Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary material

Selective production of aromatics from CO_2

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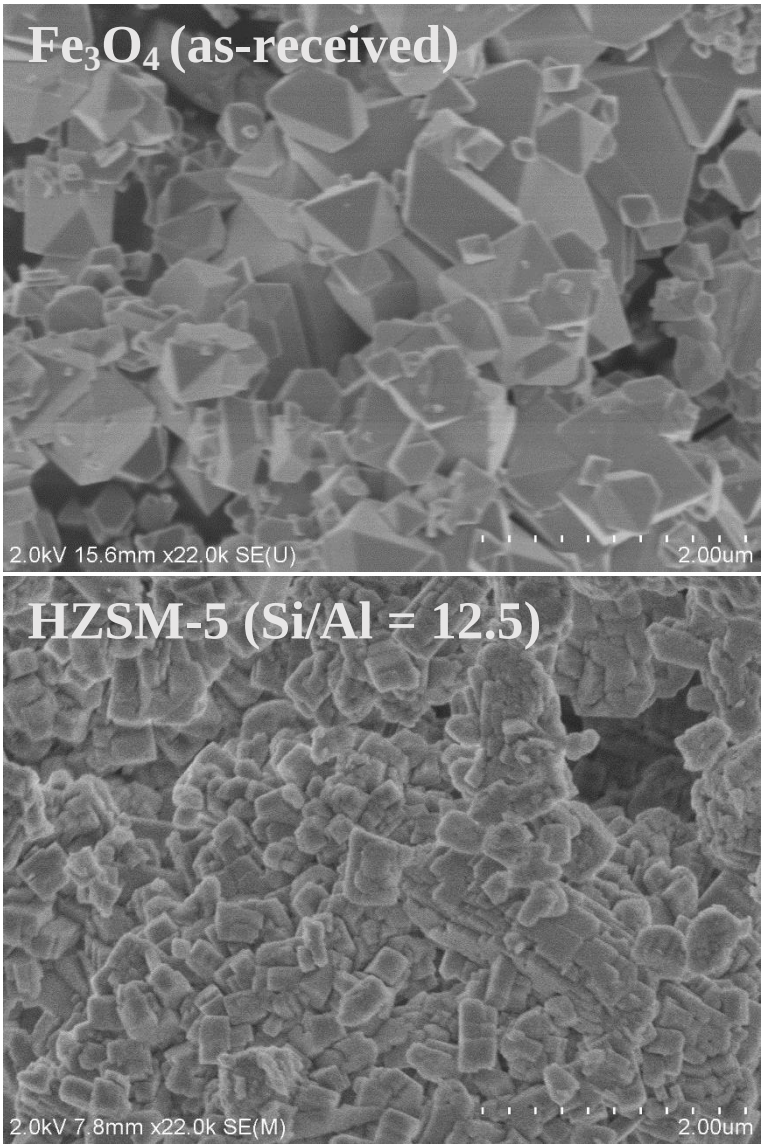

Fig. S1. SEM observations of Fe_3O_4 and HZSM-5 (Si/Al = 12.5).

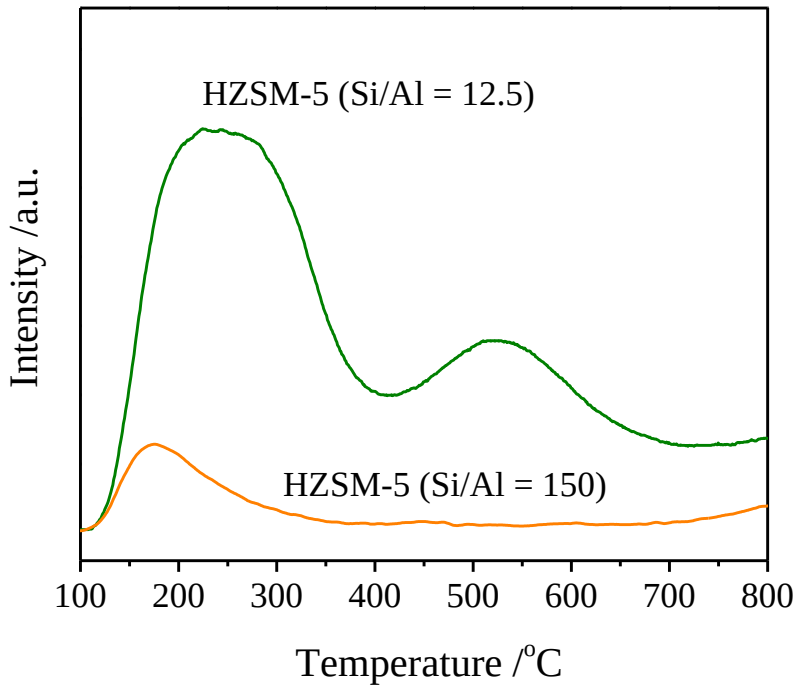

Fig. S2. NH_3-TPD profiles of fresh HZSM-5 zeolites.

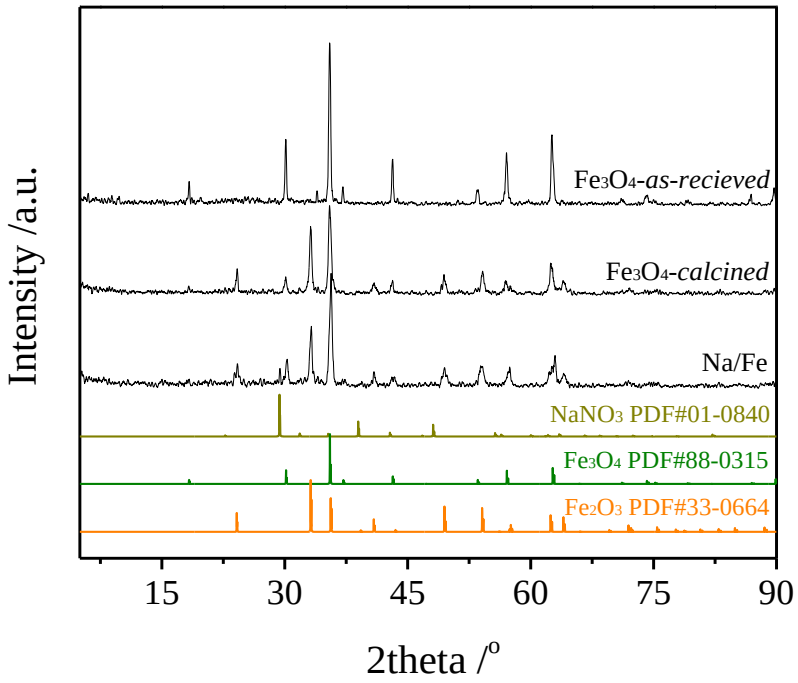

Fig. S3. XRD patterns of as-received and calcined Fe_3O_4 and Na/Fe_3O_4.

