text{O}_3:80\text{SiO}_2:21\text{TPAOH}:943\text{H}_2\text{O}$ in the gel. The resultant crystals were then applied to a 90 °C oven for 12 hours and subsequently calcined in air at a rate of 5 °C/min, held at 120 °C for 1 hour, ramped at the same rate again, held at 300 °C for 1 hour and finally ramped at the same rate to 600 °C and held for 3 hours. The resultant catalyst was then ready for reaction.

Synthesis of Pt-Zn/U-ZSM-5

Pt-Zn/U-ZSM-5 was synthesized by wetness impregnation (WI) where tetraammineplatinum (II) nitrate from Sigma Aldrich and Zn nitrate hexahydrate from Alfa Aesar were added to deionised water (DI) and stirred at RT. Prepared U-ZSM-5 support was then added to the solution to obtain 5%Zn-1%Pt/U-ZSM-5 as the final product. The mixture was stirred at RT for 3 hours and then the DI water removed by heating at 90 °C. The resulting catalyst was then dried at 90 °C for 12 hours once DI water was removed and calcined as before. The same procedure was carried out for Pt-

Zn/C-ZSM-5 synthesis using ZSM-5 (80:1) as provided by Zeolyst international. The same procedures were also used for Zn/U-ZSM-5 and Pt/U-ZSM-5 synthesis.

Synthesis of Pt-Sn/U-ZSM-5

Pt-Sn/U-ZSM-5 was synthesized by wetness impregnation (WI) where tetraammineplatinum (II) nitrate from Sigma Aldrich and Tin (IV) chloride pentahydrate from Sigma Aldrich were added to deionised water (DI) and stirred at RT. Prepared U-ZSM-5 support was then added to the solution to obtain 5%Sn-1%Pt/U-ZSM-5 as the final product. The mixture was stirred at RT for 3 hours and then the DI water removed by heating at 90 °C. The resulting catalyst was then dried at 90 °C for 12 hours once DI water was removed and calcined as before.

Synthesis of Ga-Zn/U-ZSM-5

Ga-Zn/U-ZSM-5 was synthesized by wetness impregnation (WI) where Zn nitrate hexahydrate from Alfa Aesar and Gallium (III) nitrate hydrate from Aldrich Chemistry were added to deionised water (DI) and stirred at RT. Prepared U-ZSM-5 support was then added to the solution to obtain 5%Zn-1%Ga/U-ZSM-5 as the final product. The mixture was stirred at RT for 3 hours and then the DI water removed by heating at 90 °C. The resulting catalyst was then dried at 90 °C for 12 hours once DI water was removed and calcined as before.

Catalyst performance experimental procedure

In a typical experiment, catalyst was loaded to a 100 mL Parr batch reactor system with 3 g of n-octane (98% from Sigma Aldrich) applied to a vial to ensure reactant contact with the catalyst in the gas phase. The catalyst mass was then altered following subsequent experiments to achieve conversions between 55-65%. The reactor was then pressurised to 3 MPa with CH₄ (99.9998%) from Praxair and 1 atm N₂ as internal standard. The system was then heated at a rate of 20 °C /min until 400 °C where the temperature was held for 1 hour. Upon completion, the system was cooled naturally. The liquid product was extracted and diluted with 10 mL CS₂ and applied to a carefully calibrated gas chromatography-mass spectrometer (GC-MS) as supplied by PerkinElmer (GC Claus 680 and MS Clarus SQ 8T) with a paraffin/olefin/naphthene/aromatic (PONA) column from Agilent. Gas products were analysed using a micro-GC as supplied by Agilent Technologies with 4 columns: A 10m molecular sieve 5A, 10-m alumina, 8-m CP-Sil 5 CB, and a 10-m PPU. All columns are equipped with thermal conductivity detectors. i-alkanes are mentioned throughout and refer to the feedstock with which it is associated. For example, i-alkane of n-pentane refers to i-pentane only and i-alkane of n-heptane refers to i-heptane only.

Calculations were made as follows:

$$\text{Yield of } x = \left(\frac{\text{mass of } x \text{ post reaction}}{\text{mass of feedstock fed}} \right) \times 100\% \quad (1)$$

$$\text{Conversion of } x = \left(\frac{\text{mass of } x \text{ fed} - \text{mass of } x \text{ post reaction}}{\text{mass of } x \text{ fed}} \right) \times 100\% \quad (2)$$

$$\text{Selectivity of } x = \left(\frac{C \text{ mol of } x}{\sum C \text{ mol of products}} \right) \times 100\% \quad (3)$$

Catalyst characterisation procedures

HAADF-STEM images were obtained on a FEI Talos F200X, a high-resolution scanning/transmission electron microscope (S/TEM) operated between 80 and 200kV and equipped with HAADF (high angle annular dark field) detector for Z contrast imaging and SuperX EDS detector for compositional analysis. XRD images were procured using a Rigaku Multiflex Diffractometer with Cu K α irradiation at 20 kV and 40 mA in the 2 θ region between 3° and 60°. XAS was conducted with an SM beamline (10ID-1) at the Canadian Light Source (CLS), which is equipped with a 35 nm outermost-zone plate (CXRO, Berkeley Lab). The diffraction-limited resolution for the zone plate is 30 nm. Image sequence (stack) scans over a range of spatial resolution for the zone plate is 30 nm. Image sequence (stack) scans over a range of photon energies were acquired for the same sample region at the Zn L-edge. XPS spectra were obtained using a Kratos Axis spectrometer with monochromatized Al K α ($h\nu = 1486.71$ eV) with a base pressure of $\sim 5 \times 10^{-10}$ Torr in the analysis chamber where binding energies were then referenced to the C1s energy at position 284.1 eV. N₂ physisorption measurements were made on an ASAP 2020 Plus physisorption instrument supplied by micromeritics. Vacuum outgassing at 400 °C for 2 h was followed by immersion in liquid N₂ to bring to a temperature of 77K. Brunauer-Emmett-Teller (BET) analysis was used for surface area measurements. SEM was conducted on an FEI Quanta 250 FEG variable-pressure/environmental field emission scanning electron microscope. Thermogravimetric analysis (TGA) was conducted on a PerkinElmer STA 6000 simultaneous thermal analyzer. Samples were ramped from 303 K to 1073 K at a rate of 10 °C/min in air.

