Supplementary Materials

Catalytic Conversion of Polyethylene into Aromatics with Pt/ZSM-5: Insights on Reaction Pathways and Rate-Controlling Step Regulation

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Experimental details

$H_2PtCl_6 \cdot 6H_2O$ (37.5%, Shanghai Titan Scientific Co., Ltd.) was dissolved in ultrapure water to prepare the aqueous solution as Pt precursor. $PdCl_2$ (59%, Shanghai Titan Scientific Co., Ltd.) was also dissolved in concentrated hydrochloric acid (37%, Sinopharm Chemical Reagent Co., Ltd.) to prepare the aqueous solution of chloropalladic acid (pH = 0.2) as the Pd precursor. $RuCl_3 \cdot H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$, as Ru and Ni precursor, were bought from Sinopharm Chemical Reagent Co., Ltd. Ultrapure water (18.2 MΩ) was used throughout this work.

The standard chemicals of hydrocarbons were got from Shanghai Maclin Biochemical Technology Co., Ltd. The gas standards for calibration, which include CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, n-C_4H_8, i-C_4H_8, n-C_4H_{10}, i-C_4H_{10}, c-C_4H_8, were purchased from Shanghai Haoqi Gas Co. Ltd. Real PE film (Food grade, MIAOJIE) purchased from TOP Daily Chemicals (China) Co., Ltd.

In order to prevent product condensation, the injector temperature was set at 300 ℃. The GC oven temperature was initially kept at 40 ℃ for 3 min, then heated with 5 ℃/min to 250 ℃, held for 20 min, and then heated with 5 ℃/min to 260 ℃ for 120 min. The third procedure was mainly applied to the thermal cracking of PE, to prevent the long chain product remaining in the column.

Each test condition was triplicated to ensure the repeatability and

reliability of the experiment. Pyrolysis products were qualitatively MS and quantitatively FID. For quantitative purposes, different concentrations of each compound were injected to obtain calibration curves with regression coefficient >99%. The low carbon gas hydrocarbons with carbon number less than five were quantified in the same way by TCD through the gas standard mixture. Since PE and catalyst were mixed together during in-situ catalytic cracking and could not be separated after cracking, elemental analysis (VARIO EL CUBE Elemental analyzer, Elementer, Germany) was used to measure the carbon content in the total solid residual carbon in the cup.

The yields of products were calculated using the equation (1):

$$Carbon\ yeild\ of\ a\ product\ (C\%) = \frac{Mole\ of\ carbon\ in\ product}{Total\ mole\ of\ carbon\ in\ PE} \times 100\% \quad (1)$$

Catalyst characterizations

Analysis of metal actual loadings in the catalyst by inductively coupled plasma-optical emission spectrometer (ICP-OES, Agilent 725, USA). Elemental analysis (VARIO EL CUBE Elemental analyzer, Elementer, Germany) was used to measure the carbon content in the total solid residual carbon in the cup.

The textural properties, including specific surface area, pore volume, and pore size distribution of the catalysts were measured for N_2 adsorption-desorption at 77 K using the instrument of Micromeritics

Tristar 3Flex with the Brunauer-Emmet-Teller (BET), *t*-plot and Barrett-Joyner-Halenda (BJH) method, respectively.

X-ray diffraction (XRD) patterns were collected on a D8 ADVANCE diffractometer with Cu Kα radiation working (40 kV, 100 mA) and the scanning speed of 10 °/min in the scanning angle (2θ) ranged from 5° to 80°.

Scanning electronic microscopy (SEM) images were obtained using the FEI Nova NanoSEM 450. Scanning transmission electron microscopy images were got from high-angle annular dark-field scanning transmission electron microscopy (HADDF-STEM, Thermo Fisher Talos F200X) coupled with energy dispersive spectroscopy (EDS). Aberration-corrected STEM (AC-STEM) images and fast Fourier transform (FFT) patterns were performed on a ThermoFisher Themis Z microscope. Before STEM analysis, the catalyst was ultrasonically dispersed with ethanol and then added drop on a copper grid.

The number and strength of acid/base sites on the catalysts were evaluated via NH_3 and CO_2 temperature-programmed desorption (NH_3/CO_2-TPD) using a Micromeritics Auto Chem II 2920. Firstly, about 50 mg of catalyst was weighed and placed in a U-shaped tube. The samples were dried and pretreated from room temperature to 200 ℃ by heating speed of 10 ℃/min, and purged by helium flow of 50 mL/min for 1 hour. Then the samples were cooled down to 50 ℃ and 5% NH_3/He or

CO_2/He mixture was added until adsorption saturation. After saturation, samples rose to 100 ℃, switched He flow (50 mL/min) to purge for 1 hour to remove the physical adsorption NH_3 or CO_2 on/in the sample. Finally, samples were heated up to 700 ℃ at 5 ℃/min in He flow of 50 mL/min. The signal of desorbed CO_2 or NH_3 was recorded by a thermal conductivity detector (TCD).

The distinction between Brønsted and Lewis acids of catalysts were obtained by Pyridine adsorption FT-IR (Py-IR, Bruker ALPHA, Germany). Firstly, the wafer was vacuumed to 10^{-3} Pa in-situ in an IR cell at 400 ℃ for 2 hours to make the gas molecules on the surface of the sample desorbed clean, and cooled down to room temperature, evacuated for 30 min and exposed to saturated pyridine vapor. After that, sample was rose to 150 ℃ and vacuumed to 10^{-3} Pa again, kept for 30 min, and then cooled down to room temperature, and scanned in the range of 1400 ~ 1700 cm^{-1} wave number. The infrared spectra of pyridine adsorption at 150 ℃ were recorded. Desorption was also carried out at other specified temperatures (50 ℃, 200 ℃ and 350 ℃), and corresponding spectra were collected at lower temperatures.

X-ray photoelectron spectroscopy (XPS) experiment was performed on a Thermo Fisher Nexsa spectrometer to characterize the states of Pt species on the catalyst surface with a monochromatic Al Kα X-ray source (1486.68 eV). The binding energies were calibrated using the C 1s peak

at 284.6 eV as a reference.

The dispersion of the metal was determined by CO-Chemisorption (Micromeritics Auto Chem II 2920) using CO as the probing molecule. Firstly, about 100 mg of the sample was weighed and placed in a U-shaped tube, and dried at 10 ℃/min from room temperature to 300 ℃. After that, samples were reduced at 200 ℃ under H_2 (10 Vol%)/Ar mixed gas for 2 hours, and then samples were cooled to 50 ℃. Finally, He flow (50 mL/min) blew away H_2 of the surface until the baseline was stable, and CO pulse titration was carried out until saturation.

Thermogravimetric analysis (TGA) was performed using a PerkinElmer Pyris1 thermal gravimetric analyzer. The sample was heated from room temperature to 120 ℃ at a rate of 10 ℃/min, held for 1 hour, and then continued to rise to 800 ℃ for 30 min. TG and DTG curves were recorded during the whole process.

Computational Details

To simplify the ZSM-5 model, the surface rings of ZSM-5 zeolite were cut for calculation purposes. To prevent interactions between adjacent cells, a vacuum layer with a thickness of 20 Å was introduced between the periodically repeated slabs. The dimer method was utilized to locate the transition states of elementary steps.

Supporting Tables

Table S1. The properties of the polyethylene

Properties	Value
Formula	$H(CH_2CH_2)_nH$
State	Powder (white)
M_n [a] ($g\ mol^{-1}$)	1700
M_w [a] ($g\ mol^{-1}$)	4000
Density ($g\ mL^{-1}$)	0.92
Viscosity (poise)	1.5
Melting Point (℃)	92
Acid Number (mg KOH/g)	<0.05
C [b] (wt%)	85.04
H [b] (wt%)	14.84
Ca [c] ($mg\ kg^{-1}$)	16.5
Na [c] ($mg\ kg^{-1}$)	<10
K [c] ($mg\ kg^{-1}$)	<10
P [c] ($mg\ kg^{-1}$)	<10
S [c] ($mg\ kg^{-1}$)	<10

[a] Molecular weight of the polyethylene were determined by GPC.
[b] Quantitation of carbon and hydrogen was measured on VARIO EL CUBE Elemental analyzer.
[c] Elemental compositions of polyethylene were determined by ICP-AES.

Table S2. The specific physical property parameters of catalysts

Catalysts	SiO_2/Al_2O_3	S_{Micro} [a] ($m^2\ g^{-1}$)	S_{Meso} [a] ($m^2\ g^{-1}$)	V_{Micro} [a] ($cm^3\ g^{-1}$)	V_{Meso} [a] ($cm^3\ g^{-1}$)	d [a] (nm)
ZSM-5(25)	25	0.107	0.085	2.91	0.085	3.67
ZSM-5(38)	38	0.176	0.005	2.10	0.005	2.23
ZSM-5(70)	70	0.113	0.029	2.36	0.029	2.97
Pt/ZSM-5(38)	38	0.157	0.007	2.11	0.007	2.26

[a] Textural structure was obtained by N_2 physical adsorption–desorption.

Table S3. Carbon yield of polyethylene thermal cracking products at 500 ℃

Products (Total Yield (%))	**Chemicals**	**Yield (%)**
Gas product (8.0)	Methane	2.3
	Ethane	1.9
	Ethylene	0.4
	Propane	0.4
	Propylene	0.7
	Isobutane	0.0
	N-butane	0.5
	N-butene	1.0
	Isobutene	0.7
	2-Butylene	0.1
Liquid product (91.4)	Diolefins above C_6	5.5
	Olefins above C_6	51.8
	Alkanes above C_6	34.1
Solid product [a]	Char and Coke	0.0

[a] Quantitation of carbon was measured on VARIO EL CUBE Elemental analyzer.