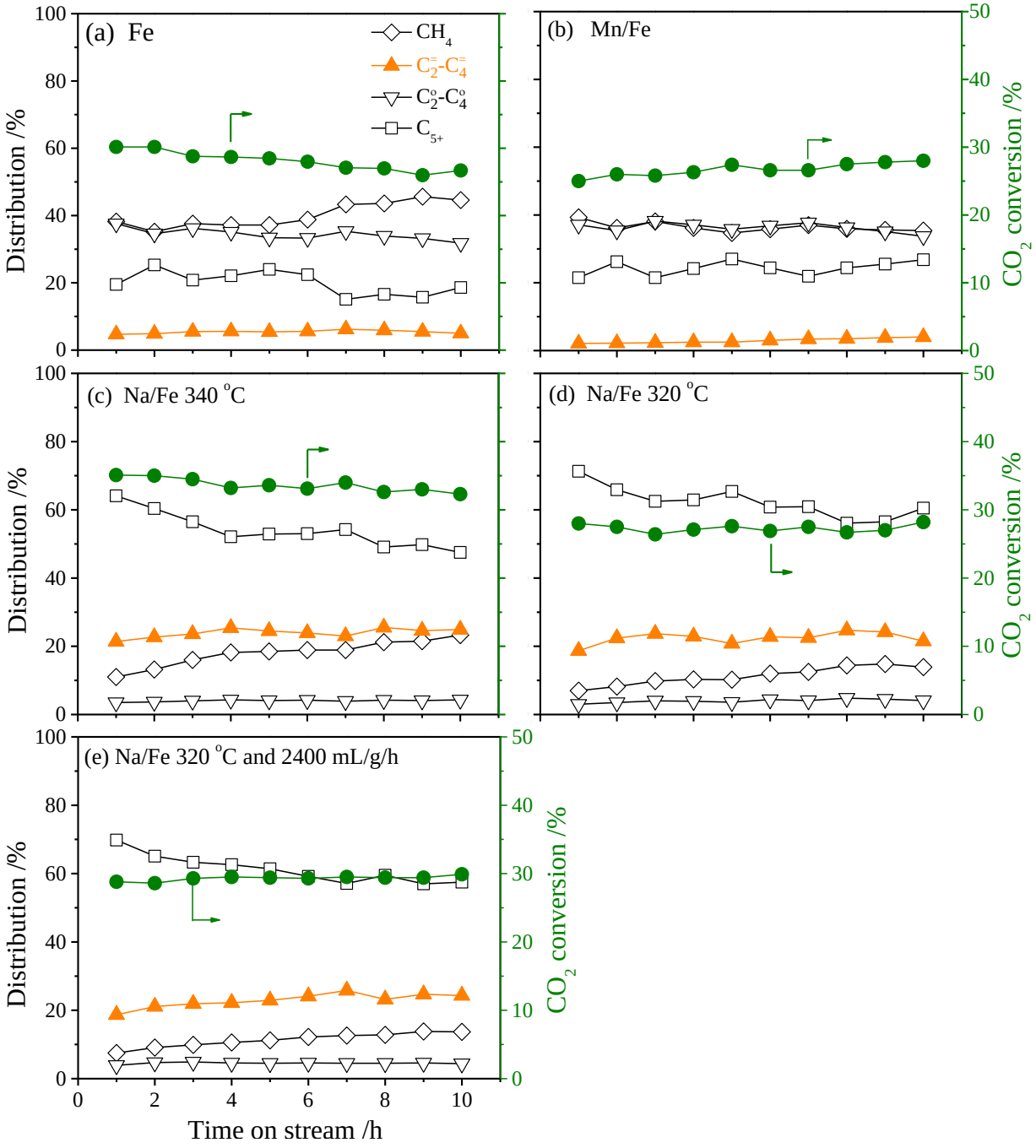

Fig. S4. Time-dependences of CO_2 conversion and hydrocarbon distribution obtained over (a) Fe, (b) Mn/Fe and (c) Na/Fe catalysts at 340 ℃, 1 MPa, 4800 mL g^{-1} h^{-1} and H_2/CO_2 ratio of 3, and (d) Na/Fe catalyst at 320 ℃ and (e) Na/Fe catalyst at 320 ℃ and 2400 mL g^{-1} h^{-1}.

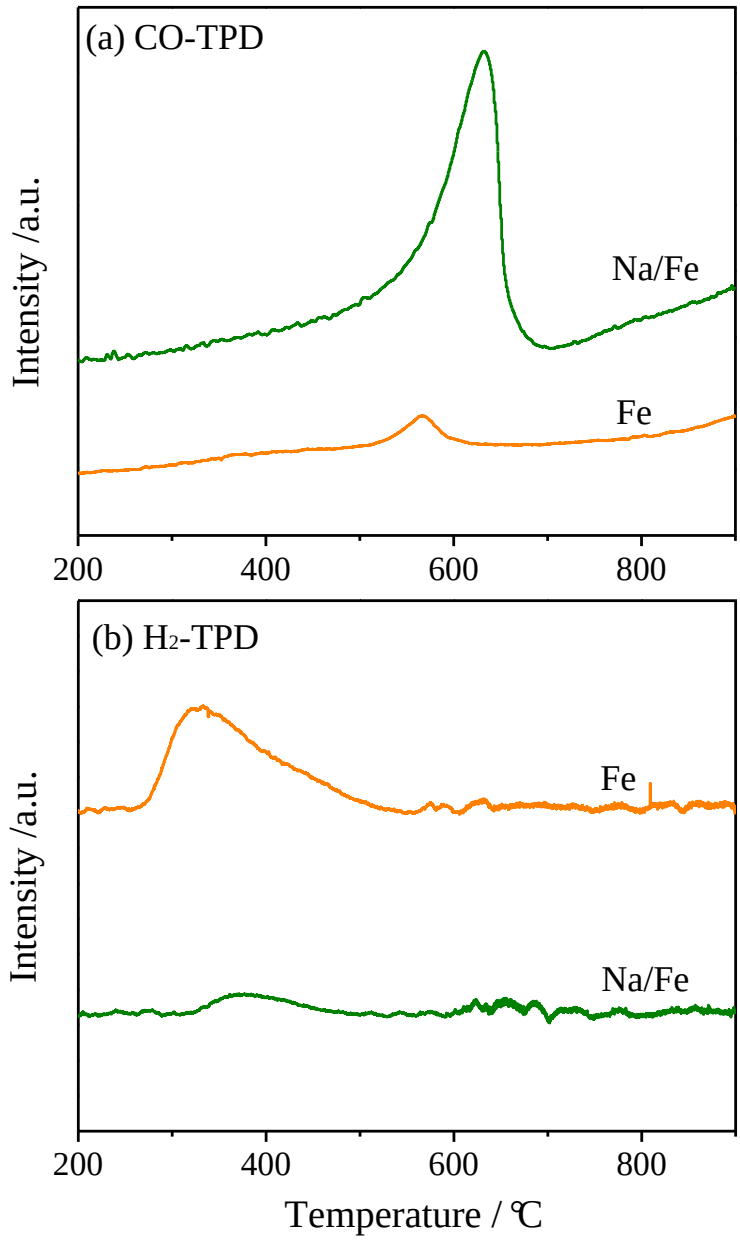

Fig. S5. CO-TPD and H_2-TPD profiles of reduced Fe and Na/Fe catalysts.