Error Calculations

Reactions were performed in triplicate. Errors bars were calculated at the 95% confidence interval (CI) assuming normal distribution.

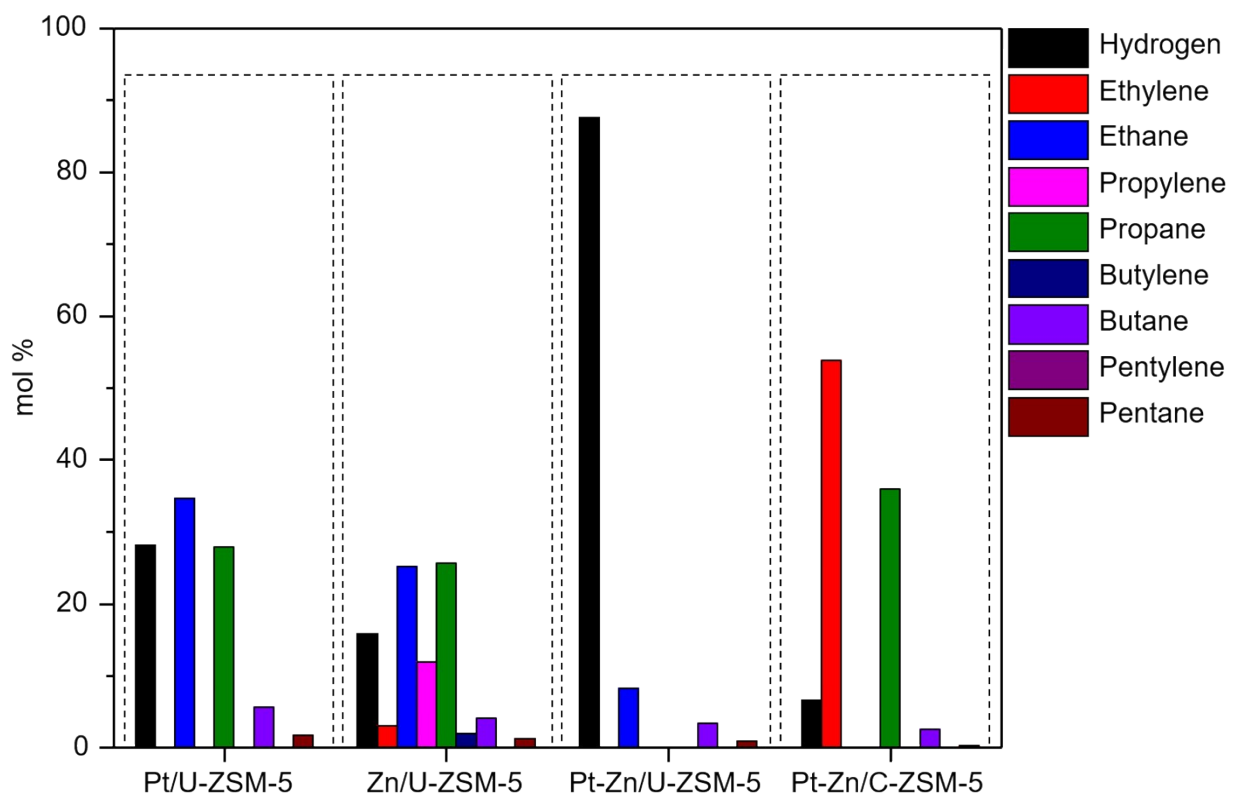


Figure S1. mol % distribution of gas products from reactions of Pt/U-ZSM-5, Zn/U-ZSM-5, Pt-Zn/U-ZSM-5, and Pt-Zn/C-ZSM-5 with n-octane at 400 °C for 1 h at 3 MPa CH₄ and 1 atm N₂.

