Supporting information

Coupling conversion of n-hexane and CO over an HZSM-5 zeolite: Tuning the H/C balance and achieving high aromatic selectivity

Changcheng Wei[ab], Qijun Yu[ab], Jinzhe Li[a], Zhongmin Liu[a]*

[a] National Engineering Laboratory for Methanol to Olefins, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

[b] University of Chinese Academy of Sciences, Beijing 100049, China

Corresponding Authors: * E-mail: liuzm@dicp.ac.cn (Z.L.).

Table S1. SiO_2/Al_2O_3 and textural properties of H-ZSM-5

	SiO_2/Al_2O_3[a]	Pore volume (cm^3g^{-1})[b]	Micropore volume (t-plot, cm^3g^{-1})[b]	BET surface area (m^2g^{-1})[b]	Micropore area (t-plot, cm^3g^{-1})[b]
HZSM-5	33.6	0.23	0.12	406	256

	Acid amount ($mmolg^{-1}$)[c]	Bronsted acid concentration ($mmolg^{-1}$)[d]	Lewis acid concentration ($mmolg^{-1}$)[d]
HZSM-5	0.82	0.67	0.15

a: SiO_2/Al_2O_3 was determined by XRF. b: BET surface area and pore volume was determined by nitrogen sorption experiments recorded at 77K on a Micromeritics ASAP-2020 analyzer. c: Acid amount was calculated from the results of NH_3-TPD. d: Bronsted acid amount and Lewis acid amount were determined by Py-FTIR.

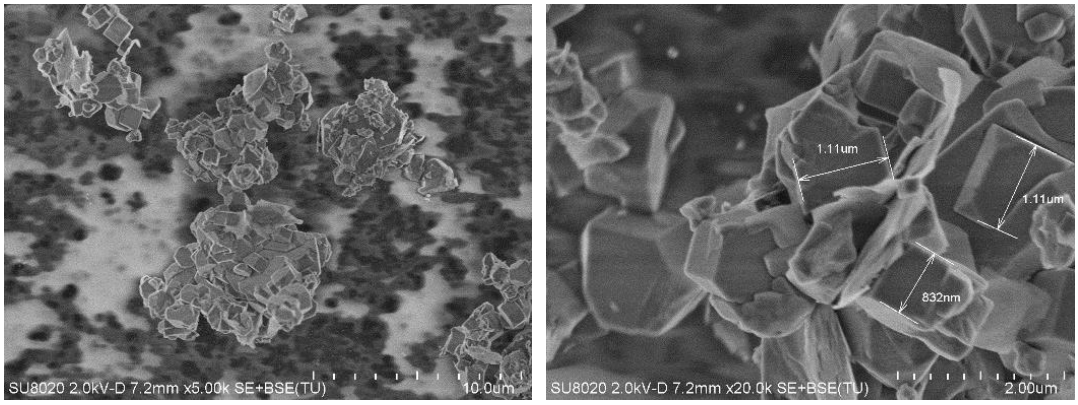

Figure S1. SEM images of HZSM-5.

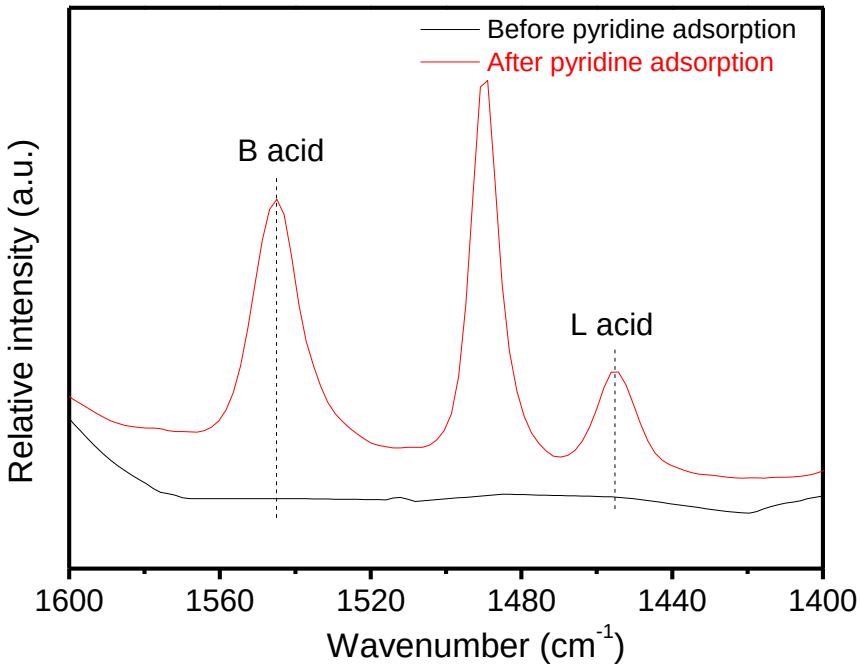

Figure S2. IR spectra recorded over HZSM-5 zeolite before pyridine adsorption (back line) and after pyridine adsorption (red line).