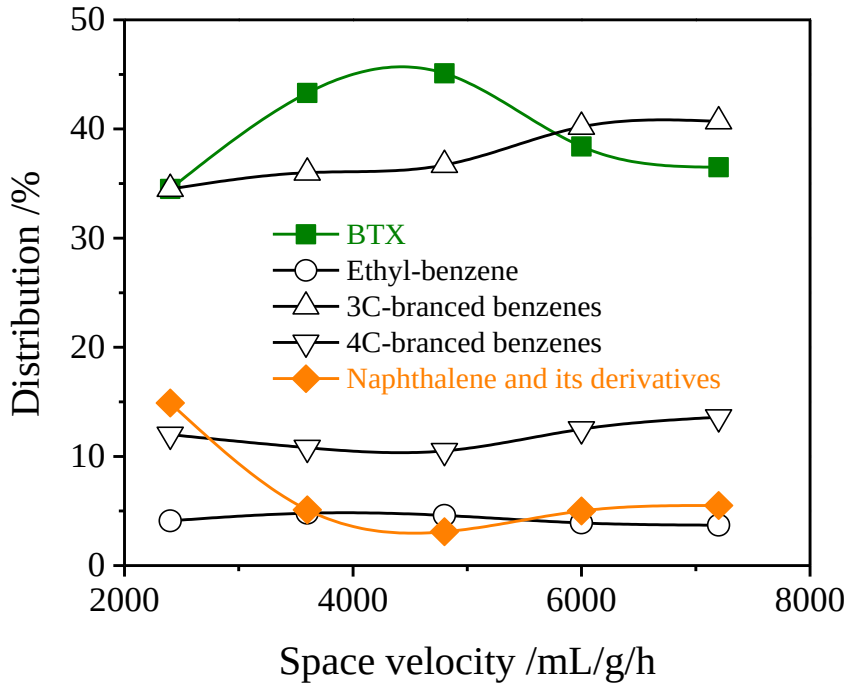

Fig. S6. Aromatic distribution obtained at different space velocities over the composite Na/Fe and HZSM-5 (Si/Al = 12.5) catalyst system.

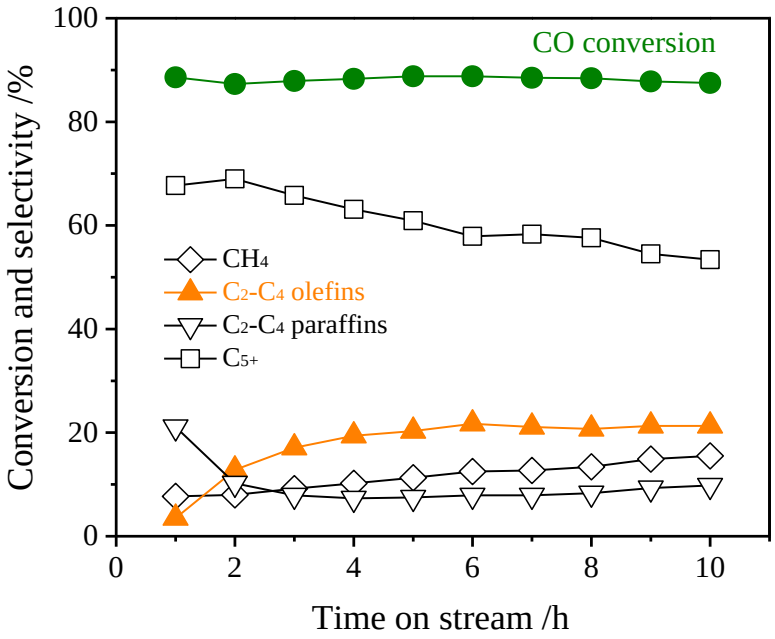

Fig. S7. Catalytic hydrogenation of CO (time-dependence of CO conversion and the CO_2-free selectivities to CH_4, $C_2^{=}$-$C_4^{=}$, C_2^{0}-C_4^{0} and C_{5+}) over the composite Na/Fe and HZSM-5 (Si/Al = 12.5) catalyst system at the conditions of 340 ℃, 1 MPa, 4800 mL g^{-1} h^{-1} and $H_2/CO = 2$.

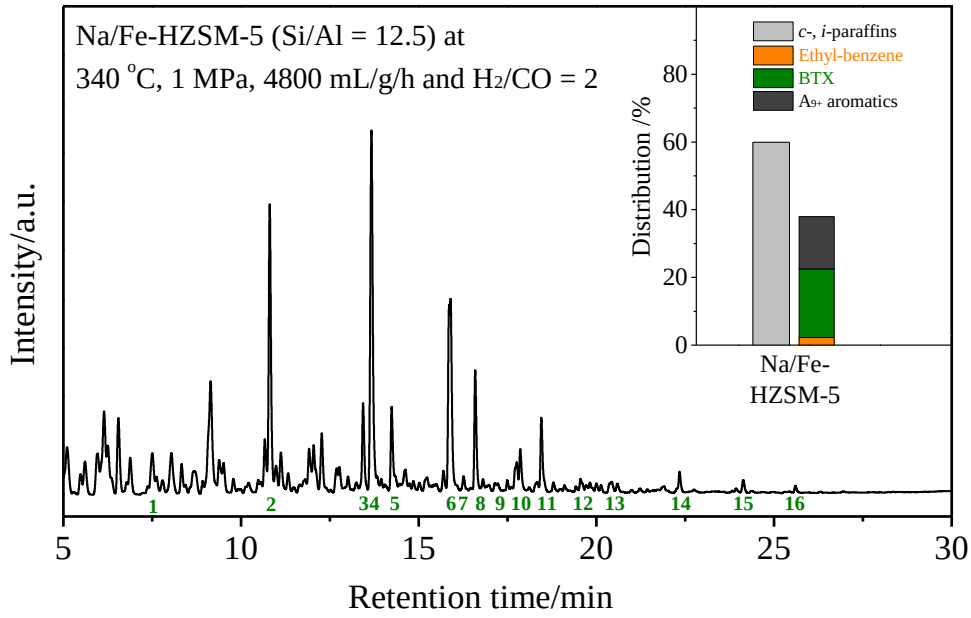

Fig. S8. GC spectrum of liquid hydrocarbon obtained from CO hydrogenation over the composite Na/Fe and HZSM-5 catalyst system at 340 ℃, 1 MPa, 4800 mL g^{-1} h^{-1} and $H_2/CO = 2$. The numbers of 1-16 present the aromatic hydrocarbons whose names are same with those in Fig. 5 in main text. The inserted figure shows the distribution of hydrocarbons by integration of the GC spectrum.