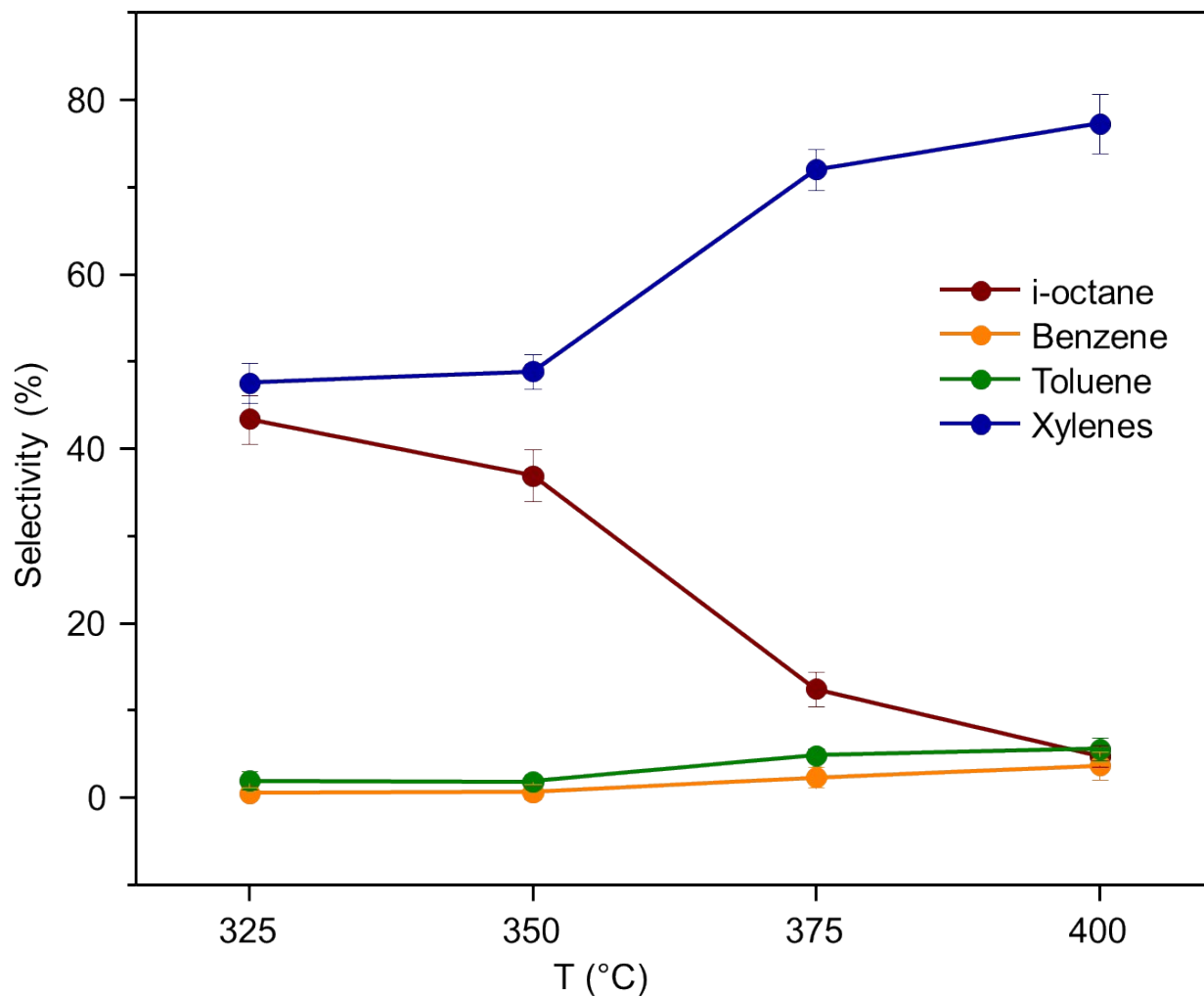


Figure S2. Selectivity towards i-octane, benzene, toluene, and xylene at different temperatures over the Pt-Zn/U-ZSM-5 catalyst. Reaction conditions: $t = 1$ h; $P = 3$ MPa CH_4 and 1 atm N_2 .