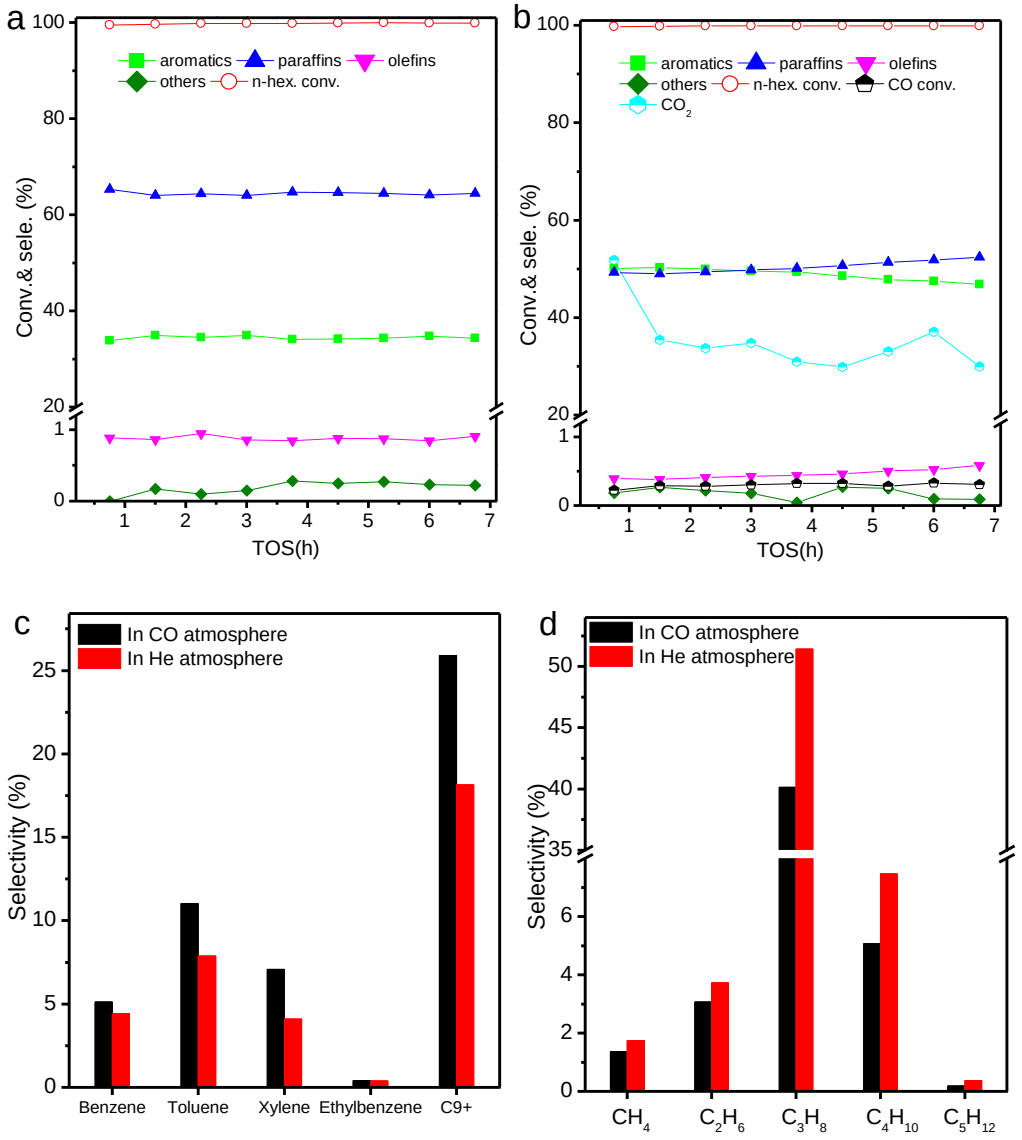

Figure S3. Contrast of the n-hexane conversion and the products selectivity with TOS for n-hexane cracking in (a) CO and (b) He atmospheres over HZSM-5. Detailed comparison of (c) aromatics and (d) paraffins. Reaction conditions: T=400 °C, n-hexane WHSV=0.17 h^{-1}, (CO + Ar $_{internal\ standard}$ + He $_{balance}$)/n-hexane=120, P=3 MPa, time on stream=3 h. PS: the C9+ aromatics are composed of indene, naphthalene, methylnaphthalene and dimethylnaphthalene. And the carbon balance was calculated, which was between 97% and 99%.