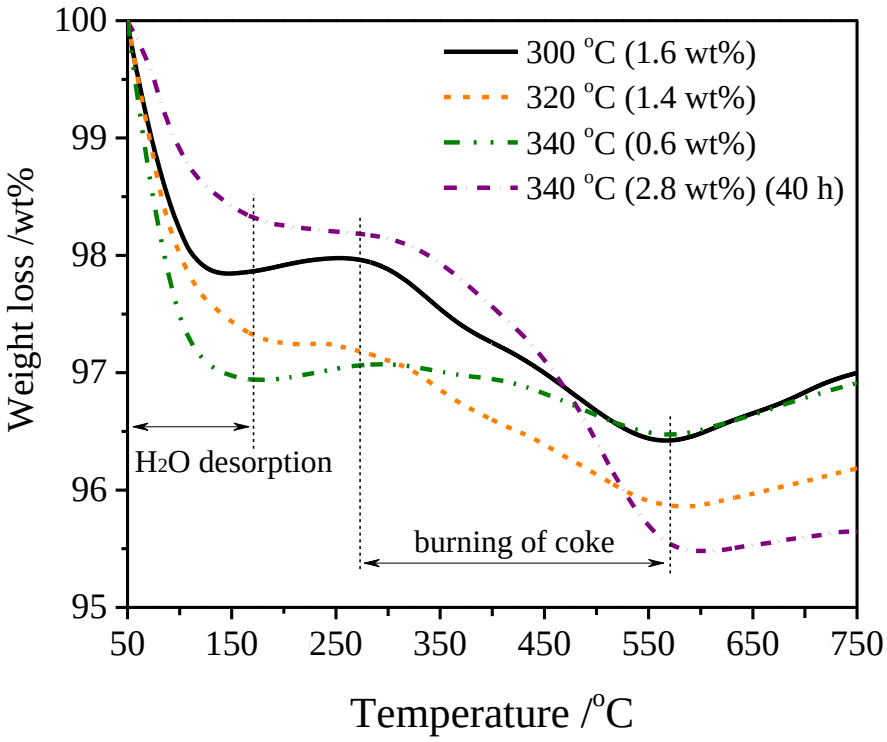

Fig. S9. TG profiles of spent HZSM-5 samples collected from tests over the composite Na/Fe and HZSM-5 (Si/Al = 12.5) catalyst system at different reaction temperatures. The first stage of weight loss is attributed to H_2O desorption and the second one is the burning of coke which is used to calculate the coke content in sample (wt%).

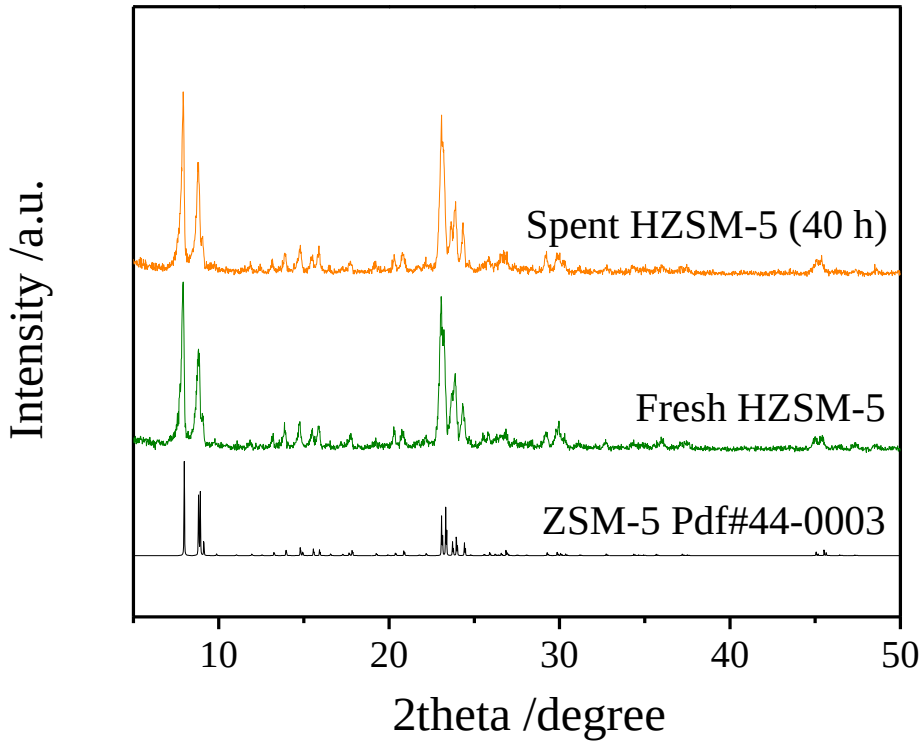

Fig. S10. XRD patterns of fresh HZSM-5 and the spent one collected after 40 h reaction (Fig. 8 in main text).

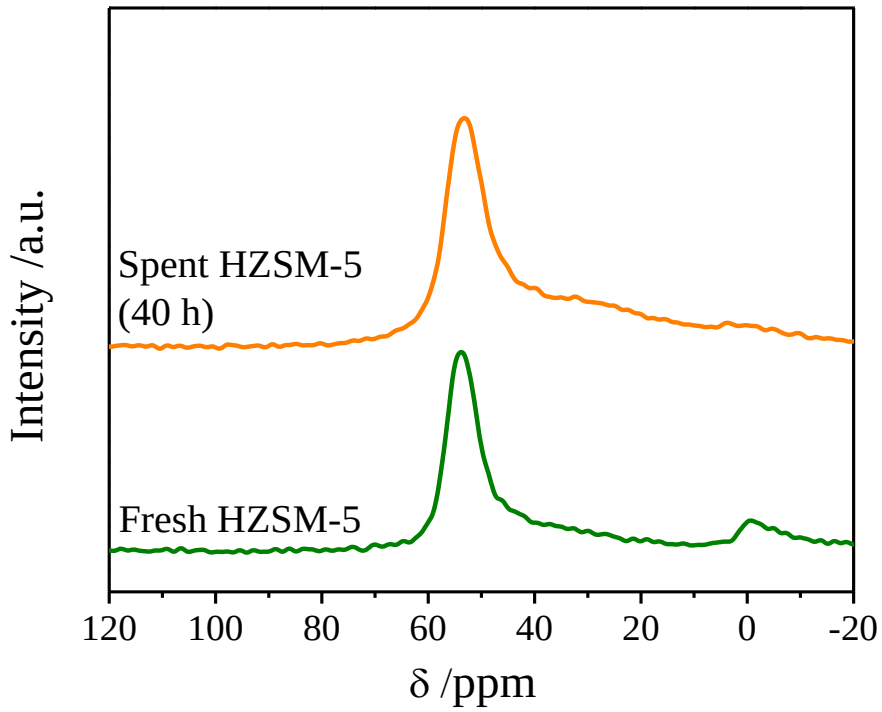

Fig. S11. ^{27}Al NMR spectrum of fresh HZSM-5 zeolite and the spent one collected from the 40-h reaction (Fig. 8 in main text).