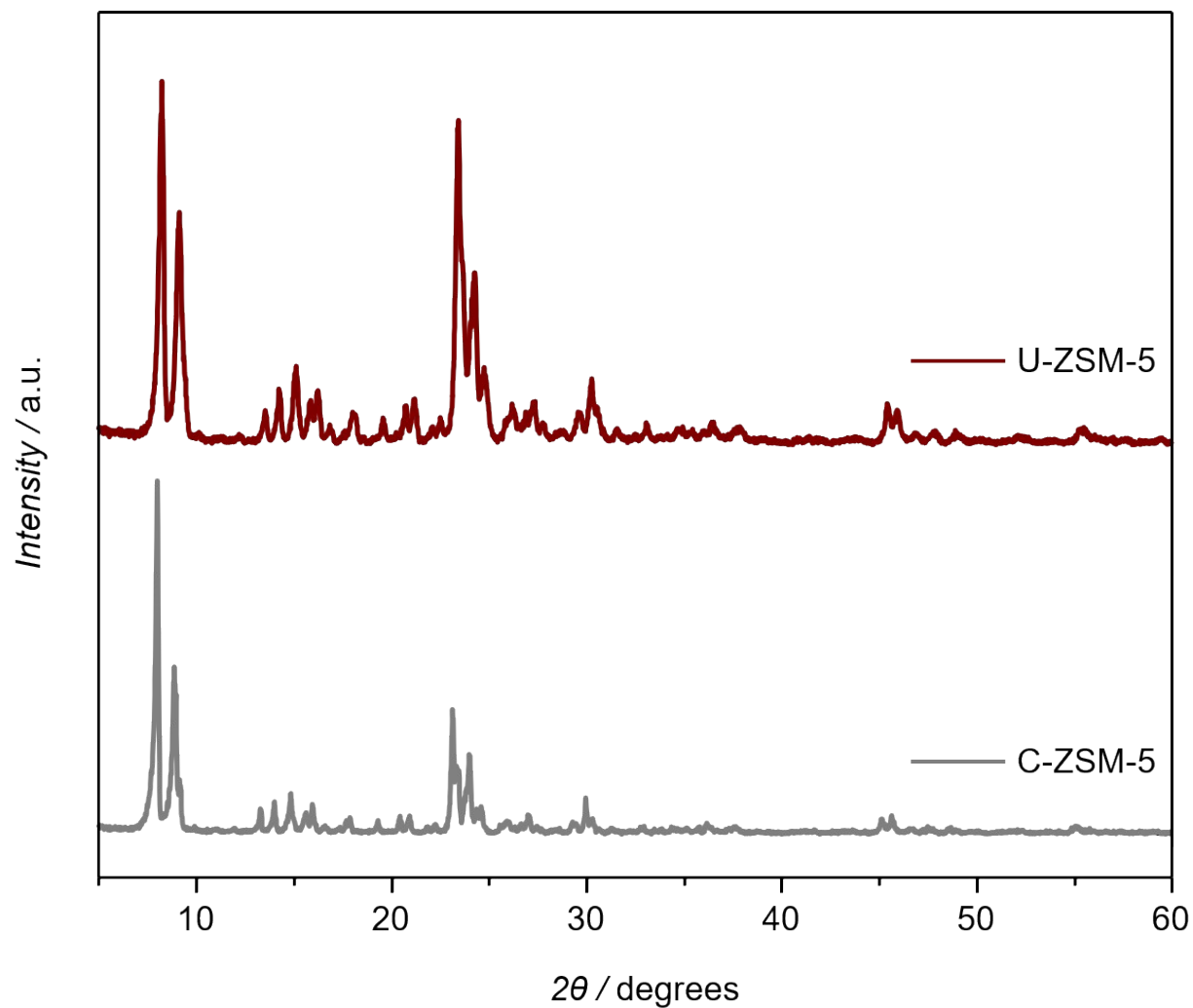


Figure S3. XRD patterns of U-ZSM-5 (red line) and C-ZSM-5 (grey line). Patterns are typical of the ZSM-5 MFI type zeolite.

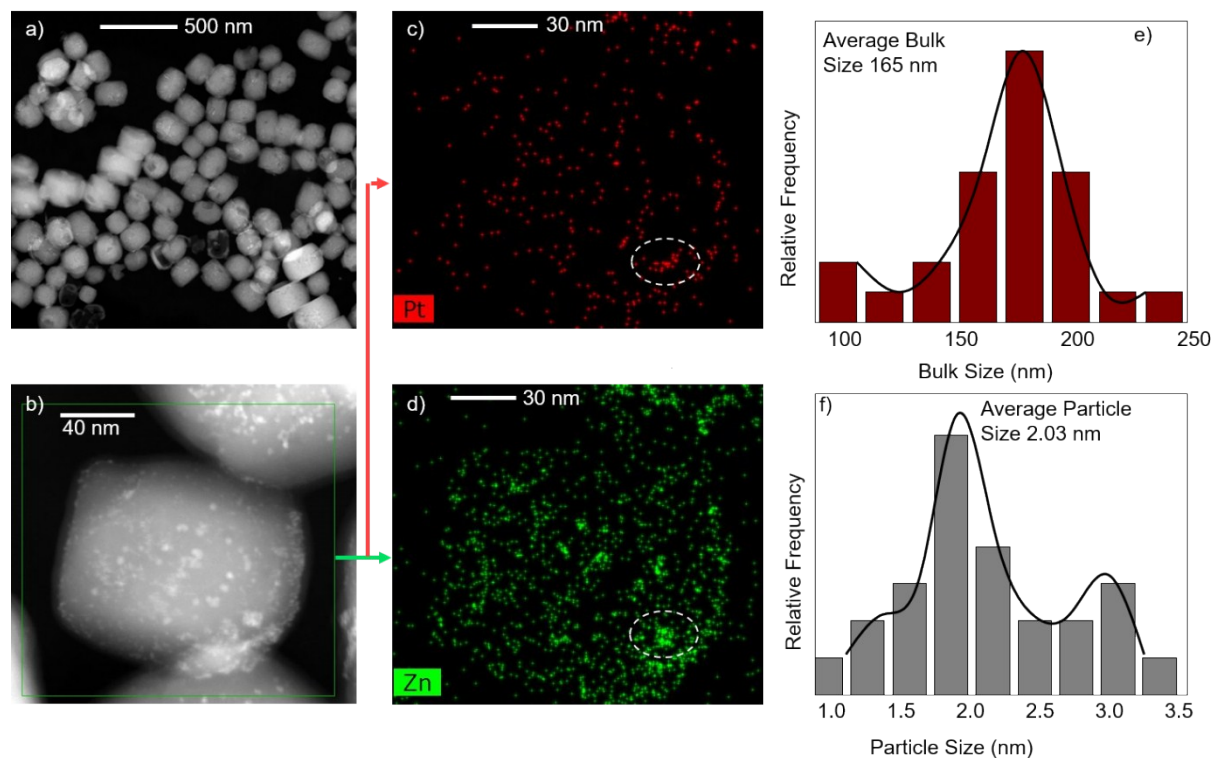


Figure S4. High-angle annular dark-field scanning transmission electron microscopy images of catalysts and particle size distributions of **a.** Pt-Zn/U-ZSM-5 particles. **b.** Pt-Zn/U-ZSM-5 single particle. **c.** well dispersed Pt nanoparticles (red) on single U-ZSM-5 particle. **d.** well dispersed Zn nanoparticles (green) on single U-ZSM-5 particle. **e.** bulk particle sizes of Pt-Zn/U-ZSM-5 (100 particle count). **f.** metal nanoparticle sizes on Pt-Zn/U-ZSM-5.