According to element conservation, the equations for the transformation of n-hexane to aromatics (toluene as an example) and different alkanes are presented.

(1) $9.5C_6H_{14} \rightarrow C_7H_8 + 12.5C_4H_{10}$

(2) $16C_6H_{14} \rightarrow 3C_7H_8 + 25C_3H_8$

(3) $3.25C_6H_{14} \rightarrow C_7H_8 + 6.25\ C_2H_6$

(4) $2C_6H_{14} \rightarrow C_7H_8 + 5CH_4$

(5) $7C_6H_{14} \rightarrow 6C_7H_8 + 25H_2$

Table S2. Theoretical value of aromatics selectivity of five reaction equations.

Reaction equation	(1)	(2)	(3)	(4)	(5)
Aromatic selectivity (C%)	12	22	36	58	100

Because the amount of hydrogen generated is very small at this temperature range, the theoretical maximum of aromatics selectivity is 58 % for sole n-hexane conversion when n-hexane completely converted to aromatics and methane.

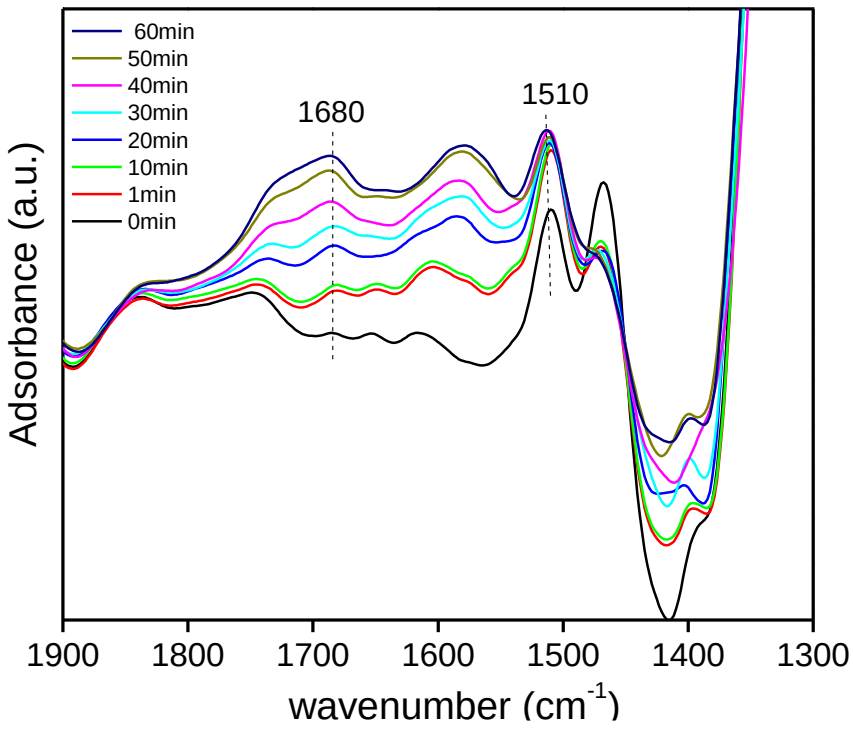

Figure S4. IR difference spectra recorded over HZSM-5 zeolite for the coupling n-hexane with carbon monoxide at 200 °C.