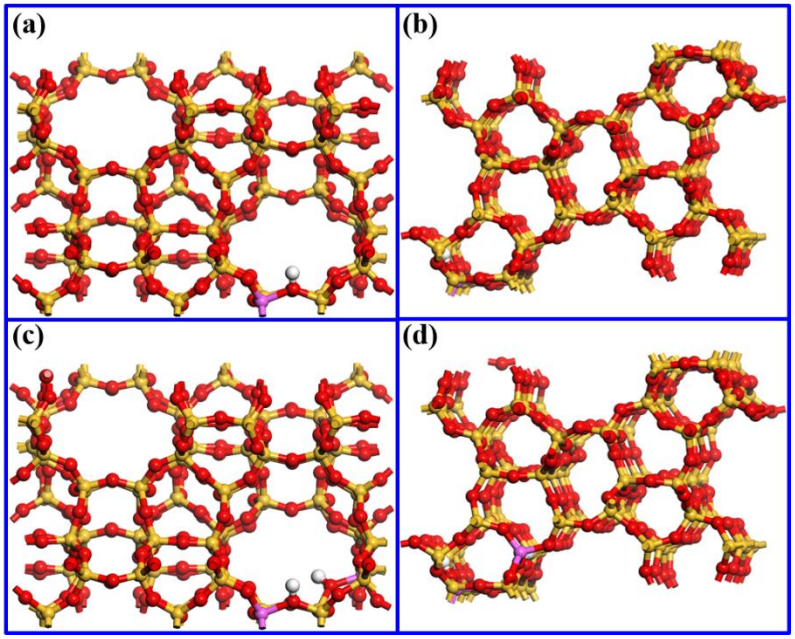

Fig. S12. Front and side views of HZSM-5 (a) and (b) and 2HZSM-5 (c) and (d). Red: O atoms; yellow: Si atoms; purple: Al atoms; white: H atoms.

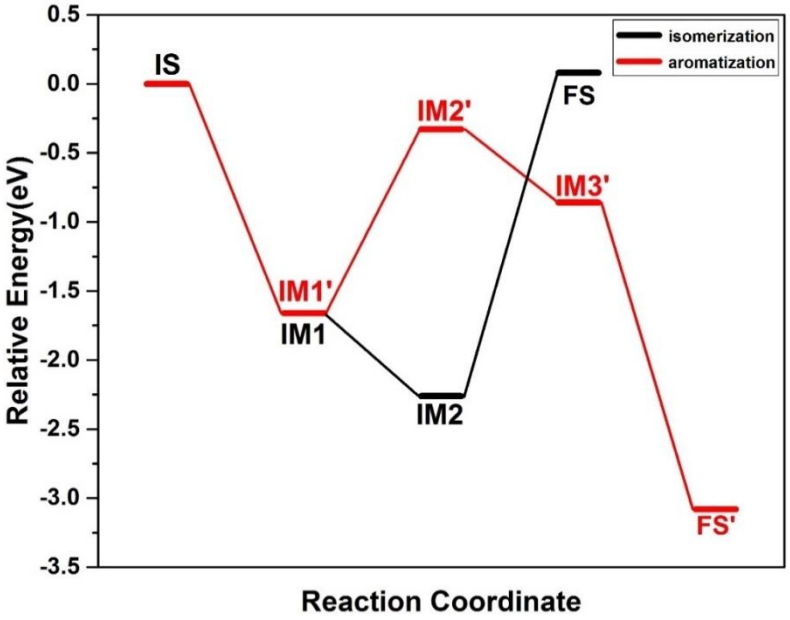

Fig. S13. Calculated energy profiles of isomerization and aromatization reactions over HZSM-5.

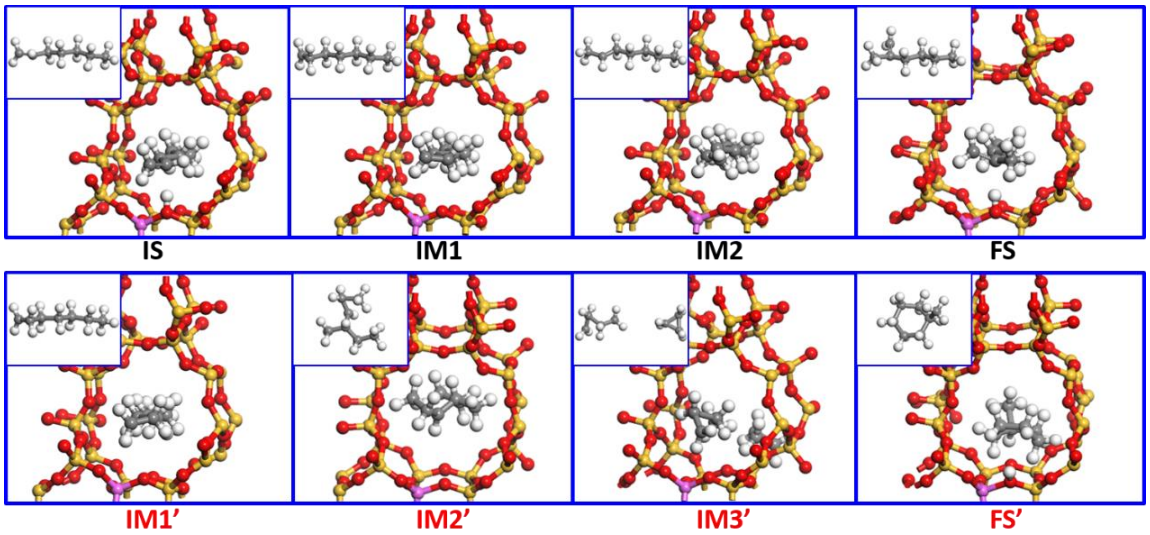

Fig. S14. Calculated intermediates in the isomerization (black) and aromatization (red) reactions over HZSM-5. Red: O atoms; yellow: Si atoms; purple: Al atoms; grey: C atoms; white: H atoms.

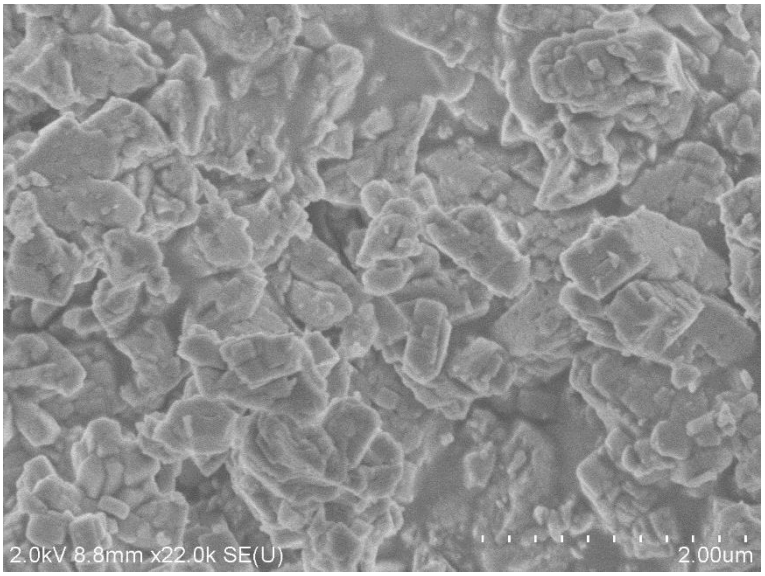

Fig. S15. SEM observation of SiO_2-coated HZSM-5 (Si/Al = 12.5) zeolite.