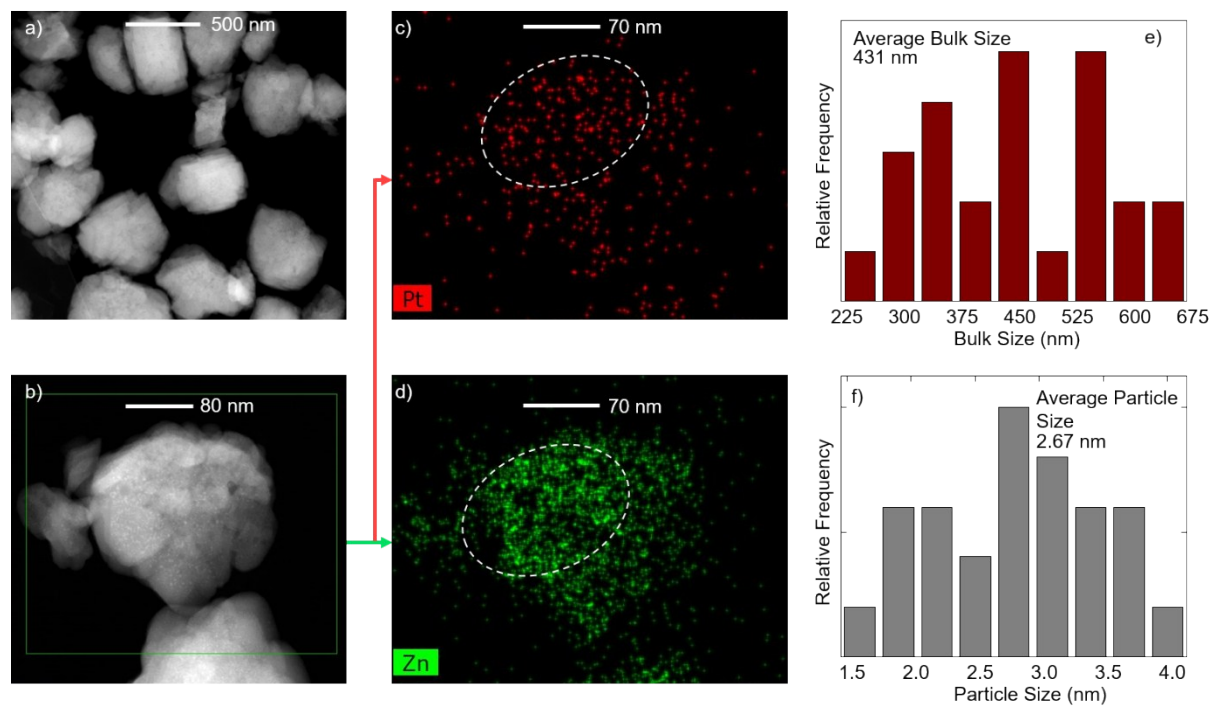


Figure S5. High-angle annular dark-field scanning transmission electron microscopy images of catalysts and particle size distributions of **a.** Pt-Zn/C-ZSM-5 particles. **b.** Pt-Zn/C-ZSM-5 single particle. **c.** well dispersed Pt nanoparticles (red) on single C-ZSM-5 particle. **d.** well dispersed Zn nanoparticles (green) on single C-ZSM-5 particle. **e.** bulk particle sizes of Pt-Zn/C-ZSM-5 (75 particle count). **f.** metal nanoparticle sizes on Pt-Zn/C-ZSM-5.