Table S4. Carbon yield of polyethylene catalytic cracking with ZSM-5 (38) at 450 ℃

Products (Total Yield (%))	**Chemicals**	**Yield (%)**
Gas product (60.7)	Methane	0.3
	Ethane	0.3
	Ethylene	4.7
	Propane	6.0
	Propylene	15.2
	Isobutane	8.7
	N-butane	5.3
	N-butene	4.0
	Isobutene	12.6
	2-Butylene	3.6
Liquid product (26.5)	Benzene	1.5
	Toluene	9.2
	Ethylbenzene	1.4
	Xylene	9.6
	Another Monocyclic Aromatic Hydrocarbon	4.0
	Polycyclic Hydrocarbons	0.8
Solid product [a]	Char and Coke	0.8

[a] Quantitation of carbon was measured on VARIO EL CUBE Elemental analyzer.

Table S5. Carbon yield of polyethylene catalytic depolymerization at 500 °C with different PE to catalyst ratio

(The mass of PE is fixed at 500μg)

PE: catalyst (Mass ratio)	Gas Product (%)	Liquid Product (%)	Solid [a] Product (%)	Total Yield (%)
1:1	45.9	20.5	1.7	68.1
1:2	64.5	24.8	1.3	90.6
1:3	69.9	26.3	1.3	97.5
1:4	68.1	30.3	1.7	100.1
1:5	65.1	30.6	1.2	96.9
1:6	65.5	33.1	1.0	99.6
1:7	62.1	32.0	1.3	95.4
1:8	59.3	32.3	2.0	93.6

[a] Quantitation of carbon was measured on VARIO EL CUBE Elemental analyzer.

Table S6. Carbon yield of polyethylene catalytic depolymerization with ZSM-5 (38) at different temperature

(The mass ratio of PE and catalyst is 1:6)

Temperature (℃)	Gas Product (%)	Liquid Product (%)	Aromatics in Liquid Products (%)	Solid [a] Product (%)	Total Yield (%)
350	68.5	19.2	19.2	3.8	91.5
450	60.7	26.5	26.5	0.8	88.0
500	65.5	33.1	26.6	1.0	99.6
550	65.3	30.7	26.8	0.8	96.8
600	63.8	28.5	24.5	0.5	92.8

[a] Quantitation of carbon was measured on VARIO EL CUBE Elemental analyzer.

Table S7. Carbon yield of polyethylene and ZSM-5 with different SiO_2/Al_2O_3 ratios (500 ℃, PE: ZSM-5 =1:6)

SiO_2/Al_2O_3	Gas Product (%)	Liquid Product (%)	Solid [a] Product (%)	Total Yield (%)
25	60.6	19.8	1.1	81.5
38	65.5	33.1	1.0	99.6
70	73.4	15.5	1.1	90.0

[a] Quantitation of carbon was measured on VARIO EL CUBE Elemental analyzer.

Table S8. Carbon yield of polyethylene and ZSM-5 loaded with different metals (500 °C, PE: Metal/ZSM-5 =1:6)

Metal	Gas Product (%)	Liquid Product (%)	BTEX in Liquid Products (%)	Solid [a] Product (%)	Total Yield (%)
Pt	32.9	60.5	50.7	3.6	97.0
Pd	44.7	43.9	34.4	5.7	94.3
Ni	33.8	49.3	37.0	10.1	93.2
Ru	68.4	30.4	22.9	2.6	101.4

[a] Quantitation of carbon was measured on VARIO EL CUBE Elemental analyzer.

Table S9. Carbon yield of polyethylene and ZSM-5 with different loads of Pt (500 ℃, PE: Pt/ZSM-5 =1:6)

Pt [a] (wt%)	**0.04**	**0.60**	**1.40**	**4.60**
Alicyclic Hydrocarbon	0.6	0.3	0.0	0.1
Aliphatic Hydrocarbons	2.0	1.0	0.3	0.5
Benzene	3.0	4.1	5.4	4.7
Toluene	16.1	20.8	23.3	21.0
Ethylbenzene	1.7	1.7	1.2	1.1
Xylene	15.3	19.8	20.8	15.8
Another Monocyclic Aromatic Hydrocarbon	4.2	4.0	2.5	2.3
Polycyclic Hydrocarbons	2.9	4.0	7.1	4.0
Total Liquid Product (%)	45.8	55.7	60.6	49.5
Gas Product (%)	54.2	39.3	32.9	36.8
Solid [b] Product (%)	1.9	3.6	3.6	3.8
Total Yield (%)	102.0	98.6	97.1	90.1
Metal [c] dispersion (%)	74.8	68.1	37.4	22.7

[a] Quantitation of Pt was determined by ICP-AES.

[b] Quantitation of carbon was measured on VARIO EL CUBE Elemental analyzer.

[c] Metal dispersion was calculated based on the CO chemisorption data from Micromeritics Auto Chem II 2920.

Table S10. Carbon yield of polyethylene and Pt/ZSM-5 (38) at different temperature (PE: Pt/ZSM-5 =1:6)

Temperature (℃)	Gas Product (%)	Liquid Product (%)	Aromatics in Liquid Products (%)	Solid [a] Product (%)	Total Yield (%)
350	15.9	51.2	41.9	25.8	92.9
450	30.9	62.3	61.8	5.0	98.2
500	32.9	60.5	60.2	3.6	97.0
550	31.7	59.7	59.4	2.6	94.0
600	31.2	54.0	53.6	2.7	87.9

[a] Quantitation of carbon was measured on VARIO EL CUBE Elemental analyzer.

Table S11. Carbon yield of polyethylene catalytic depolymerization with Pt/ZSM-5 (38) at 450 ℃ (PE: Pt/ZSM-5 =1:6)

Products (Total Yield (%))	**Chemicals**	**Yield (%)**
Gas product (30.9)	Methane	3.6
	Ethane	0.4
	Ethylene	5.1
	Propane	8.3
	Propylene	4.9
	Isobutane	1.3
	N-butane	3.6
	N-butene	0.7
	Isobutene	2.3
	2-Butylene	0.7
Liquid product (62.3)	Aliphatic hydrocarbon	0.1
	Alicyclic hydrocarbon	0.4
	Benzene	5.5
	Toluene	24.2
	Ethylbenzene	1.1
	Xylene	22.7
	Another Monocyclic Aromatic Hydrocarbon	2.0
	Polycyclic Hydrocarbons	6.3
Solid product [a]	Char and Coke	5.0

[a] Quantitation of carbon was measured on VARIO EL CUBE Elemental analyzer.

Table S12. Comparison of product distribution from catalytic pyrolysis of PE film (food grade) and PE powder over the Pt/ZSM-5 (38) at 450 ℃ (PE: Pt/ZSM-5 =1:6)

Feedstock	Yield of gas product (%)	Yield of liquid product (%)	Yield of solid [a] product (%)	Yield of aromatics (%)	Yield of BTX (%)
PE powder (Sigma-Aldrich)	30.9	62.3	5	61.8	52.4
PE film, food grade (MIAOJIE)	38.6	59.8	2.7	59.7	53.2

[a] Quantitation of carbon was measured on VARIO EL CUBE Elemental analyzer.

Table S13. BTX yield during recyclability test for the catalytic pyrolysis of PE over the Pt/ZSM-5 (38) at 400 ℃ (PE: Pt/ZSM-5 =1:6)

Test	Benzene (%)	Toluene (%)	Xylene (%)	BTX (%)
Run1	5. 9	26.7	29.0	61.6
Run2	7.2	23.2	26.8	57.1
Run3	7.7	21.1	24.1	52.9
Run4	7.3	20.6	25.5	53.3

Supporting Figures

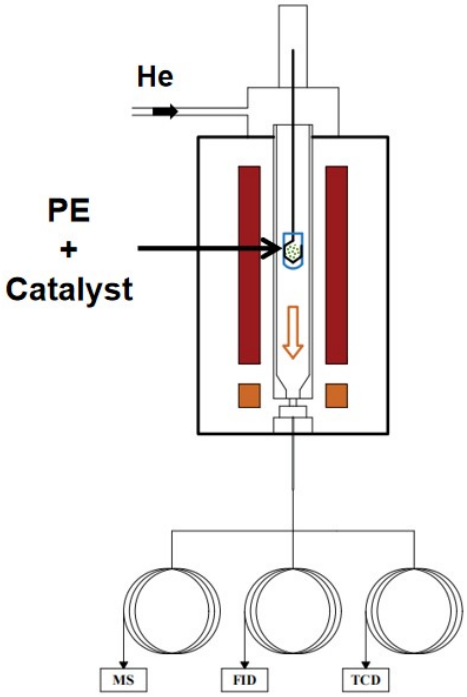

Figure S1. The configuration of pyrolysis in micropyrolyzer with online GC/MS-FID-TCD