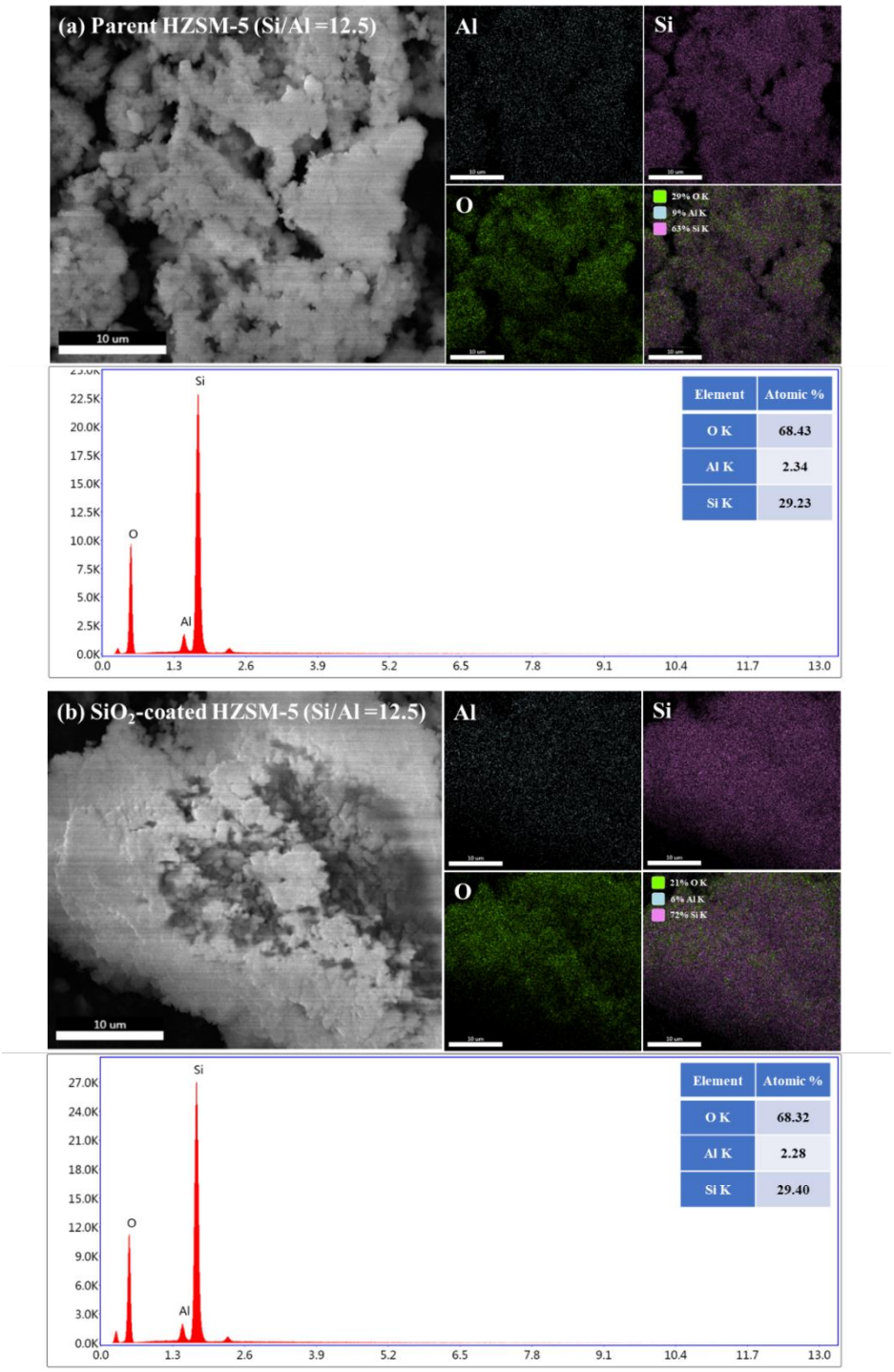

Fig. S16. SEM images and EDS analysis of parent HZSM-5 and its SiO_2-coated sample.

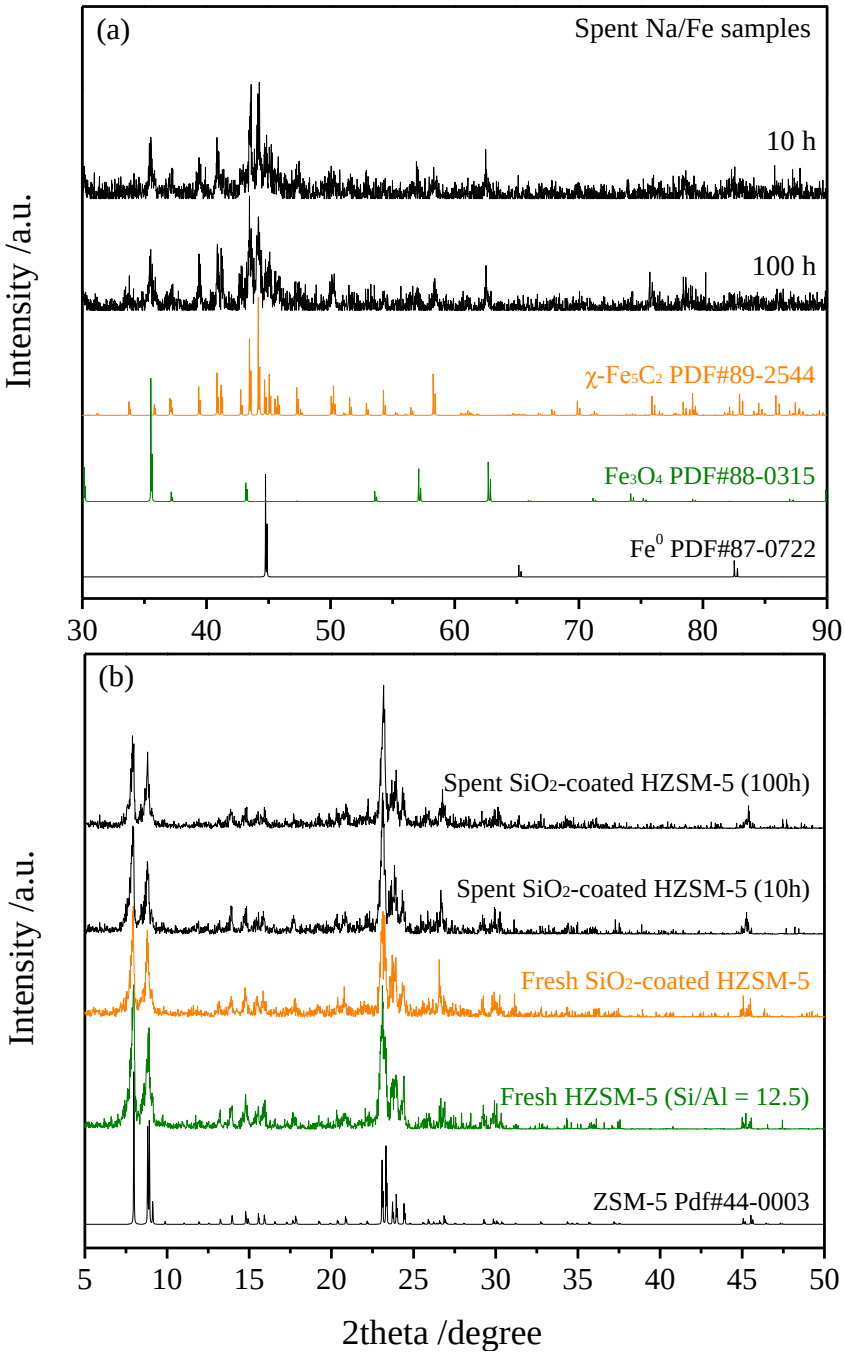

Fig. S17. XRD patterns of (a) spent Na/Fe catalyst samples collected from the tests of 10 h and 100 h and (b) fresh HZSM-5 (Si/Al = 12.5), fresh and spent SiO_2-coated HZSM-5 samples collected from the tests of 10 h and 100 h.