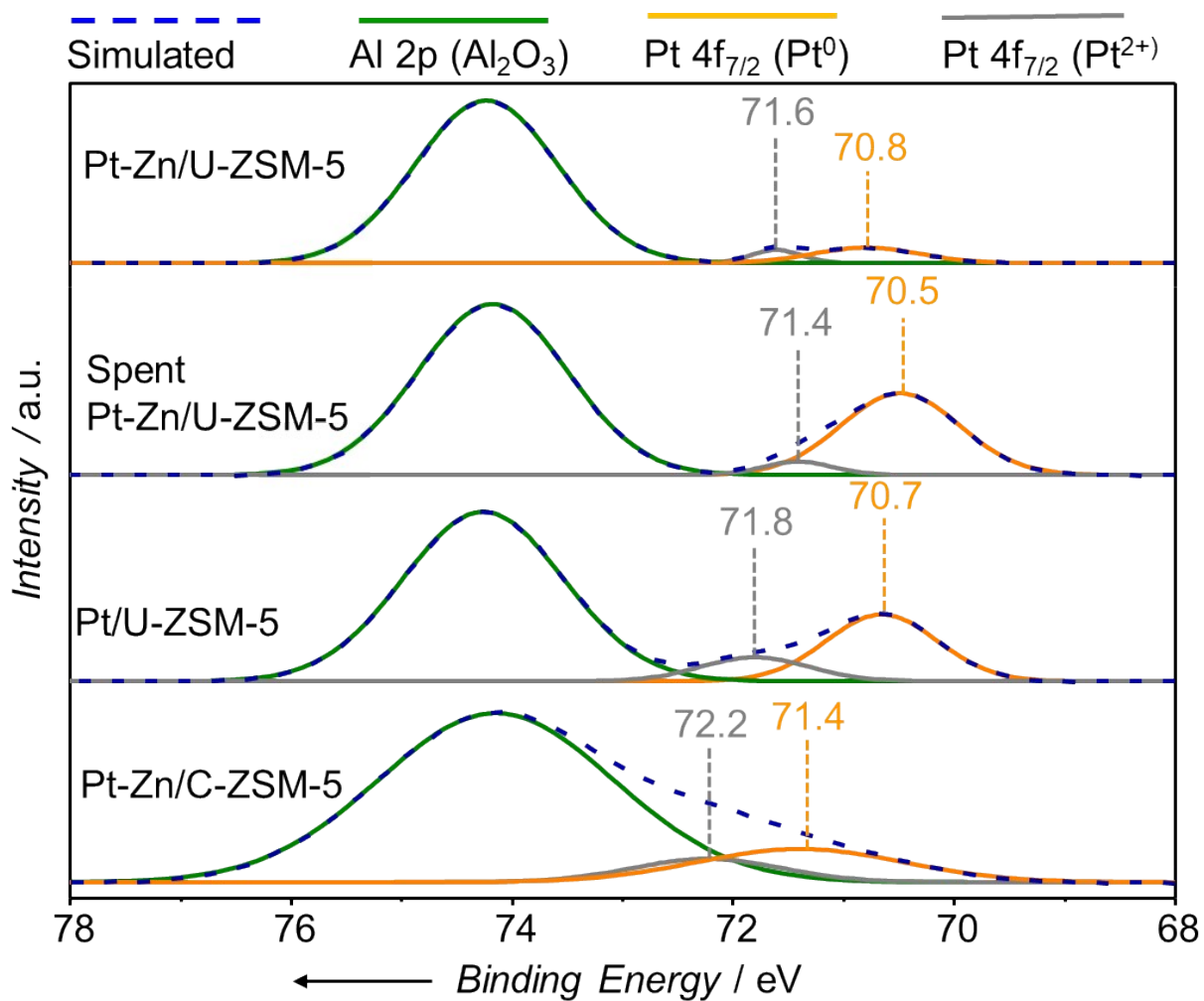


Figure S6. Simulated data for Al 2p, and Pt4f7/2 regions of XPS spectra for spent Pt-Zn/U-ZSM-5 following reaction.

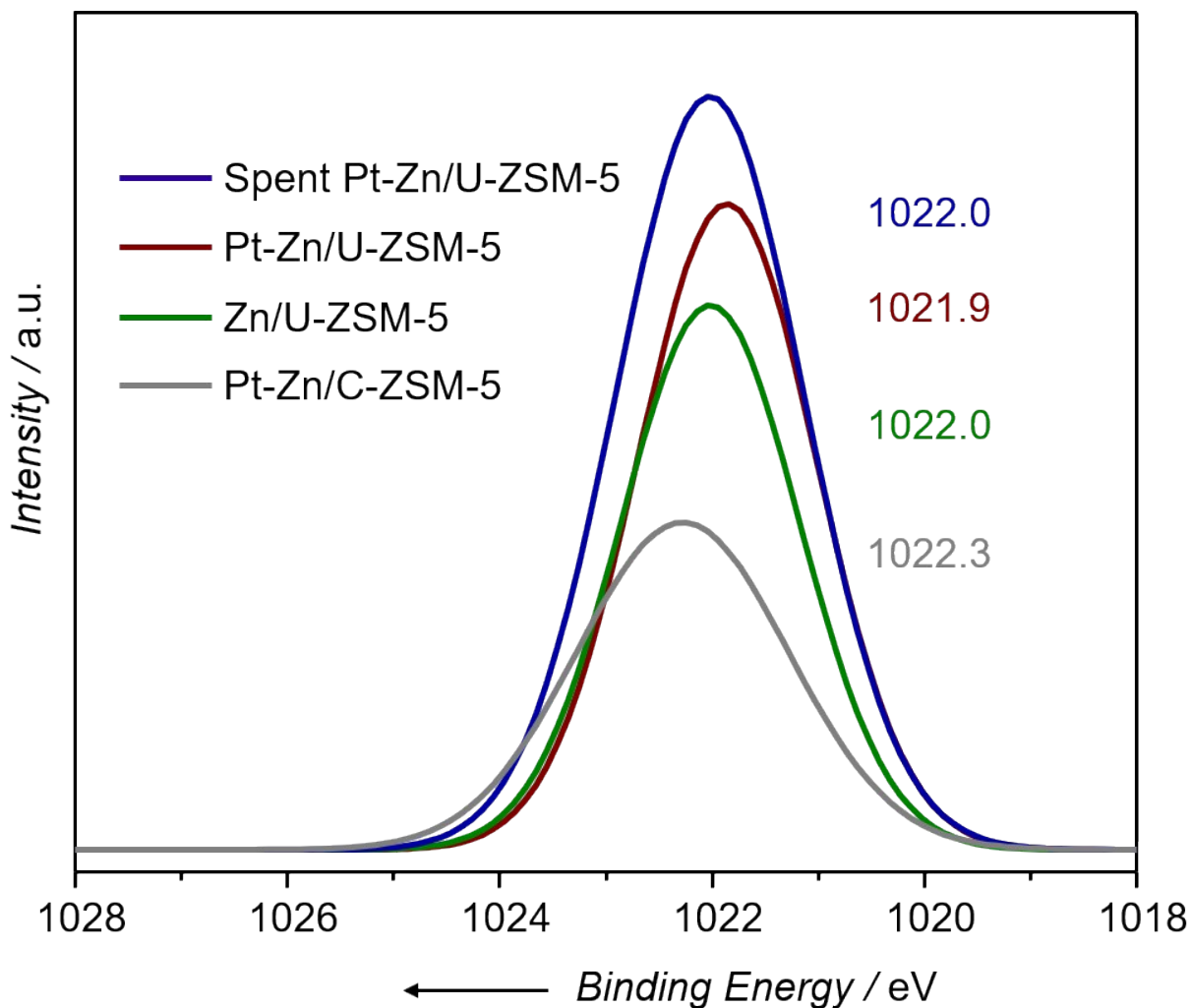


Figure S7. Simulated data for Zn 2p_{3/2} region of XPS spectra for Spent Pt-Zn/U-ZSM-5 following reaction with n-octane at 400 °C for 1 h under 30 MPa CH₄ (blue line), Pt-Zn/U-ZSM-5 (red line), Zn/U-ZSM-5 (green line), and Pt-Zn/C-ZSM-5 (grey line) catalysts.