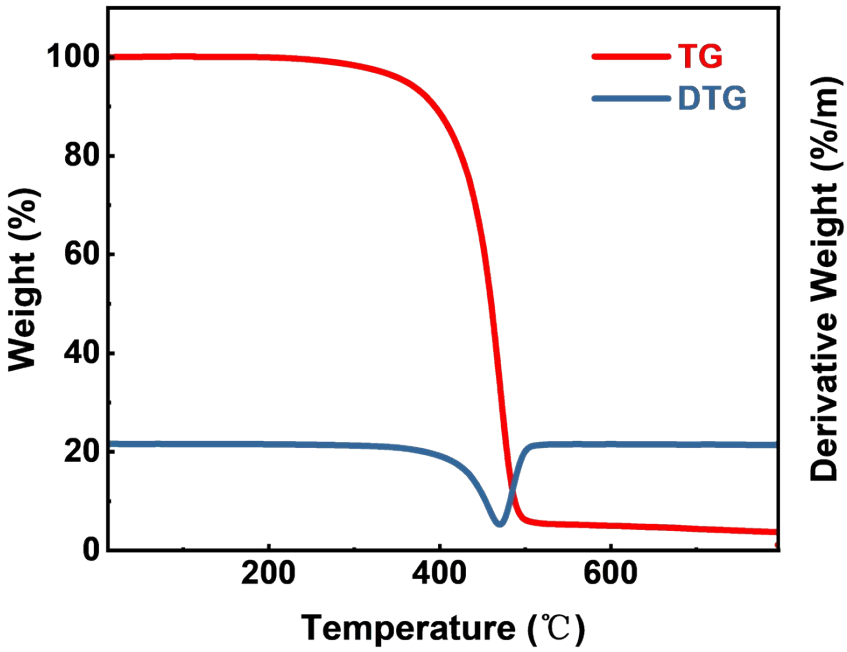

Figure S2. Thermogravimetric analysis of PE in N_2 atmosphere

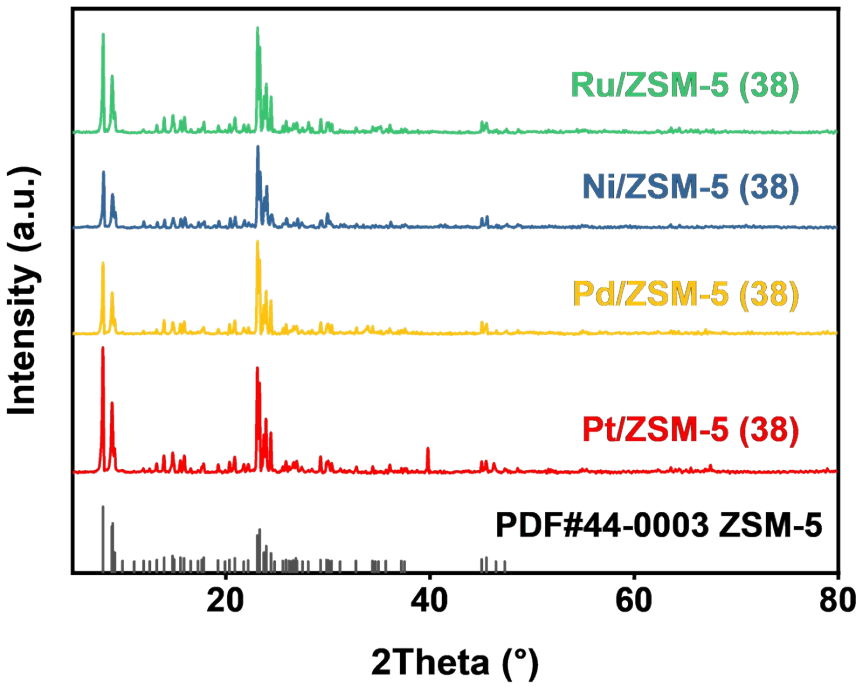

Figure S3. XRD patterns of ZSM-5 (38) catalysts supported by Pt, Pd, Ni and Ru

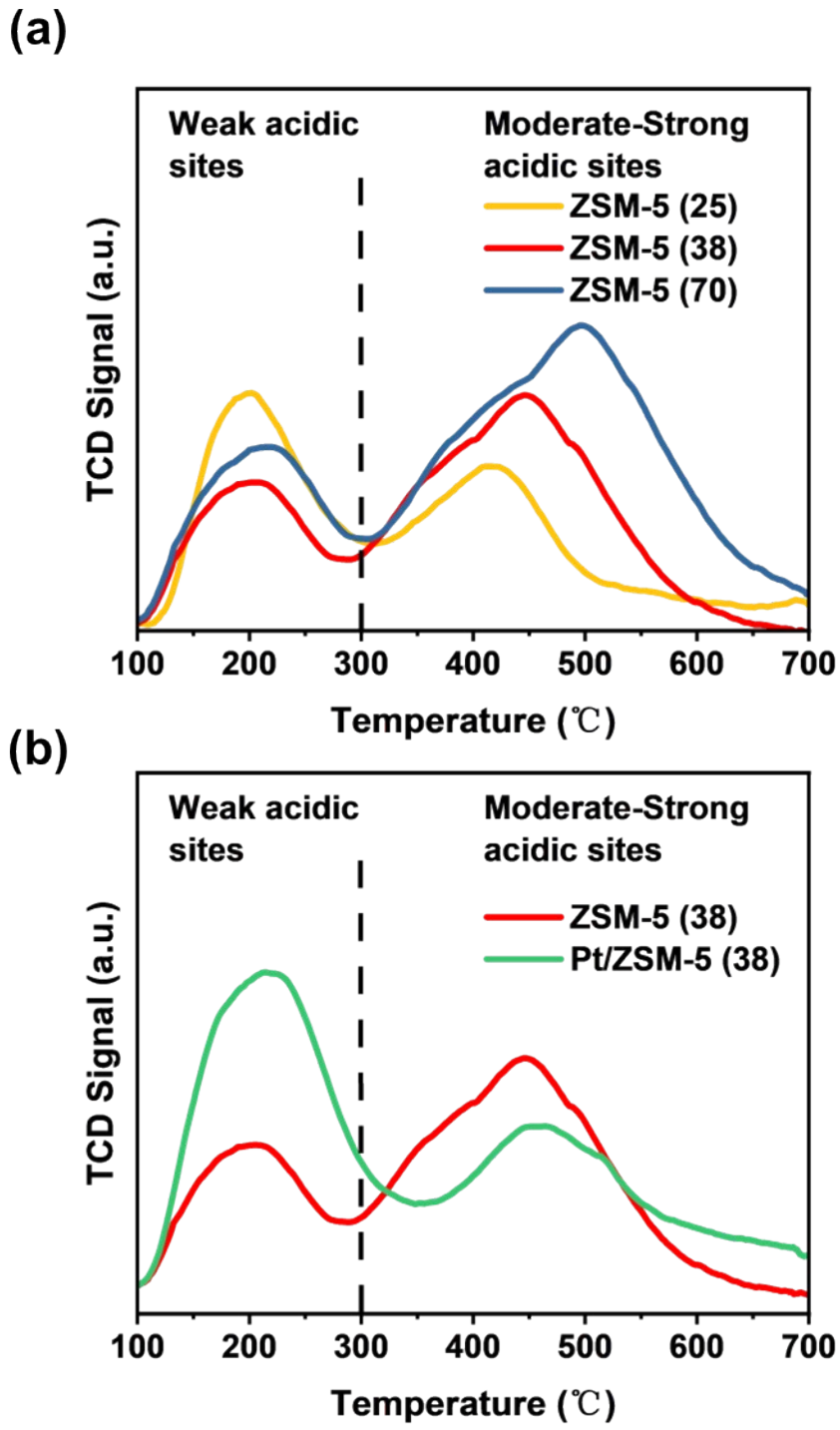

Figure S4. NH_3-TPD profiles of (a) ZSM-5 with different SiO_2/Al_2O_3 ratios and (b) Pt/ZSM-5 (38) catalysts

