

Electronic Supplementary Information

Breaking the Fischer-Tropsch synthesis selectivity: Direct conversion of syngas to gasoline over hierarchical Co/H-ZSM-5 catalysts

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Experimental

Materials

Amorphous SiO₂ with surface area and pore volume of 293 m² g⁻¹ and 1.35 cm³ g⁻¹, respectively, was provided by Fuji Silysia Chemical LTD (CARiACT Q-10). ZSM-5 zeolite in ammonium form with nominal Si/Al of 40 was purchased from Zeolyst (CBV 8014). NaOH pellets, 1 M tetrapropylammonium hydroxide (TPAOH) solution and Co(NO₃)₂·6H₂O were purchased from Sigma-Aldrich. NH₄NO₃ was provided by Merck. All chemicals were used without any further purification steps.

Synthesis

Ammonium form of ZSM-5 was calcined at 823 K for 5 h to obtain the parent H-ZSM-5. Desilication of H-ZSM-5 powder was carried out in 1 M NaOH or TPAOH aqueous solutions in a capped vessel ($\text{volume}_{\text{base solution}}/\text{weight}_{\text{parent H-ZSM-5}} = 8 \text{ cm}^3 \text{ g}^{-1}$) and under stirring at 343 K for 1 h in oil bath. This treatment was followed by immediate quenching in an ice bath and centrifugation to separate the zeolite powder from solution. The residue of the desilicating agent was removed from zeolite crystallites by subsequent redispersion in deionized water and centrifugation cycles until neutral pH was reached. In the case of NaOH treatment, the zeolite was ion exchanged with an excess of 0.1 M NH₄NO₃ at room temperature for 15 min in three additional cycles and thoroughly washed. Mesoporous H-ZSM-5 samples were then kept overnight at 333 K followed by drying at 393 K for 12 h and calcination at 823 K for 5 h.

Amorphous SiO₂, parent H-ZSM-5 as well as mesoporous zeolite samples were employed as catalyst supports and loaded with 10 wt% of Co, applying incipient wetness impregnation of Co(NO₃)₂·6H₂O aqueous solution. Before impregnation, all the supports were dried overnight at 393 K. Only in the case of parent H-ZSM-5, two impregnation steps were required (due to its low pore volume) in between of which the sample was dried at 333 K for 5 h. After impregnation, samples were kept overnight in desiccator at room temperature and dried at 393 K for 12 h. Finally, the

catalysts were calcined at 673 K for 2h. For all the above mentioned drying and calcination steps a heating rate of 2 K min⁻¹ and static air conditions were applied.

Characterization

N₂ Physisorption experiments were performed in an Autosorb-6B unit (Quantachrome Instruments) at liquid nitrogen temperature (77 K). Prior to the experiment, all samples were degassed overnight in an Autosorb Degasser unit (Quantachrome Instruments) under vacuum at 623 K.

The X-Ray Diffraction (XRD) patterns were recorded in Bragg-Brentano geometry in a Bruker D8 Advance diffractometer equipped with a Vantec position sensitive detector and graphite monochromator. Measurements were performed at room temperature, using monochromatic Co K α radiation ($\lambda = 0.179026$ nm) in the 2θ region between 10° and 100° with a step size of 0.035°. The samples were placed on a Si {510} substrate and rotated during measurements. All patterns were background-subtracted to eliminate the contribution of air scatter and possible fluorescence radiations.

Elemental analysis was done by inductively coupled plasma optical emission spectrometry (ICP-OES technique) with PerkinElmer Optima instruments. Transmission Electron Microscopy (TEM) with a field emission gun was done by a FEI Tecnai TF20 microscope operated at 200kV using a carbon coated Cu grid.

Temperature Programmed NH₃ Desorption was measured by an AutoChem II Chemisorption Analyzer (Micromeritics). *Ca.* 0.200 g of the zeolite support was first degassed under He flow at 673 K for 1 h and then saturated with NH₃ at 473 K during 1 h, under 1.65% NH₃ in He flow. The gas mixture was then switched back to He and the sample was purged at 473 K for 1 h to remove the weakly adsorbed NH₃ molecules. Desorption was recorded afterwards under He flow, from 473 to 873 K with a heating rate of 10 K min⁻¹. All the flow rates were adjusted to 25 cm³_{STP} min⁻¹.

Thermogravimetric Analysis (TGA) was performed on a Mettler Toledo TGA/SDTA851^e equipment, where 0.018–0.044 g of fresh and spent catalysts were screened for the change in their mass while heated from 298 to 1123 K with a heating rate of 5 K min⁻¹ under 100 cm³_{STP} min⁻¹ of air flow.