Figure S7 shows peaks of Zn species with +2 oxidation state (positioned at ~1022 eV) in all cases. It is typical for wet impregnated ZSM-5 to contain Zn²⁺ species in the form of isolated Zn²⁺ and [ZnOZn]²⁺ cations¹. The small shift towards the higher binding energy of 1022.3 eV in the case of Pt-Zn/C-ZSM-5 would indicate Zn(OH)₂ if the shift was more significant, suggesting that these species did not decompose to ZnO species as expected during the calcination step and so is excluded from the possible reasons. The binding energy (BE) shift of Pt-Zn/C-ZSM-5 may be attributed to stronger binding of Zn²⁺ species to the framework oxygen of the zeolite, understandably resulting in a pronounced oxidation state and increased BE. This stronger interaction between Zn²⁺ species and the support framework could be a result of the change in support morphology, nominally the larger and less uniform bulk sizes of C-ZSM-5 support. Peak intensity of Pt-Zn/C-ZSM-5 (grey) is reduced compared to all U-ZSM-5 cases, suggesting higher

amounts of Zn^{2+} species on the surface of U-ZSM-5 catalysts. Potential Zn migration to the surface of the catalyst during the reaction could be the cause of the increased intensity of spent Pt-Zn/U-ZSM-5 (blue) compared to the fresh catalyst (red).

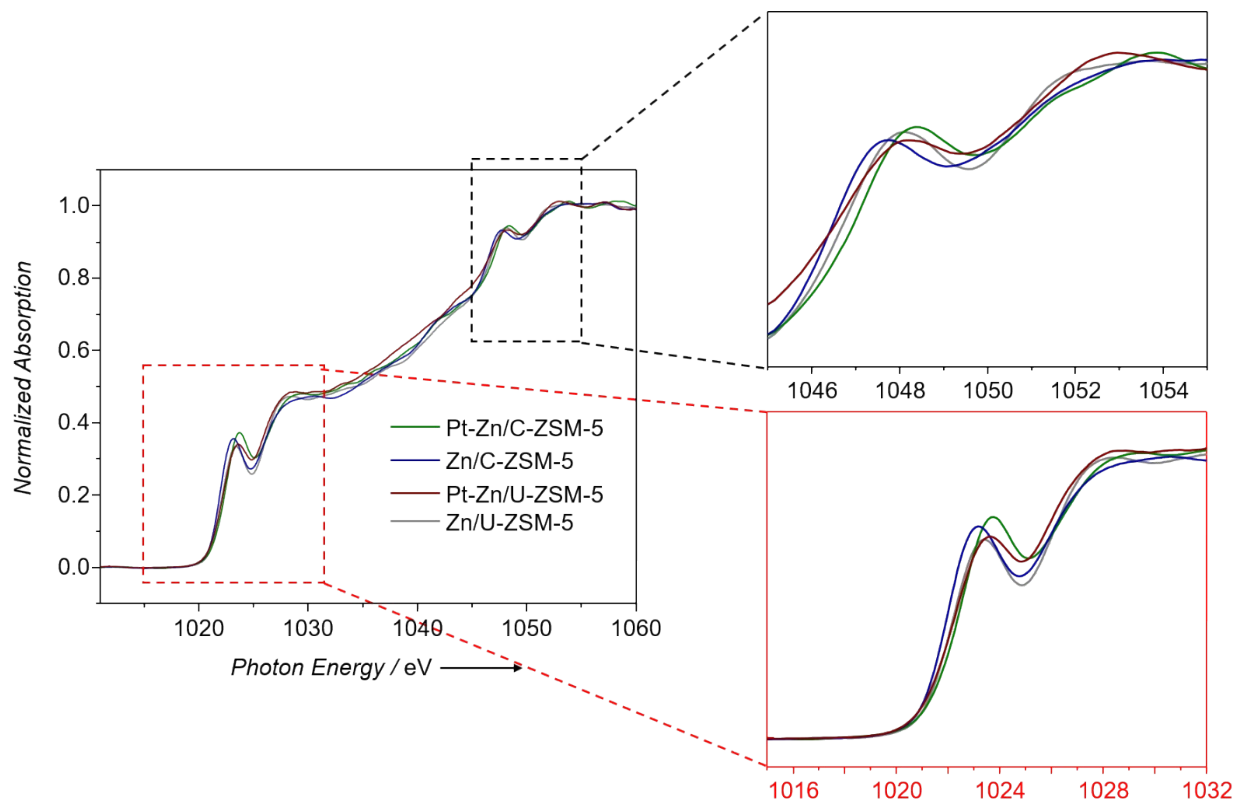


Figure S8. Zn-L_{II} and L_{III} edge XAS spectra of Pt-Zn/C-ZSM-5 (green line), Zn/CZSM-5 (blue line), Pt-Zn/U-ZSM-5 (red line), and Zn/U-ZSM-5 (grey line) with magnification on L_{III} (red border) and L_{II} (black border) regions.