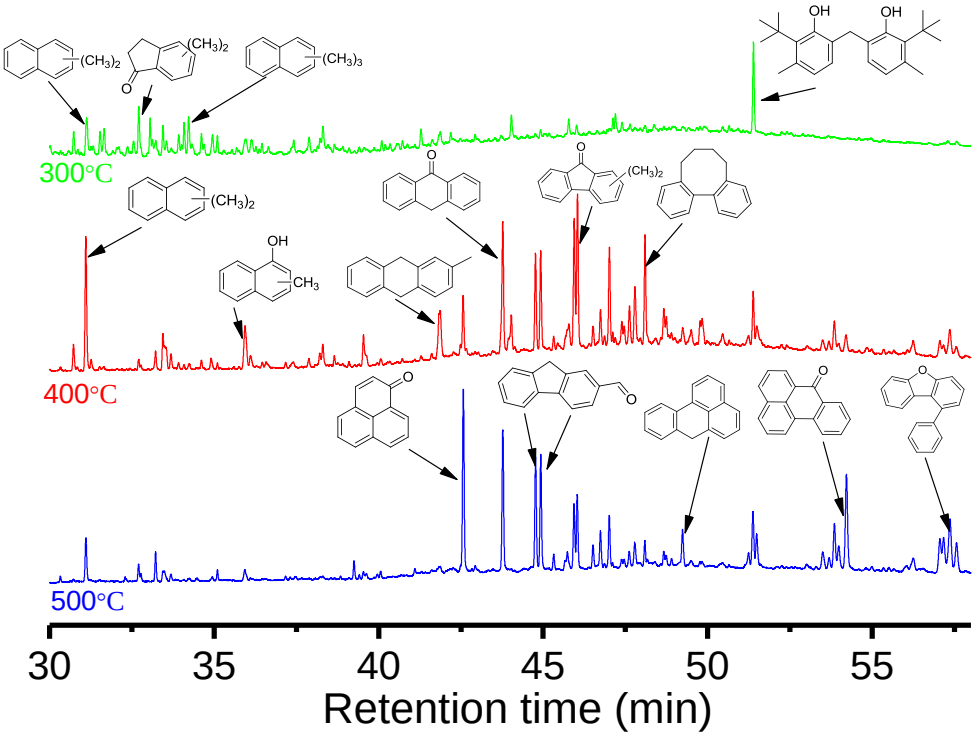

Figure S5. GC-MS results (retention time from 30 min to 58 min) of retained species at different temperature for the coupling reaction.