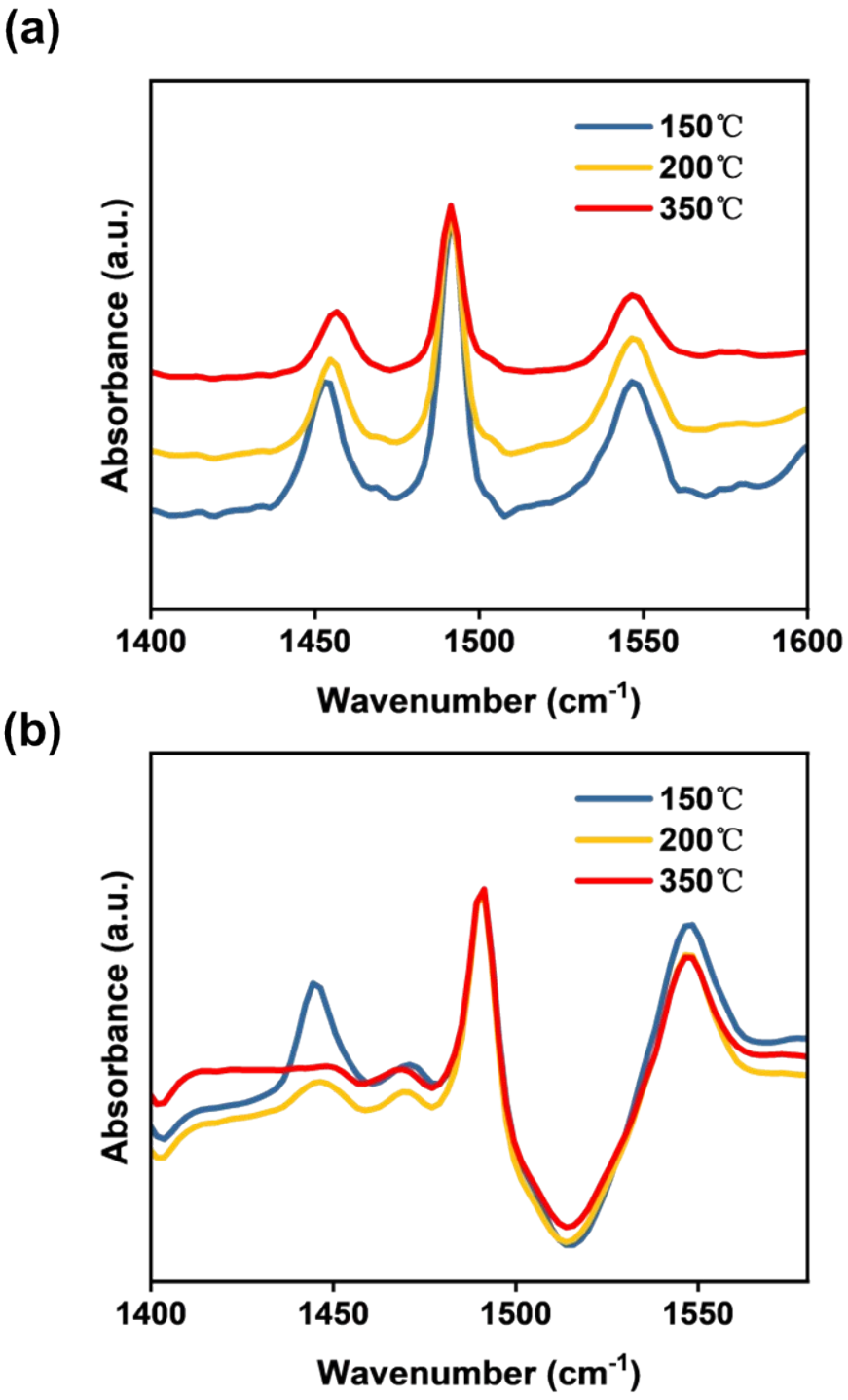

Figure S5. Pyridine-IR spectra of (a) ZSM-5 (25) and (b) ZSM-5 (70) catalysts

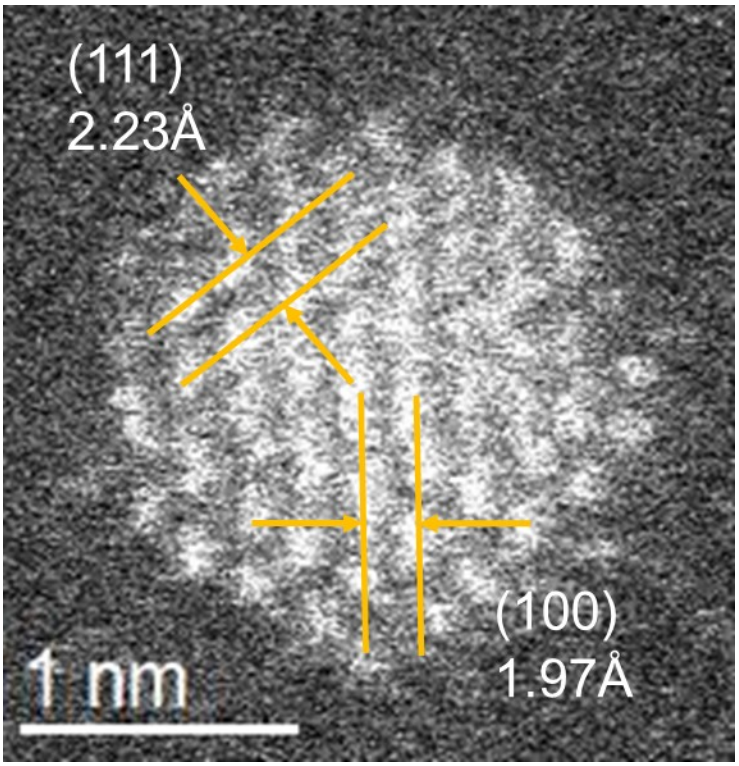

Figure S6. AC-HAADF-STEM image of Pt nanoparticle

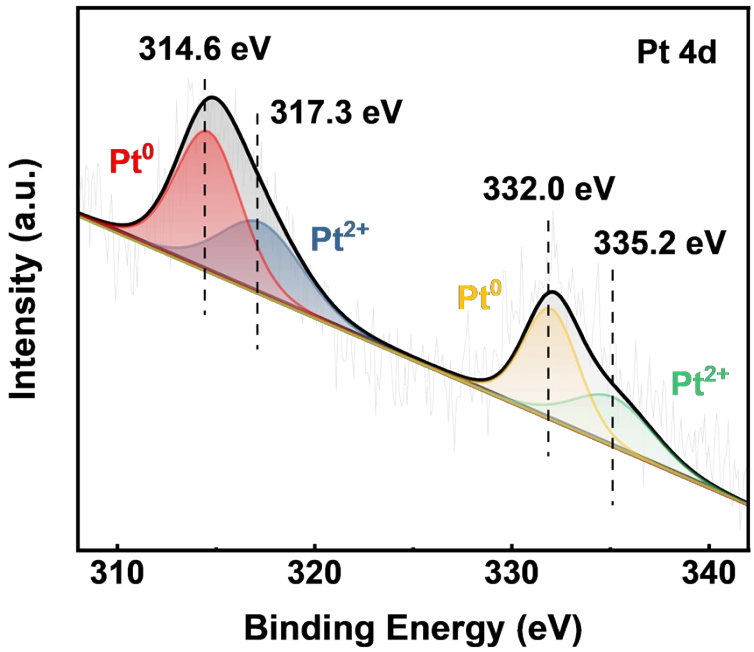

Figure S7. XPS analysis of Pt/ZSM-5 (38) catalyst of Pt $4d_{3/2}$ and $4d_{5/2}$