Fischer-Tropsch Synthesis (FTS)

FTS experiments were performed in a six-flow fixed-bed microreactor setup, shown schematically in Fig. S1a, which allowed running six reactions in parallel under similar feed composition, process temperature and conditions of separation/analysis equipments. The reactor consisted of five heating blocs with separate temperature controllers to ensure a flat isothermal zone along the glass-lined reactor inserts with inner diameter of 4 mm (see Fig. S1b). In order to

stabilize the process pressure at high conversion levels, trace of an inert gas (N_2) was injected downstream the reactor to each flow. This inert was used as an internal standard for the online gas analysis.

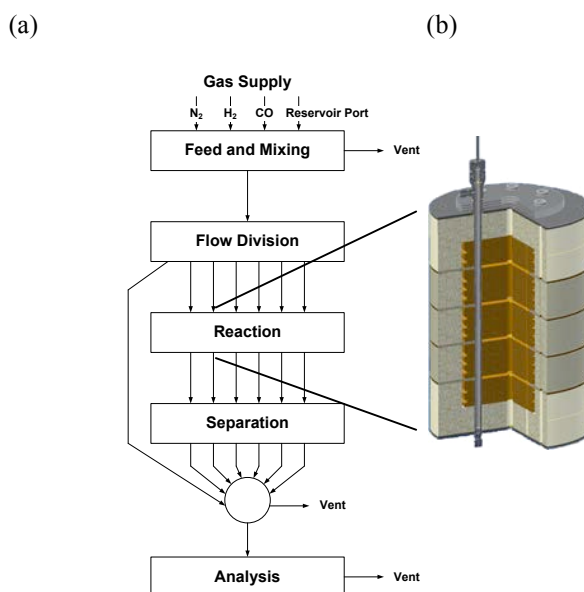


Fig. S1 Overall process flow scheme of the “six-flow fixed-bed microreactor Fischer-Tropsch synthesis” setup (a). Schematic drawing of the five heated zones fixed-bed microreactor oven (b). The three grey zones indicate the isothermal region.

For all experiments, 0.5 g of fresh catalyst particles were fixed in the reactor inserts using quartz wool. Samples were first activated *in-situ* by $80 \text{ cm}^3_{\text{STP}} \text{ min}^{-1}$ of H_2 at 673 K for 12 h at atmospheric pressure followed by cooling down to 453 K under H_2 flow. After increasing the pressure to the process value (15 bar), CO was gradually introduced to the feed stream at 453 K in order to reach its final concentration ($H_2/CO = 2$) in 1 h. Subsequently, the reactor was heated to the process temperature (513 or 493 K). A rate of 2 K min^{-1} was applied for all the heating/cooling steps.

During the experiment, heavy hydrocarbons (waxes) were collected by gas/liquid separators at 448 K and reaction pressure. Lighter hydrocarbons and water were collected in cold traps at *ca.* 278 K and atmospheric pressure. After separation from water, these hydrocarbons as well as the waxes were weighted, dissolved in CS_2 and analyzed offline by a simulated distillation (SimDis) GC (Hewlett Packard 5890, Series II) equipped with an FID and HP-1 column ($7.5 \text{ m} \times 0.53 \text{ mm}$, Film Thickness $2.65 \mu\text{m}$), using He as carrier gas. During the analysis, the oven temperature was ramped from 35 to 350 K (14 K min^{-1}) and kept at the final temperature for 5 min.

Permanent gases as well as light hydrocarbons in the gas phase were analyzed online by a Compact GC (Interscience), equipped with three columns and detectors in parallel, applying He as carrier gas. In the first column (Carboxen 1010, $10 \text{ m} \times 0.32 \text{ mm}$) N_2 , CO, CH_4 and CO_2 were separated at 333 K and analyzed by TCD. In the second column (Al_2O_3/KCl , $10 \text{ m} \times 0.32 \text{ mm}$) and FID detection, separation between all C1–C4 components was achieved at

434 K. In the third column (RTx-1 0.5 μ m, 15 m \times 0.32 mm) C5–C10 hydrocarbons were separated at 353 K and analyzed by FID.

A pseudo-steady catalytic behavior was attained after 20 h on-stream (see Fig. S7a) when selectivity data were collected and the carbon balance was satisfied by $100 \pm 5\%$. CO conversion, carbon selectivity and molar fraction of each product were defined by equations (1), (2) and (3), respectively, where X_{CO} stands for CO conversion, F indicates the molar flow, S is the carbons selectivity of a product with n carbon number and y is its molar fraction.