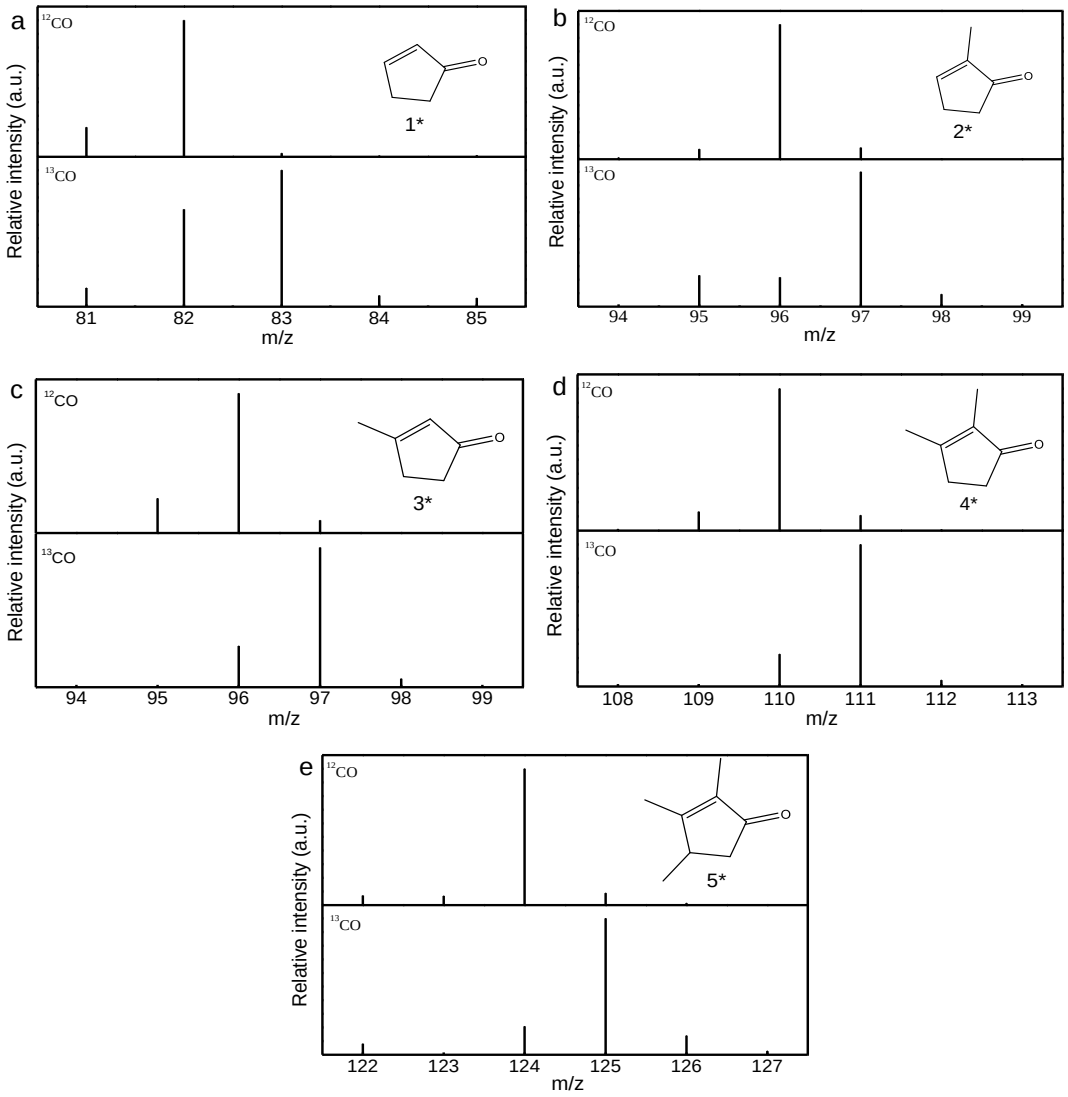

Figure S6. MS spectra of 2-cyclopenten-1-one (a), 2-methyl-2-cyclopenten-1-one (b), 3-methyl-2-cyclopenten-1-one (c), 2,3-dimethyl-2-cyclopenten-1-one (d) and 2,3,4-trimethyl-2-cyclopenten-1-one (e) in ^{13}CO (bottom) and ^{12}CO (top) of the retained species in spent zeolite for the coupling reaction of n-hexane and CO. Reaction conditions: T=250 °C; n-hexane WHSV=1.2 g*g^{-1}h^{-1}; CO/n-hexane=21; P=1 bar. The catalysts were removed at 10 min during the reaction.

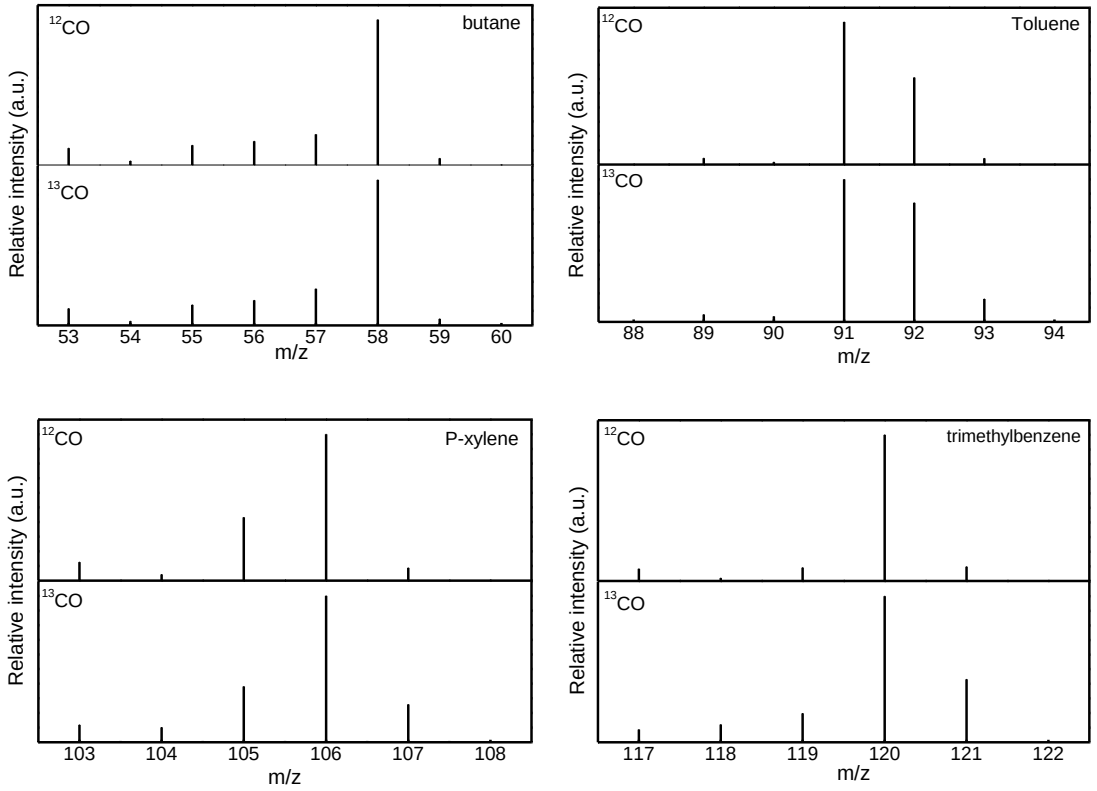

Figure S7. Contrast of MS spectra of butane, toluene, p-xylene and 1,2,3-trimethybenzene of the products in ^{13}CO (bottom) and ^{12}CO (top) atmosphere for the coupling reaction at 250 °C.