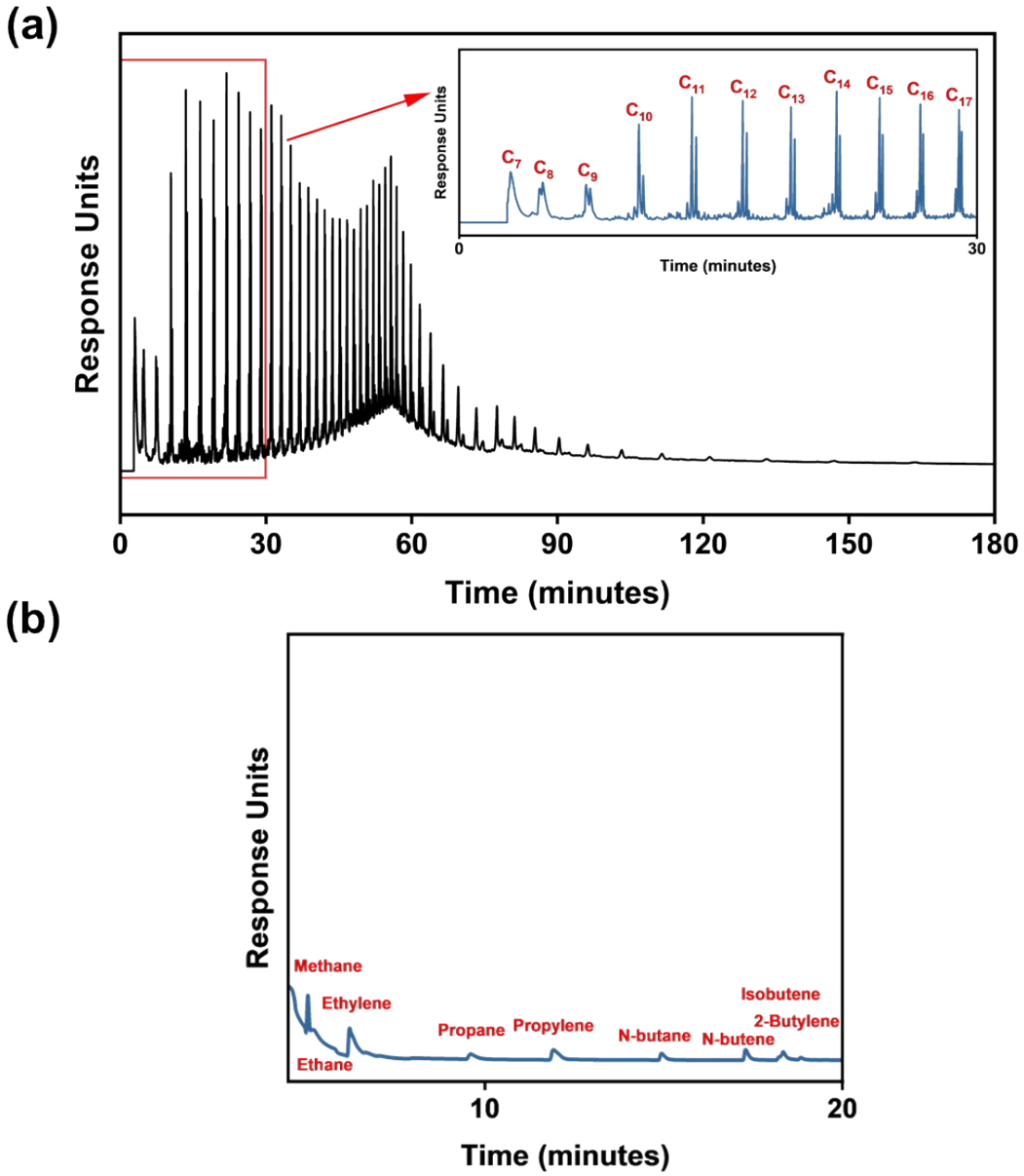

Figure S8. (a) FID and (b) TCD spectrogram analysis of PE pyrolysis at 500 ℃

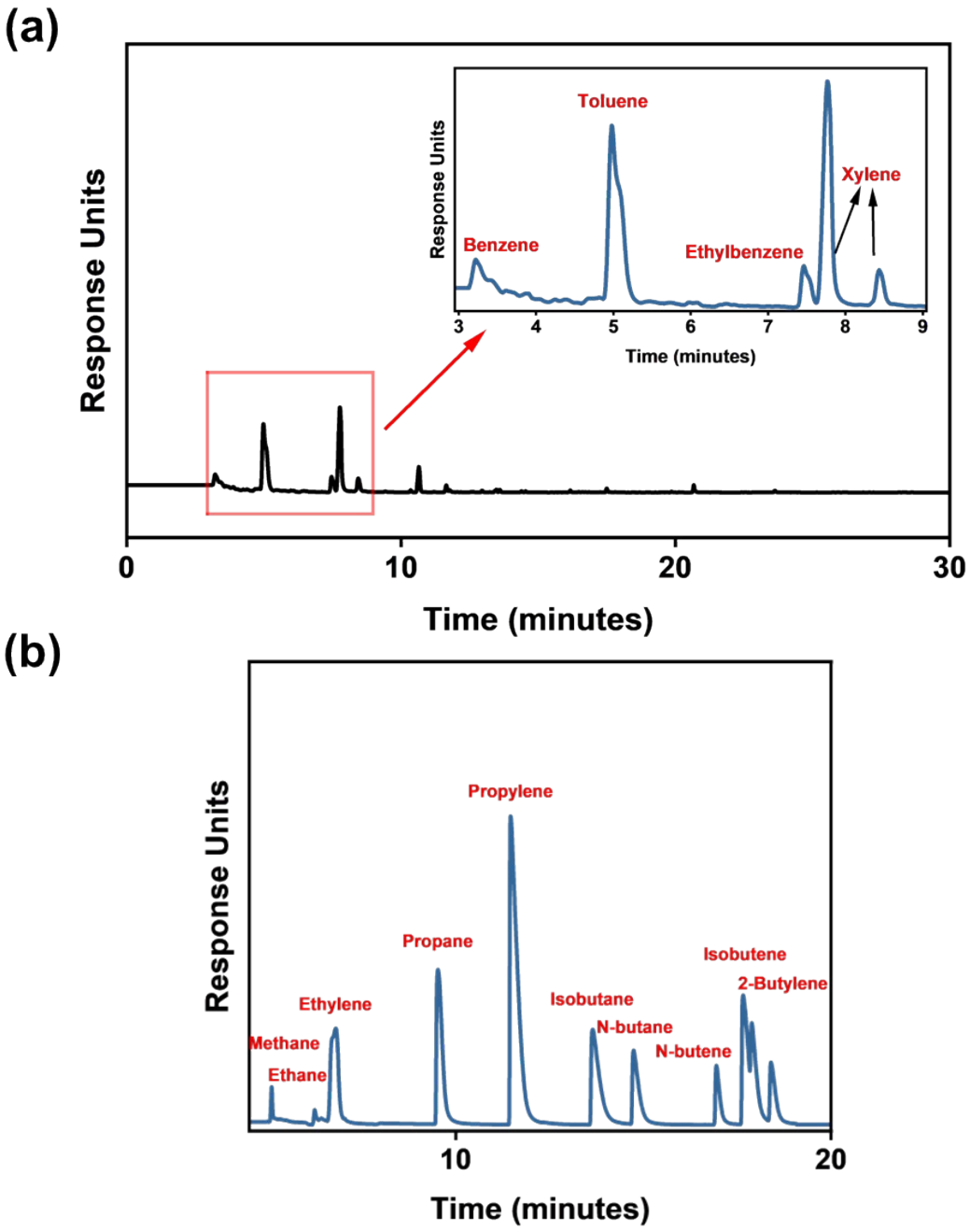

Figure S9. (a) FID and (b) TCD spectrogram analysis of PE catalytic cracking with ZSM-5 (38) catalyst at 450 ℃

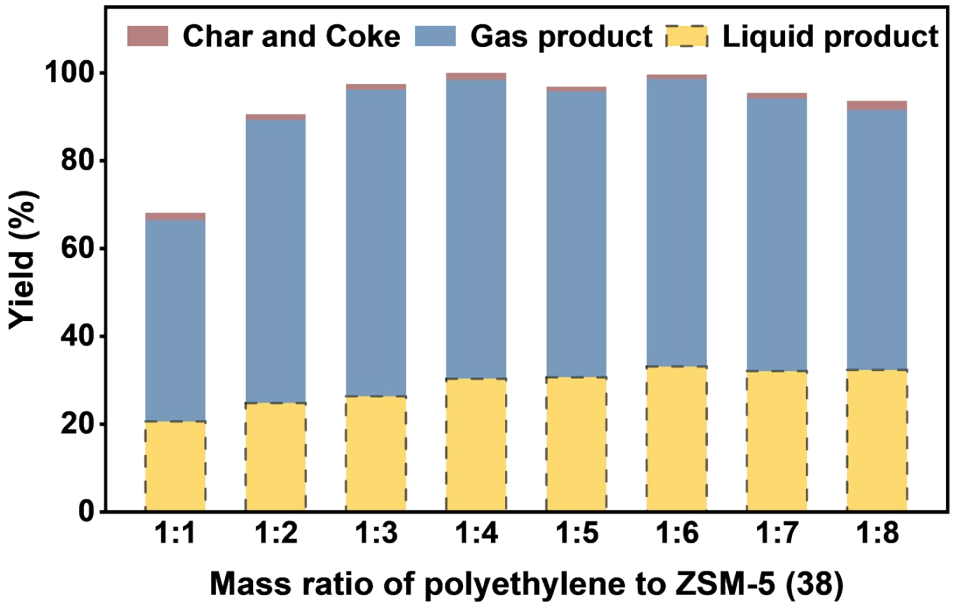

Figure S10. Product distribution of different proportions of PE and ZSM-5 (38) catalyst at 500 ℃

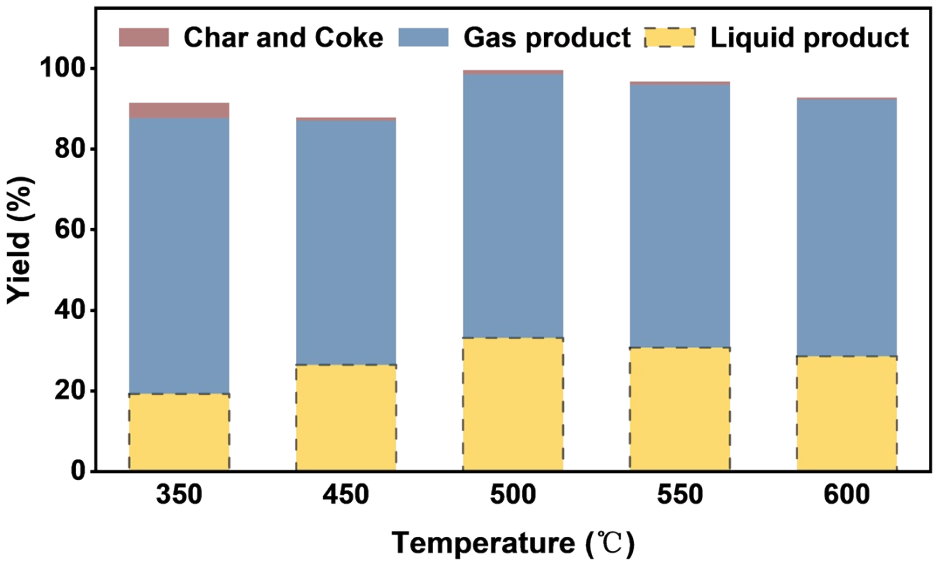

Figure S11. Product distribution of PE and ZSM-5 (38) catalyst at different catalytic pyrolysis temperatures (PE: Catalyst =1:6)

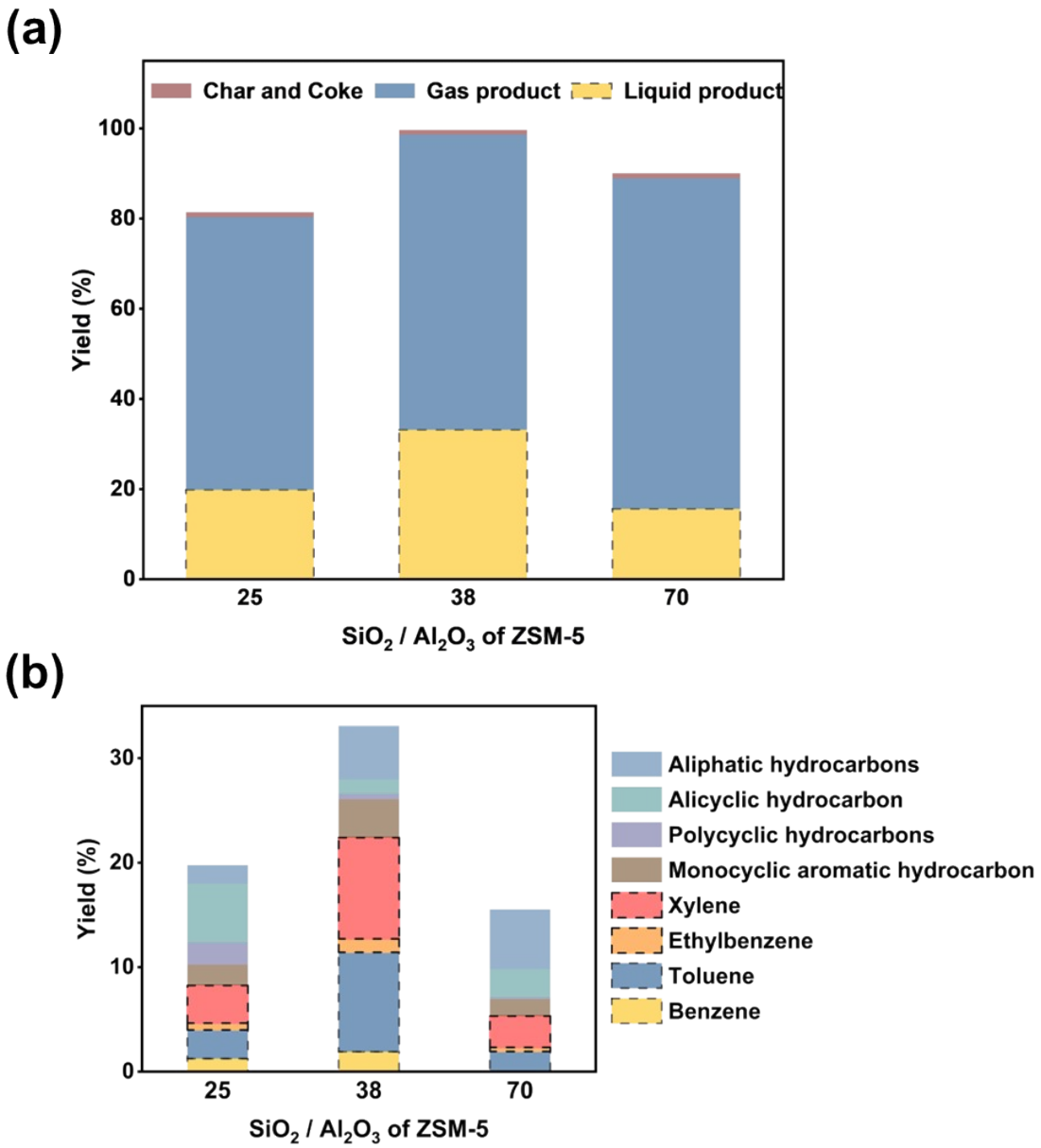

Figure S12. (a) Total product distribution and (b) liquid product distribution of PE and ZSM-5 catalysts with different SiO_2/Al_2O_3 ratios (500 °C, PE: ZSM-5 =1:6)