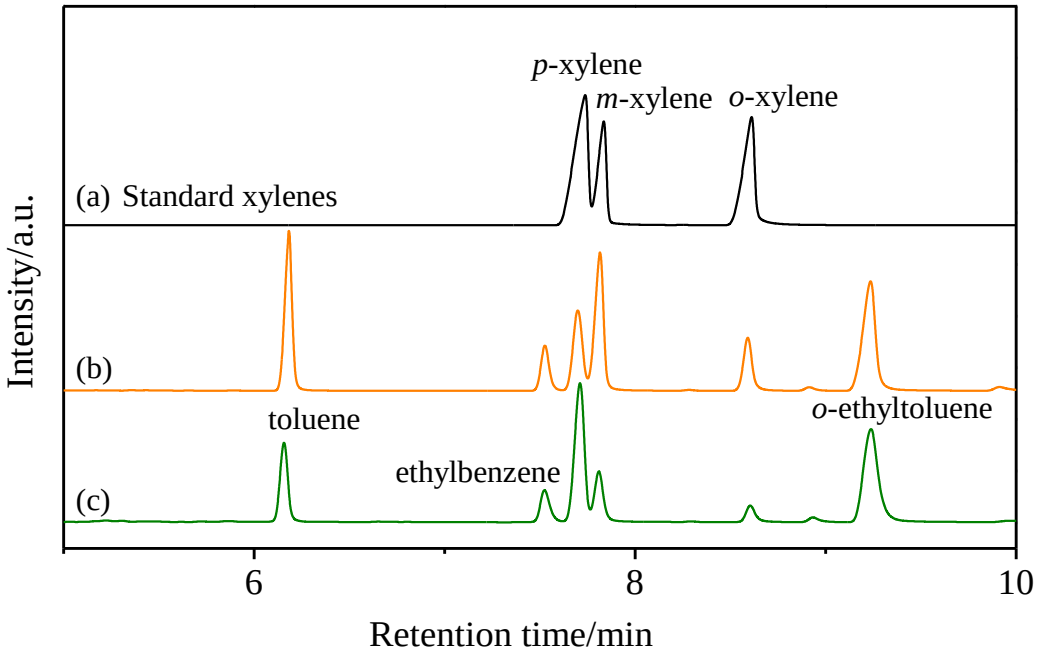

Fig. S18. GC spectrum of liquid hydrocarbon product separated by a FFAP capillary column. (a) standard xylenes (black line); (b) sample obtained from the 40-h test over the composite Na/Fe and HZSM-5 catalyst system (orange line); (c) sample obtained from the 10-h test over the Na/Fe and SiO_2-coated HZSM-5 catalyst system (green line).

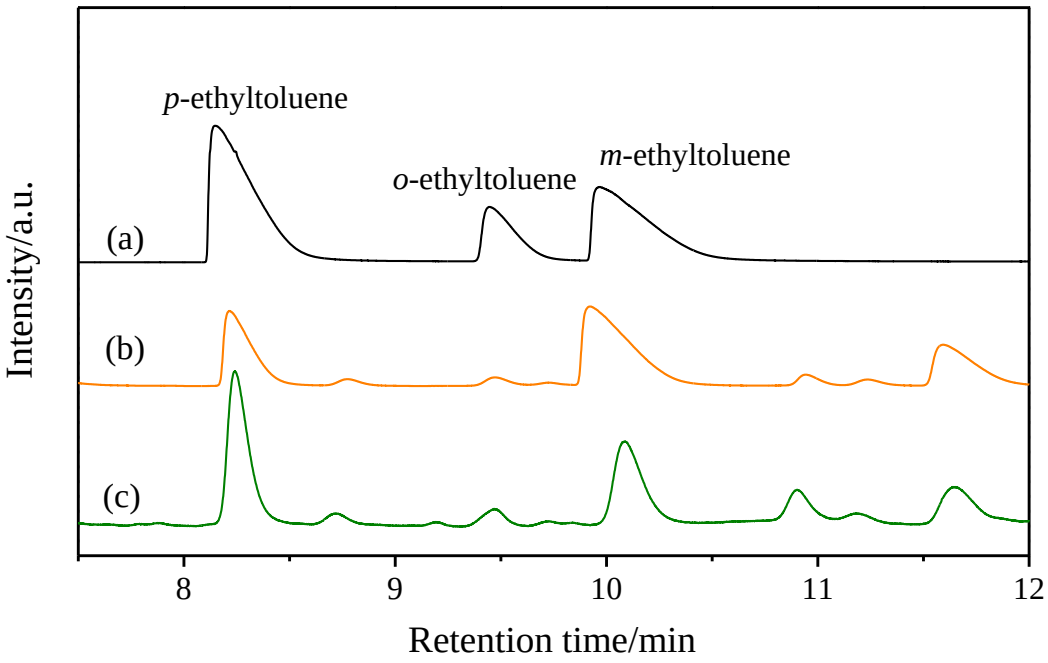

Fig. S19. GC spectrum of liquid hydrocarbon product separated by a Bentone-34 capillary column under a condition of initial temperature of 50 ℃ maintaining for 3 min, heating rate of 2 ℃ min^{-1} to final temperature of 90 ℃: (a) standard ethyltoluene mixture (black line); (b) sample obtained from the 40-h test over the composite Na/Fe and HZSM-5 catalyst system (orange line); (c) sample obtained from the 10-h test over the composite Na/Fe and SiO_2-coated HZSM-5 catalyst system (green line).