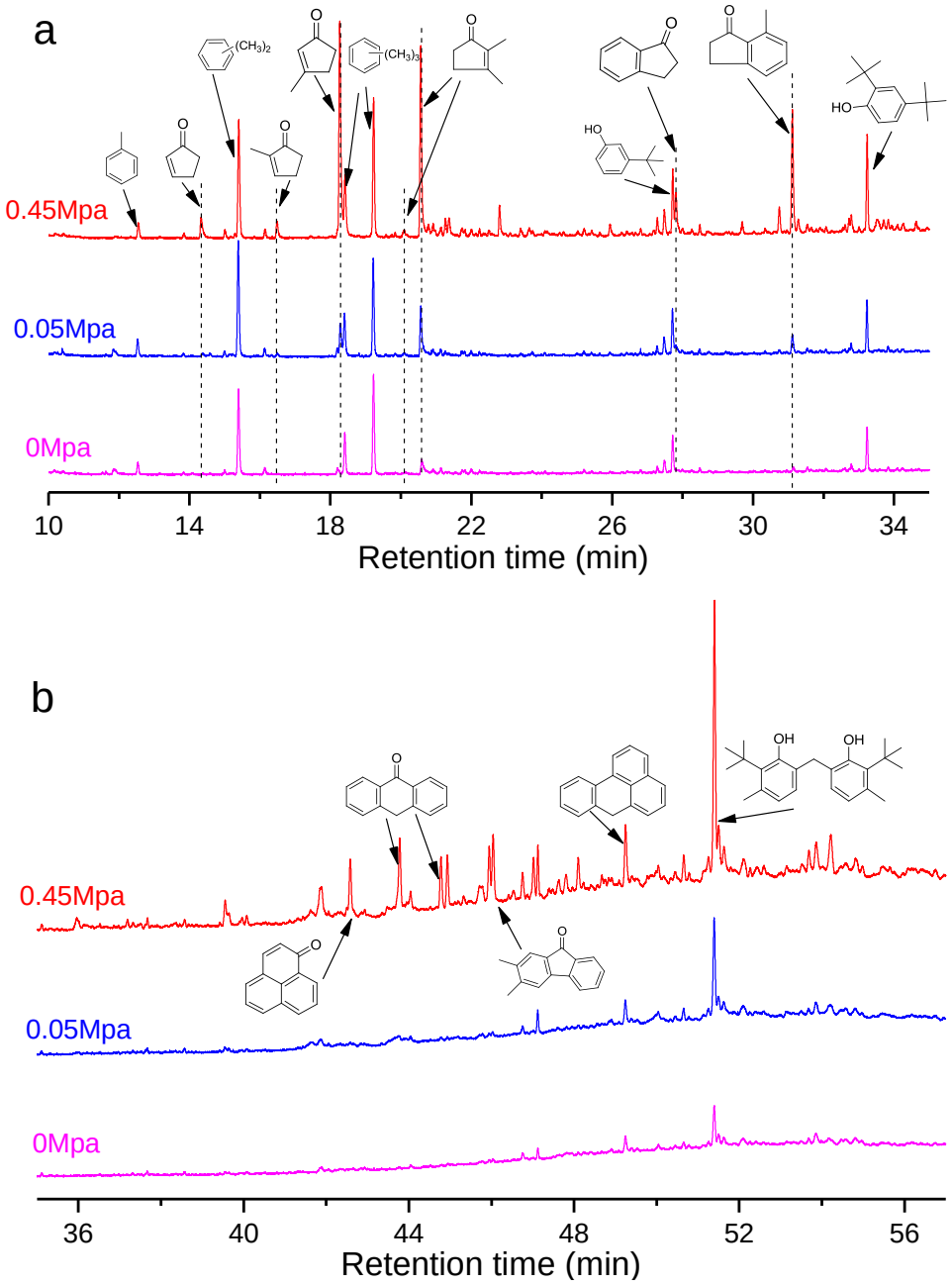

Figure S8. GC-MS analysis of retained species at different CO partial pressure for the coupling C3H6 with CO over HZSM-5. (a) Retention time from 0 min to 35 min, (b) Retention time from 35 min to 58 min.