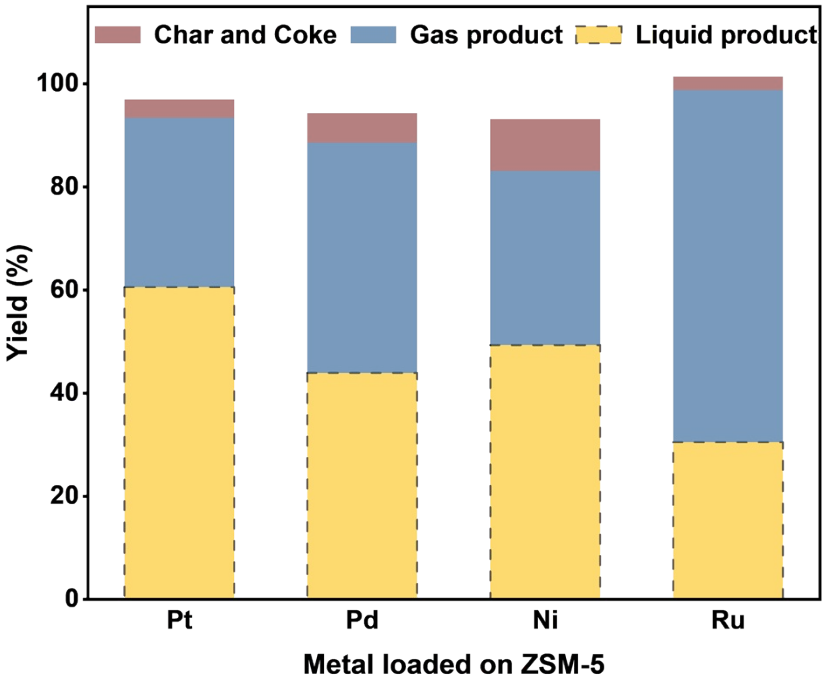

Figure S13. Product distribution of PE and ZSM-5 catalysts loaded with different metal (500 ℃, PE: Catalyst =1:6) The metal loadings of Pt, Pd, and Ni on ZSM-5 are 1.4%, 1.6%, and 1.9%, respectively.

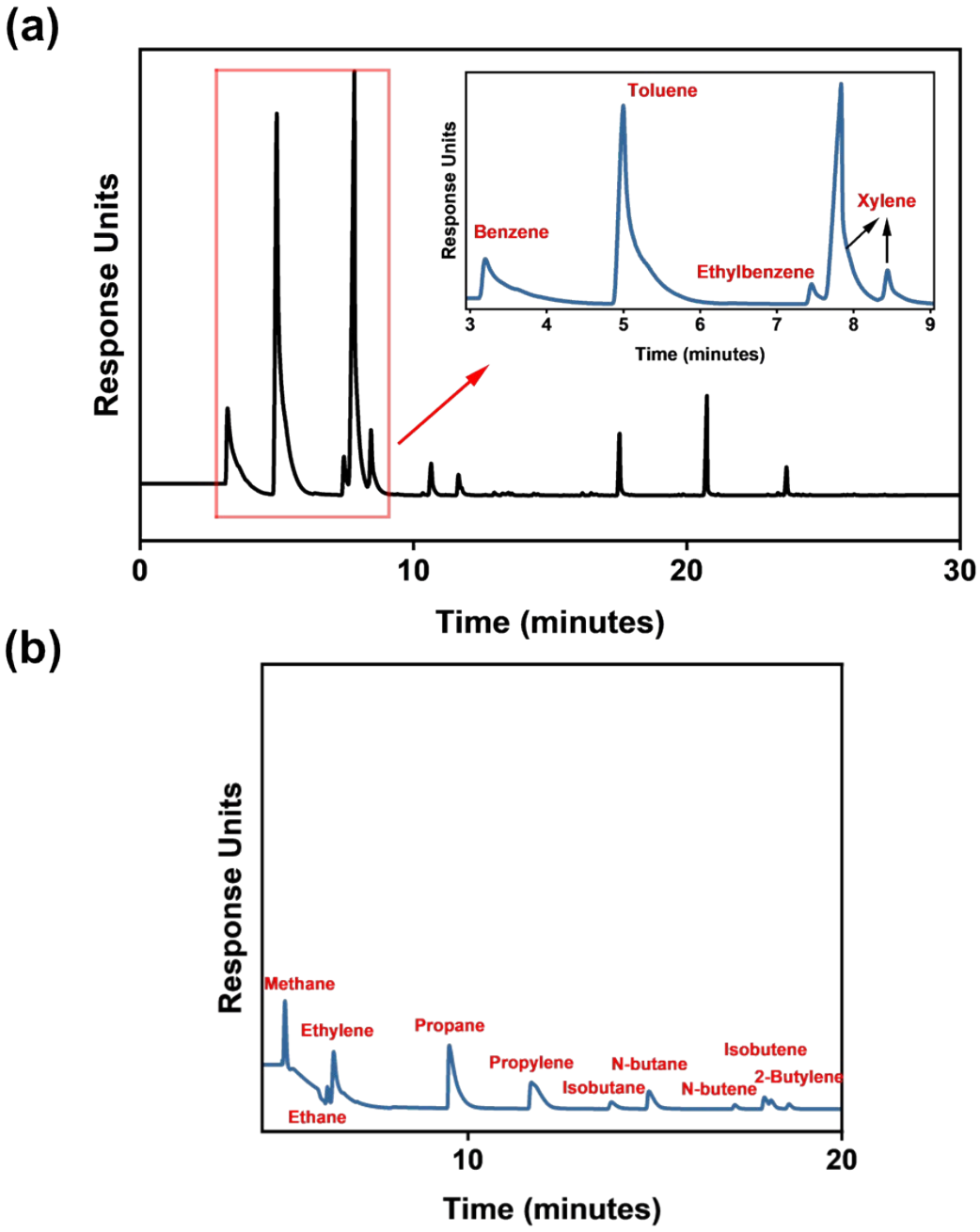

Figure S14. (a) FID and (b) TCD spectrogram analysis of PE catalytic cracking with Pt/ZSM-5 (38) catalyst at 450 ℃

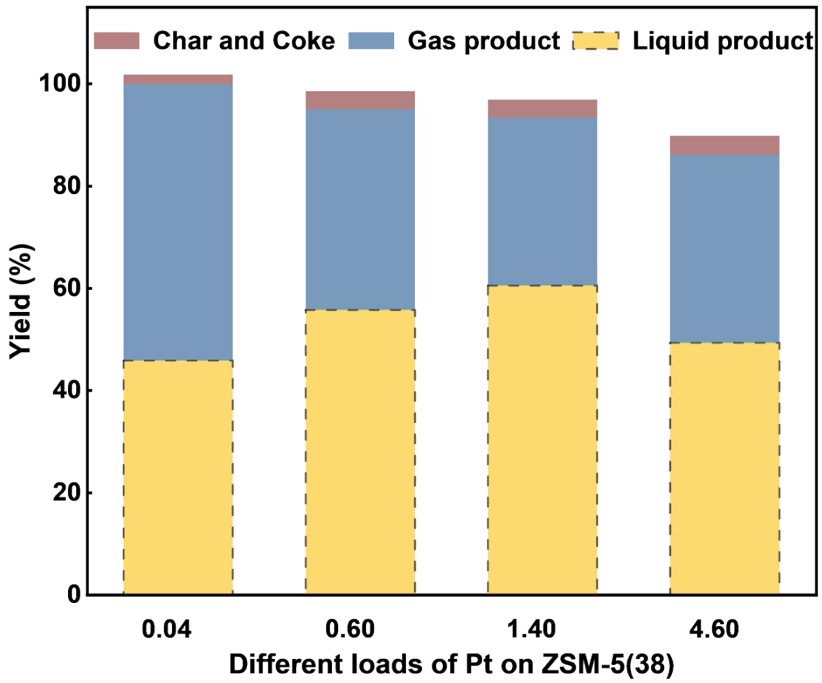

Figure S15. Product distribution of PE and ZSM-5 catalysts with different loads of Pt (500 ℃, PE: Catalyst =1:6) The dispersions of Pt on ZSM-5 (38) are 74.8%, 68.1%, 37.4%, and 22.7%, respectively (from left to right).