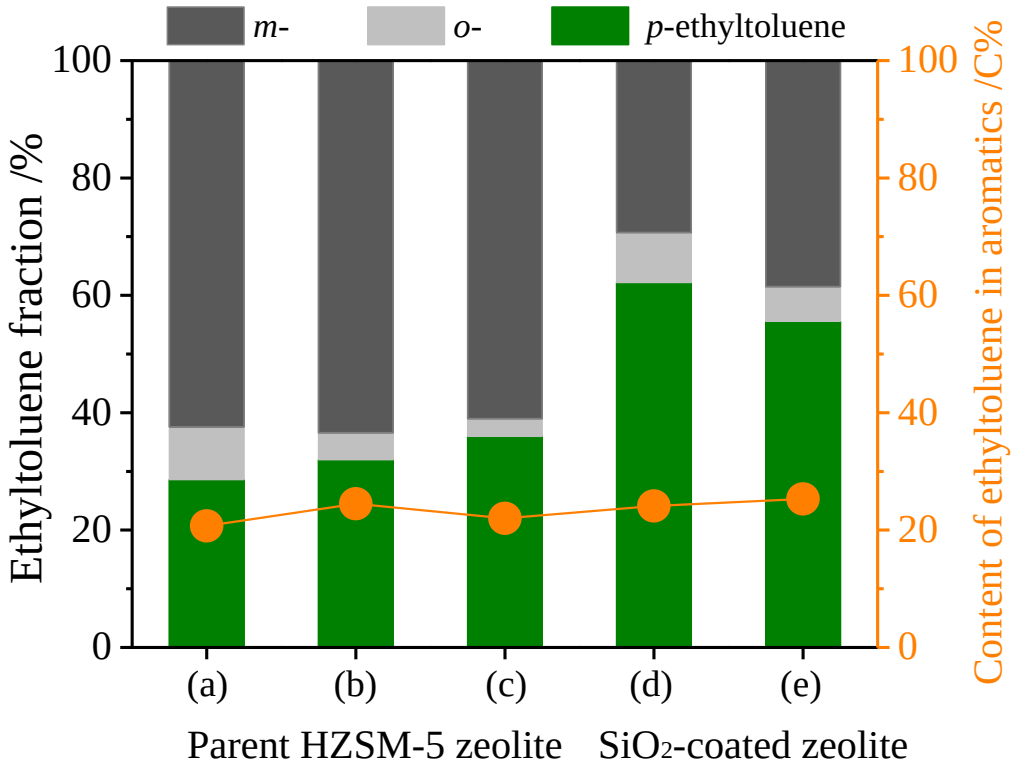

Fig. S20. Distribution of *m*-, *o*- and *p*-ethyltoluene (bar) in total ethyltoluene and the content of the ethyltoluene (●) in total aromatics obtained over the composite Na/Fe and HZSM-5 (Si/Al = 12.5) catalyst system (weight ratio of 1:0.5) at 340 ℃, 4800 mL g^{-1} h^{-1}, H_2/CO_2 = 3 and (a) 1 MPa; (b) 2 MPa; (c) 1 MPa for 40 h; and over the composite Na/Fe and SiO_2-coated HZSM-5 (Si/Al = 12.5) catalyst system at the same reaction condition (1 MPa) for (e) 10 h and (f) 100 h.

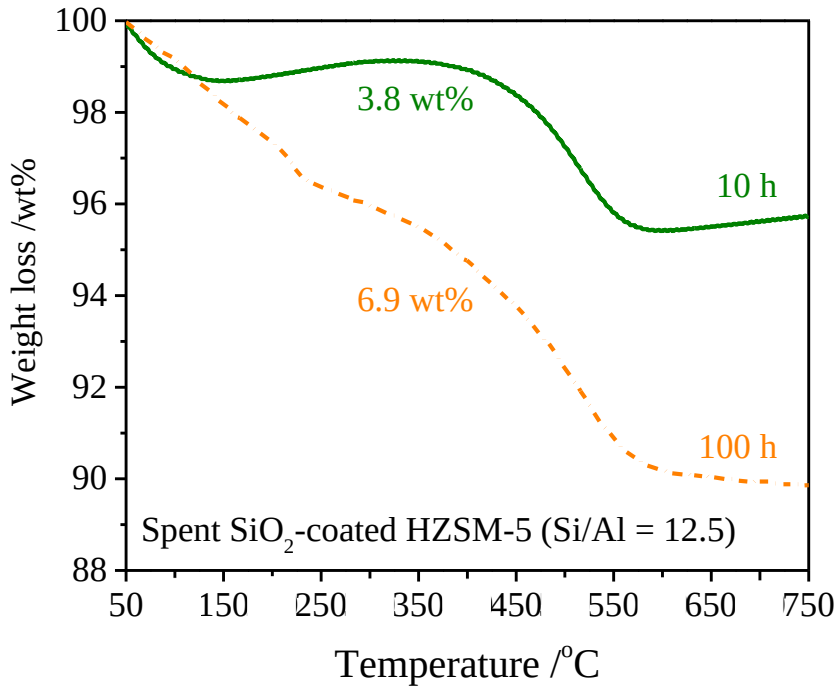

Fig. S21. TG profiles of spent SiO_2-coated HZSM-5 samples collected from 10 h and 100 h tests over the composite Na/Fe and SiO_2-coated HZSM-5 (Si/Al = 12.5) catalyst system at 340 ℃, 1 MPa, 4800 mL g^{-1} h^{-1}.

Table S1. Hydrogenation of CO or CO_2 over the composite Na/Fe and HZSM-5 catalyst systems.

Feed [a]	Composite Na/Fe and HZSM-5 system and reaction duration	CO_2 or CO conv. /%	CO or CO_2 sel. /C%	Hydrocarbon distribution /C%						Aromatic content in C_{5+} liquid phase /C%
				CH_4	$C_2^=$-$C_4^=$	*n*-C_2^0-C_4^0	*i*-C_4^0	Liquid phase		
								C_{5+} [b]	Aromatics	
H_2/CO = 2	Si/Al = 12.5, 10 h	88.2	41.5	13.8	20.8	8.0	0.6	34.2	22.6	39.8
H_2/CO_2 = 3	Si/Al = 12.5, 40 h	32.3	21.9	28.7	6.9	12.0	7.3	6.6	38.5	85.3
H_2/CO_2 = 3	Si/Al = 150, 10 h	32.0	23.1	20.9	27.1	5.0	0.3	18.4	28.3	60.5
H_2/CO_2 = 3	SiO_2-coated, 10 h	30.9	26.8	22.4	21.9	7.8	2.1	4.1	44.7	91.6
H_2/CO_2 = 3	SiO_2-coated, 100 h	30.6	27.1	34.4	25.4	8.0	0.6	9.4	22.2	70.3

[a] Reaction condition: 340 ℃, 1 MPa, 4800 mL g^{-1} h^{-1}; [b] Nonaromatic hydrocarbons including *iso*-paraffins mainly and *cyclo*-paraffins.

Table S2. Aromatic distribution in total aromatic hydrocarbons (related with Table S1).

Feed [a]	Composite Na/Fe and HZSM-5 system and reaction duration	Aromatic fraction in total aromatic hydrocarbons /C%								
							3C-branched benzenes	4C-branched benzenes		Branched naphthalene
H_2/CO = 2	Si/Al = 12.5, 10 h	4.4	17.7	6.1	24.8	6.3	25.7	12.0	0.7	2.3
H_2/CO_2 = 3	Si/Al = 12.5, 40 h	1.5	17.6	6.1	28.5	8.6	28.2	7.4	0.8	1.3
H_2/CO_2 = 3	Si/Al = 150, 10 h	1.9	7.9	4.0	21.1	3.9	33.5	24.1	2.1	1.5
H_2/CO_2 = 3	SiO_2-coated, 10 h	0.6	13.8	6.3	35.8	3.3	28.2	8.9	1.2	1.9
H_2/CO_2 = 3	SiO_2-coated, 100 h	0.9	9.8	6.9	29.5	5.9	30.2	14.3	1.1	1.4

[a] Reaction condition: 340 ℃, 1 MPa, 4800 mL g^{-1} h^{-1}.