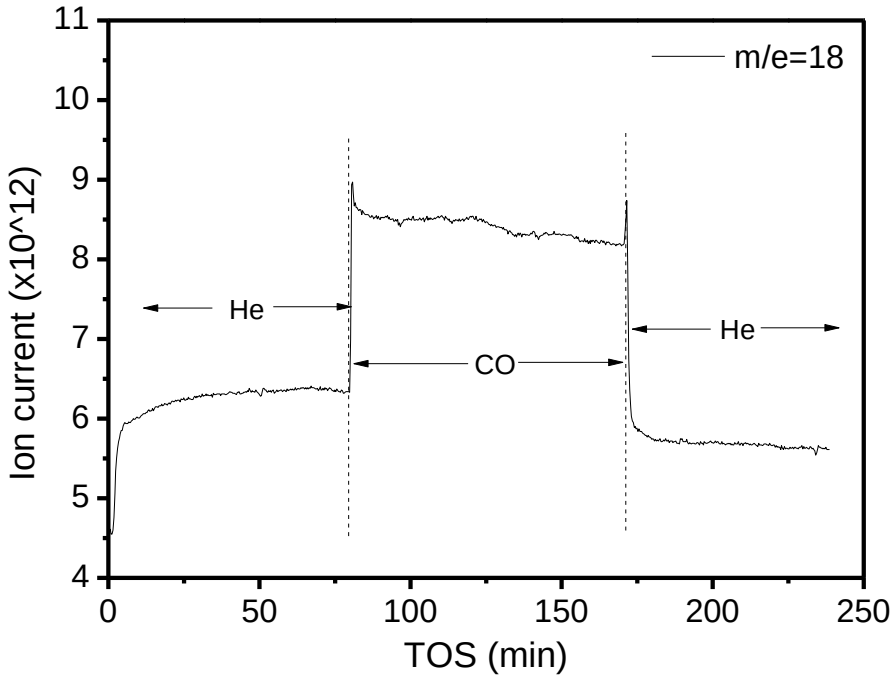

Figure S9. The m/e=18 signals of on-line mass spectrometry as a function of TOS. Reaction conditions: T=500 ºC; n-hexane WHSV=2.44 h^{-1}, He or CO/n-hexane=94, P=1 bar, n-hexane reacted in He atmosphere for 80 min before switching to CO for 80 min, and then switching to He for 70 min.

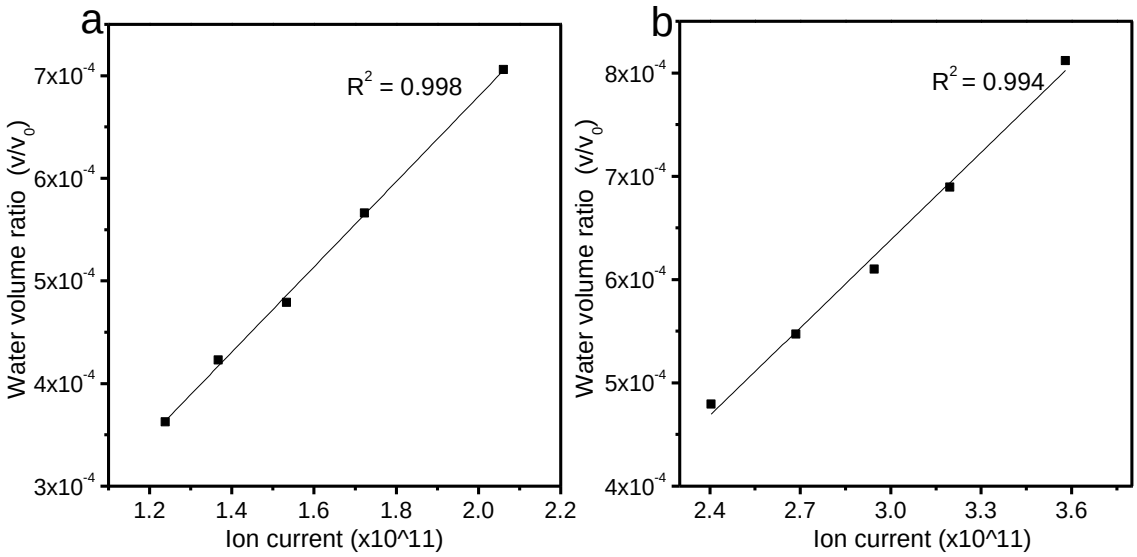

Figure S10. The water volume ratio as a function of the signal of m/e=18 in He (a) and CO (b) atmospheres.