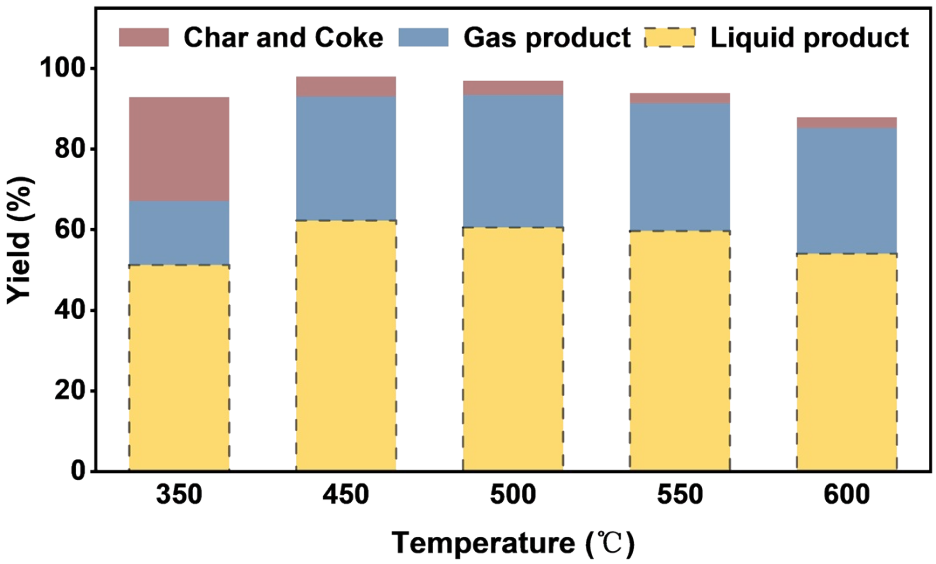

Figure S16. Product distribution of PE and Pt/ZSM-5 (38) catalyst at different temperature (PE: Catalyst =1:6)

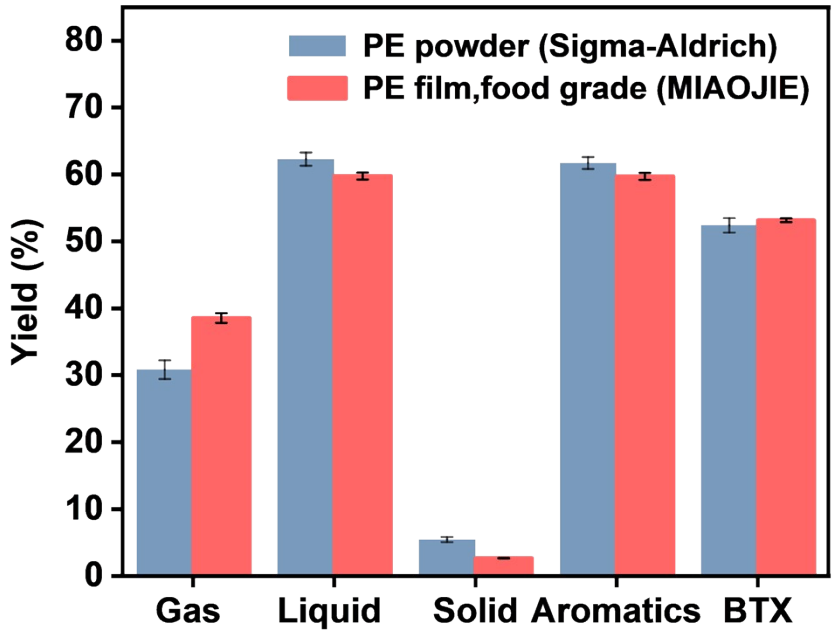

Figure S17. Product distribution from catalytic pyrolysis of different commercial PE over the Pt/ZSM-5(38) at 450°C

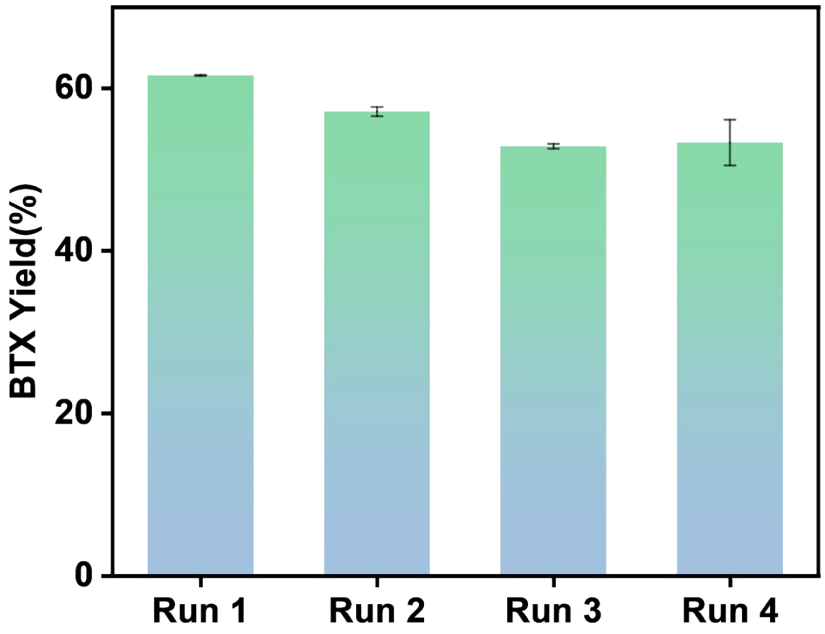

Figure S18. Recyclability test for the catalytic pyrolysis of PE over the Pt/ZSM-5 (38) at 400 ℃

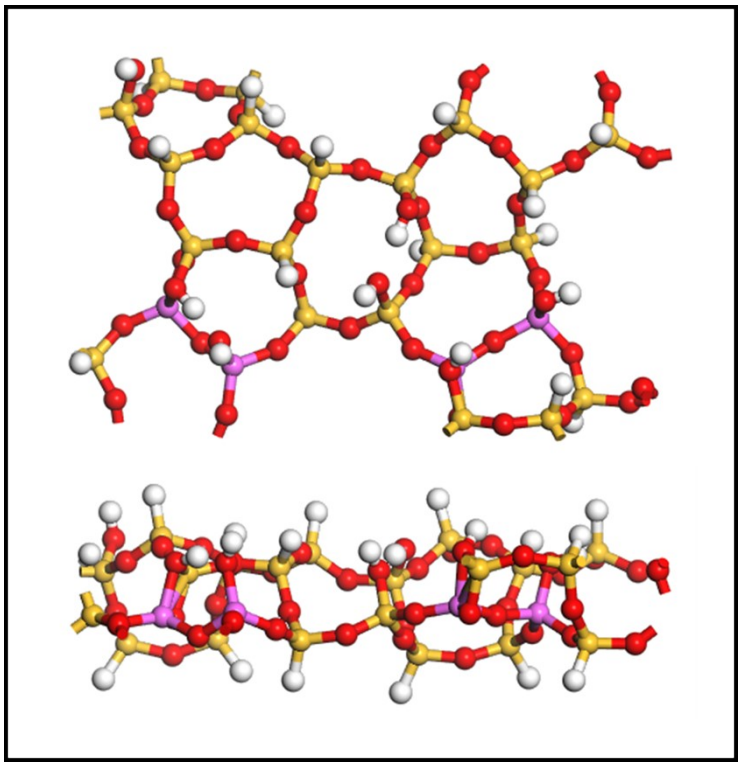

Figure S19. Optimized structure of ZSM-5

(Pink: Al, Yellow: Si, Red: O)

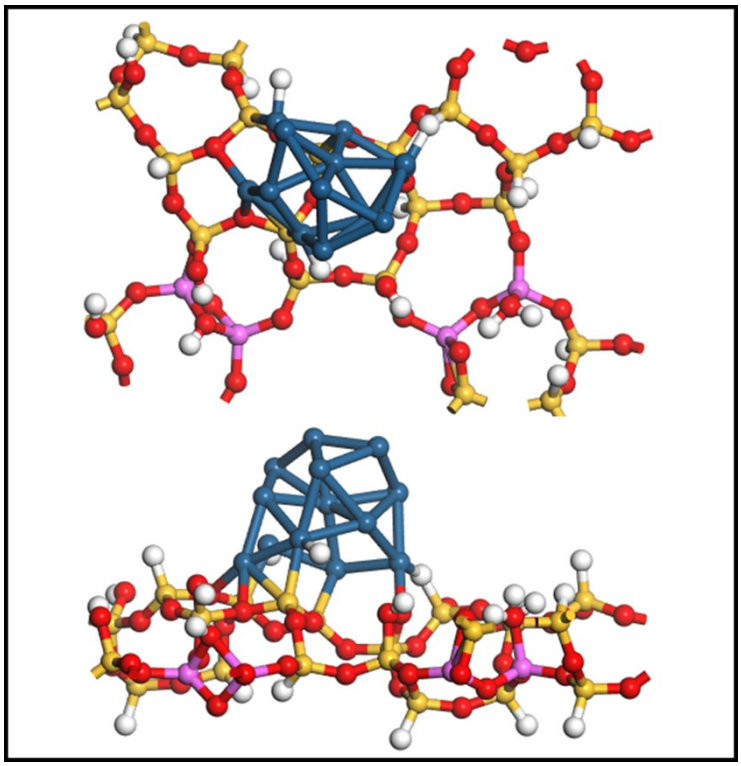

Figure S20. Optimized structure of Pt/ZSM-5

(Pink: Al, Yellow: Si, Red: O, Blue: Pt)