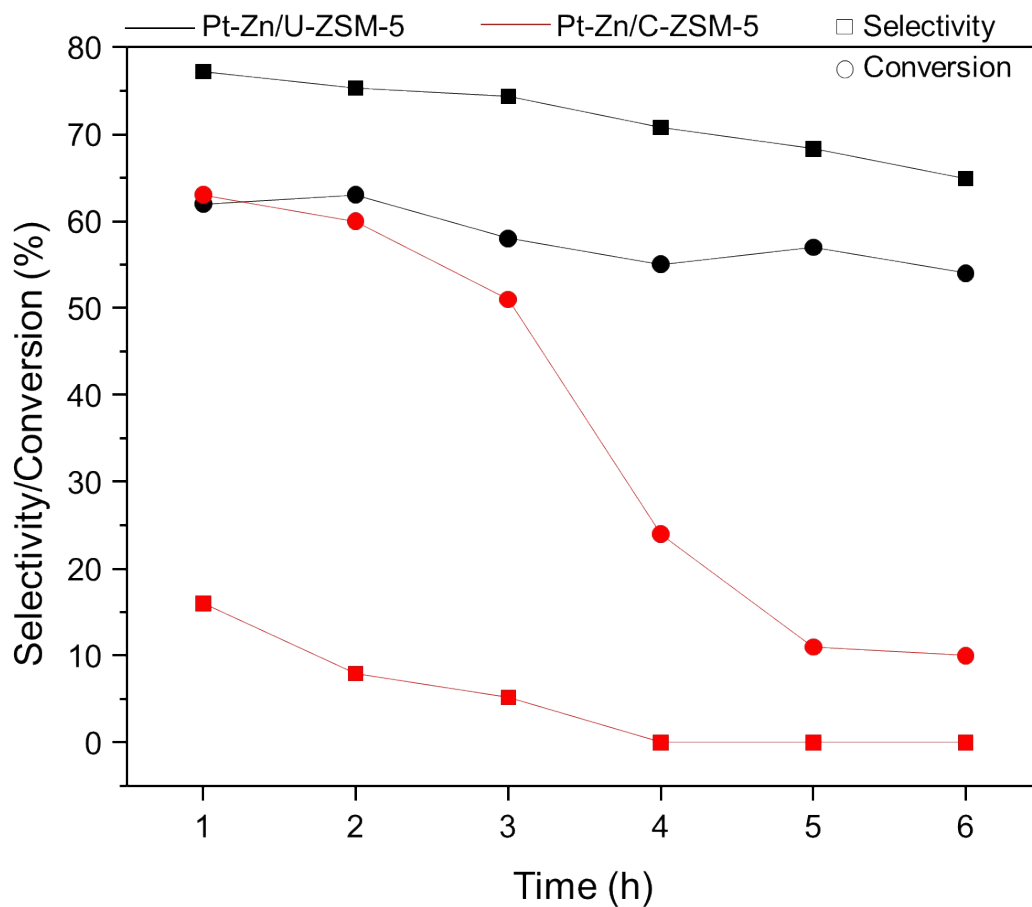


Figure S9. Selectivity and Conversion of Pt-Zn/U-ZSM-5 and Pt-Zn/C-ZSM-5 as a function of time. Catalysts were not reactivated after 1 h reactions with the exception of drying at 130°C in flowing air for 3 h to remove any physisorbed species. Reaction conditions; 400°C, 3 MPa CH₄, 3 g of n-octane, 1 h reaction time intervals. Catalyst loading to achieve initial 60% conversion with no catalyst reactivation.

Table S1. Product selectivity for the reaction of n-octane at 3 MPa CH₄ and 400 °C for 1 h over varying catalysts.

Product ^[a]	U-ZSM-5	C-ZSM-5	Pt-Zn/U ^[b]	Pt-Zn/C ^[c]
benzene	6.3	5.0	3.6	4.9
toluene	5.2	7.6	5.6	17.0
xylene	5.0	9.7	77.2	16.0
i-alkanes	0.0	0.0	6.0	0.0
n-alkanes	0.1	0.1	0.0	0.0
alkenes	77.4	1.5	0.0	0.0
cycloalkanes	1.5	0.0	0.4	0.0
>C ₈ aromatics	0.0	10.9	0.7	14.0
C ₁ -C ₅ alkanes	3.4	54.8	6.6	27.8
C ₁ -C ₅ alkenes	1.2	0.0	0.0	20.4

[a] C₁-C₅ = gas products. [b] Pt-Zn/U = Pt-Zn/U-ZSM-5. [c] Pt-Zn/C = Pt-Zn/C-ZSM-5.

Table S2. Nitrogen adsorption data for C-ZSM-5 and U-ZSM-5 supports to obtain BET surface area (m²/g).

Catalyst	BET Surface Area (m ² /g)		
	External	Microporous	Total
C-ZSM-5	109	292	401
U-ZSM-5	176	171	347

Table S3. Effect of different synthesis batches of Pt-Zn/U-ZSM-5 at the same reaction conditions and catalyst weight loadings; 400°C, 3 MPa CH₄, 0.5 g catalyst, 3 g of n-octane, 1 h reaction time. Batch # volumes refer to the Teflon-lined autoclave used during hydrothermal treatment.

Batch #	BTX Selectivity (%)	i-octane Selectivity (%)	Conversion (%)
1 – 100 mL	86.4	4.7	62
2 – 100 mL	81.7	5.1	58
3 – 100 mL	85.1	5.6	63
4 – 500 mL	77.8	11.9	51

References

- 1 A. A. Gabrienko, S. S. Arzumanov, A. V. Toktarev, I. G. Danilova, I. P. Prosvirin, V. V. Kriventsov, V. I. Zaikovskii, D. Freude, A. G. Stepanov, *ACS Catal.* 2017, **7**, 1818-1830.