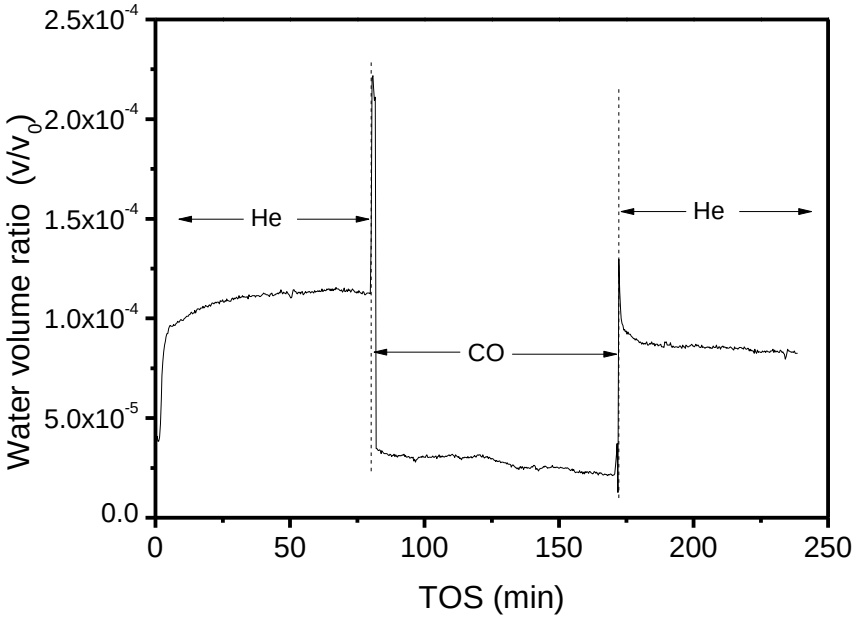

Figure S11. The water volume ratio calculated from the calibration curve as a function of TOS.

Table S3. Thermodynamics equilibrium of water-gas shift reaction at different temperature.

$CO + H_2O = CO_2 + H_2$

Temperature /°C	453	477	501	524	548
CO volume ratio	9.3E-01	9.3E-01	9.3E-01	9.3E-01	9.3E-01
CO2 volume ratio	6.6E-03	6.6E-03	6.6E-03	6.6E-03	6.6E-03
H2 volume ratio	6.6E-03	6.6E-03	6.6E-03	6.6E-03	6.6E-03
H2O volume ratio	6.4E-06	7.8E-06	9.4E-06	1.1E-05	1.3E-05

Assuming that the conversion of carbon monoxide is 0.7% (<1%), which could generate 0.7% volume of water.

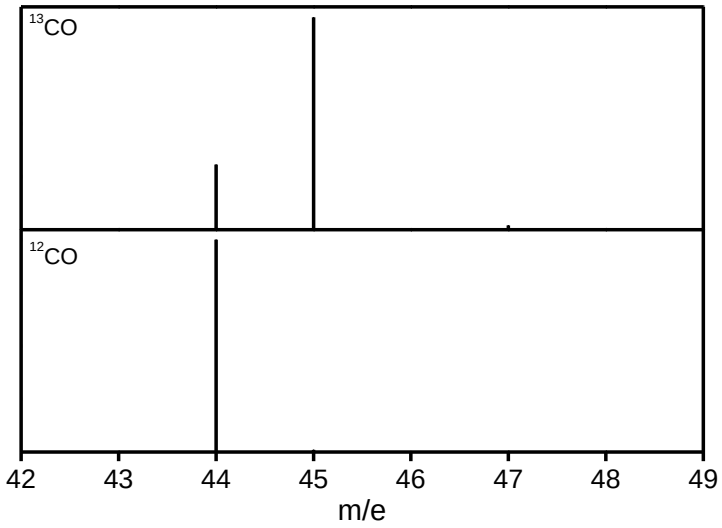

Figure S12. Contrast of MS spectra of CO_2 of the effluent products in ^{12}CO (bottom) and ^{13}CO (top) atmosphere for the coupling reaction.