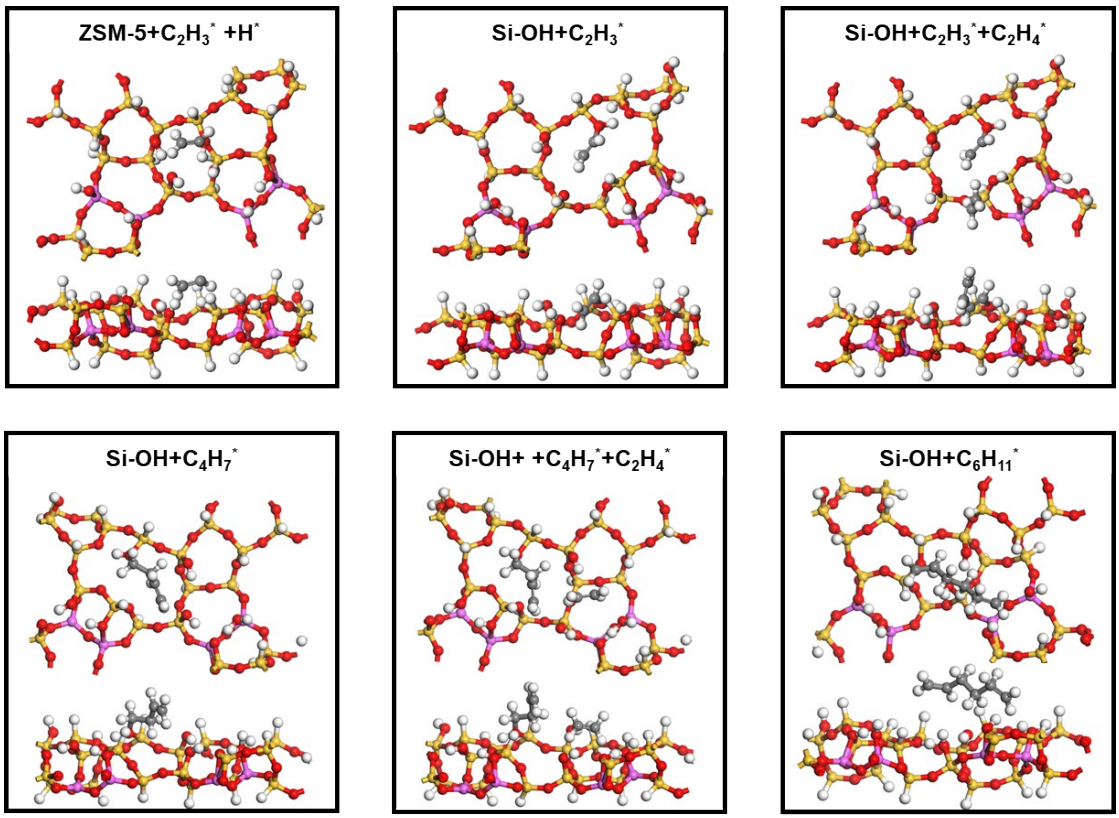

Figure S21. Optimized structures of reactant and intermediates associated with ethane dehydrogenation over ZSM-5

(Pink: Al, Yellow: Si, Red: O, Grey: C, White: H)

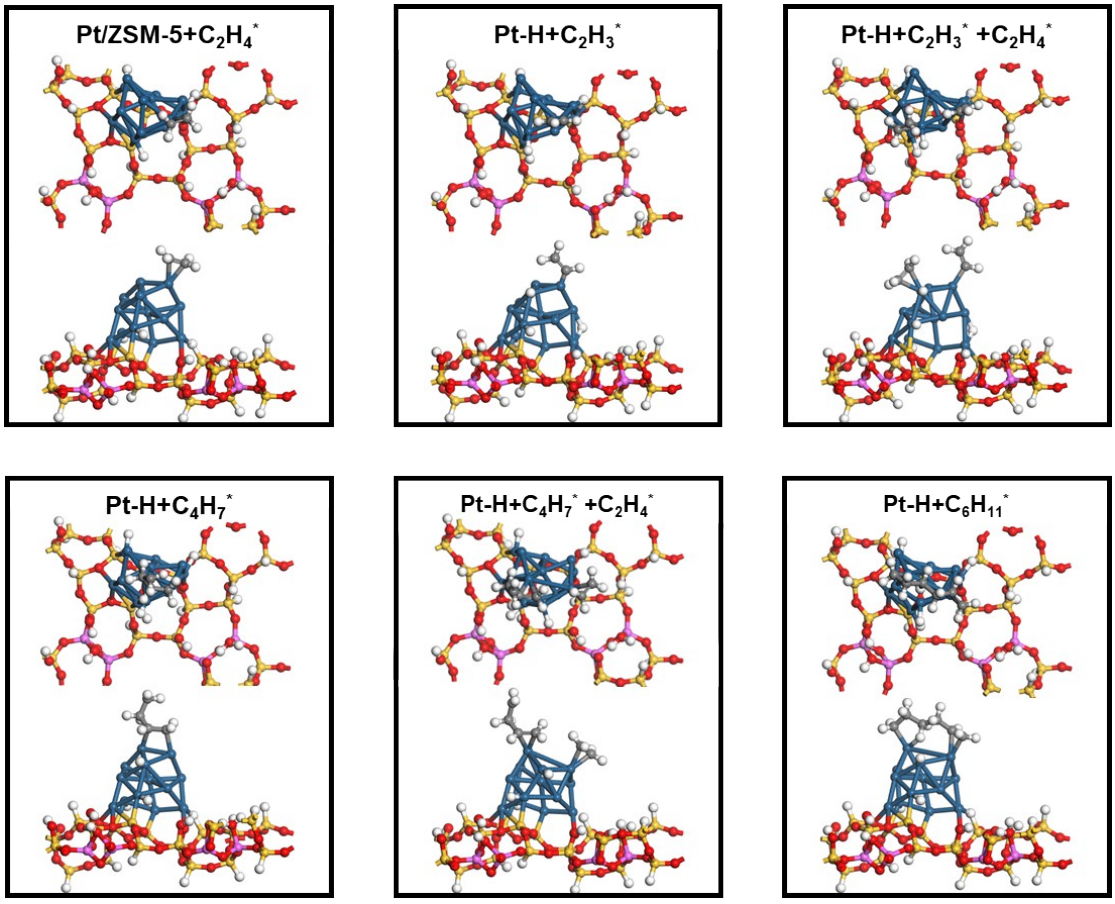

Figure S22. Optimized structures of reactant and intermediates associated with ethane dehydrogenation over Pt/ZSM-5 (Pink: Al, Yellow: Si, Red: O, Grey: C, White: H, Blue: Pt)

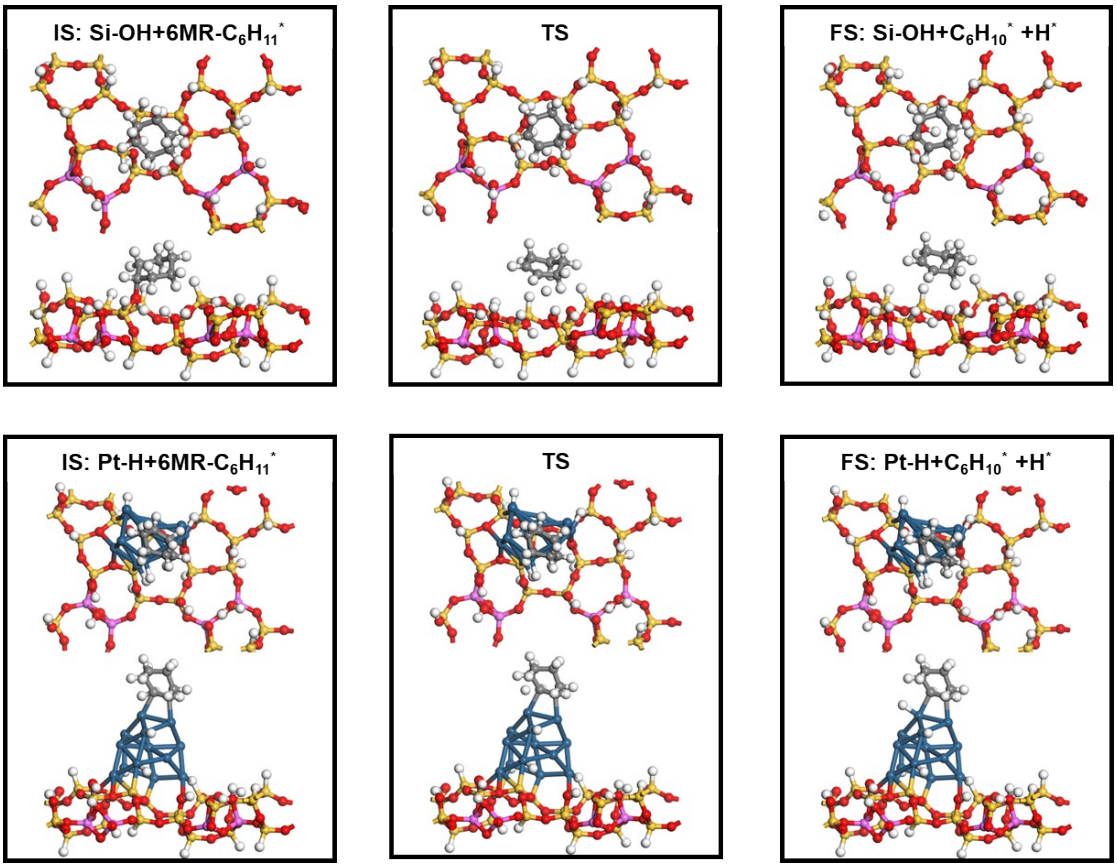

Figure S23. Optimized structures of initial state, transition state and final state associated with ethane dehydrogenation over ZSM-5 (top) and Pt/ZSM-5 (bottom) (Pink: Al, Yellow: Si, Red: O, Grey: C, White: H, Blue: Pt)