$$X_{\text{CO}} = \frac{F_{\text{in,CO}} - F_{\text{out,CO}}}{F_{\text{in,CO}}} \times 100 \quad (1), \quad S_{\text{C}_n} = \frac{nF_{\text{C}_n}}{F_{\text{CO}_2} + \sum_{n=1}^N nF_{\text{C}_n}} \times 100 \quad (2), \quad y_{\text{C}_n} = \frac{F_{\text{C}_n}}{\sum_{n=1}^N F_{\text{C}_n}} \quad (3)$$

n-Hexane Hydroprocessing

Acidic catalyzed reactions of *n*-C6 were performed in a continuous fixed-bed stainless-steel reactor. 0.25 g of the alkaline treated H-ZSM-5 particles (mesoH-ZSM-5(a)) were fixed in the reactor center (3.9 mm inner diameter) by quartz wool. The catalyst was treated overnight under H₂ flow at 673 K and atmospheric pressure. After cooling down to 513 K the pressure was increased to 15 bar and subsequently a mixture of *n*-C6, H₂ and N₂ was fed to the reactor ($WHSV = 359.7 \text{ mol kg}^{-1}_{\text{cat}} \text{ h}^{-1}$, Molar composition: H₂/*n*-C6 = 9.0, N₂/H₂ = 2.0). After 20 h on-stream, data collection started at different reaction temperatures. The reactor was kept for 3 h at each temperature before measurements. The product stream was analyzed online by a Compact GC (Interscience), equipped with Porabond Q column at 363 K (10 m \times 0.32 mm) and FID, using He as the carrier gas. Yield of the hydrocarbon products (Y_{C_n}) was defined by equation (4):

$$Y_{\text{C}_n} = \frac{n}{6} \frac{F_{\text{C}_n}}{F_{\text{in},n\text{-C6}}} \times 100 \quad (4)$$

Results

Table S1 Textural and chemical properties of the supports and catalysts.

Support/Catalyst	$S / \text{m}^2 \text{g}^{-1}$		$V / \text{cm}^3 \text{g}^{-1}$			Co		Si/Al ^f
	total ^a	meso ^b	total ^c	micro ^d	meso ^e	wt% ^f	$d_{\text{Co}}^g / \text{nm}$	
SiO ₂	293	248	1.35	0.02	1.34	n.a. ^h	n.a.	n.a.
Co/SiO ₂	223	200	1.03	0.01	1.03	9.73	14	n.a.
H-ZSM-5	460	52	0.26	0.18	0.08	n.a.	n.a.	41
Co/H-ZSM-5	388	38	0.22	0.16	0.06	9.63	13	40
mesoH-ZSM-5(a)	580	309	1.20	0.12	1.08	n.a.	n.a.	16
Co/mesoH-ZSM-5(a)	467	257	0.87	0.09	0.78	9.91	7	16
mesoH-ZSM-5(o)	683	414	0.64	0.12	0.52	n.a.	n.a.	24
Co/mesoH-ZSM-5(o)	574	344	0.53	0.10	0.43	9.02	10	22

^a BET surface area; ^b Mesopore surface area obtained from *t*-plot; ^c Total pore volume; ^d Micropore volume obtained from *t*-plot; ^e Mesopore volume calculated from $V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$; ^f Obtained from ICP-OES; ^g Co crystallite size calculated from $d(\text{Co}^0) = 0.75d(\text{Co}_3\text{O}_4)$, where $d(\text{Co}_3\text{O}_4)$ was derived from XRD, applying the Scherrer equation; ^h Not applicable.

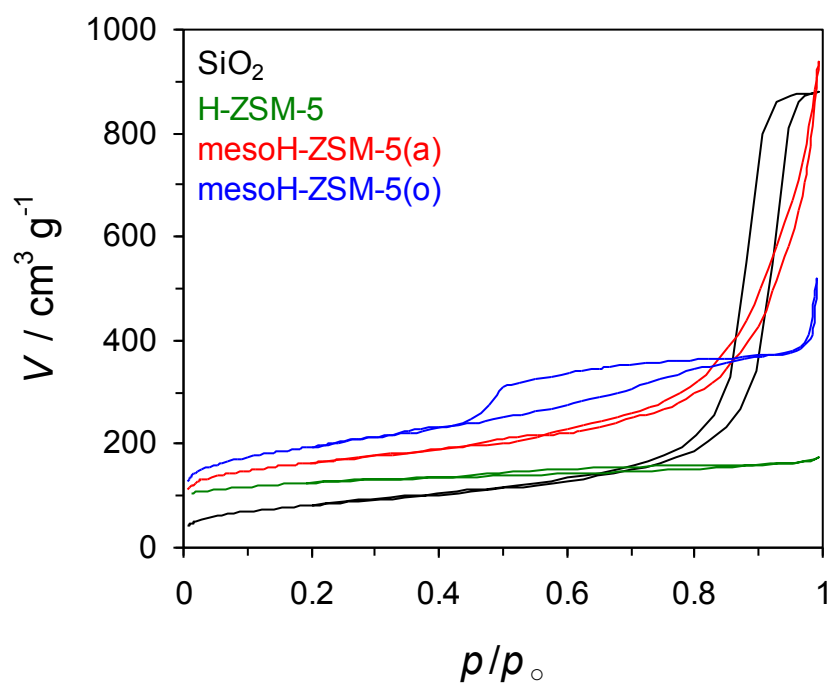


Fig. S2 N₂ physisorption isotherms of supports.

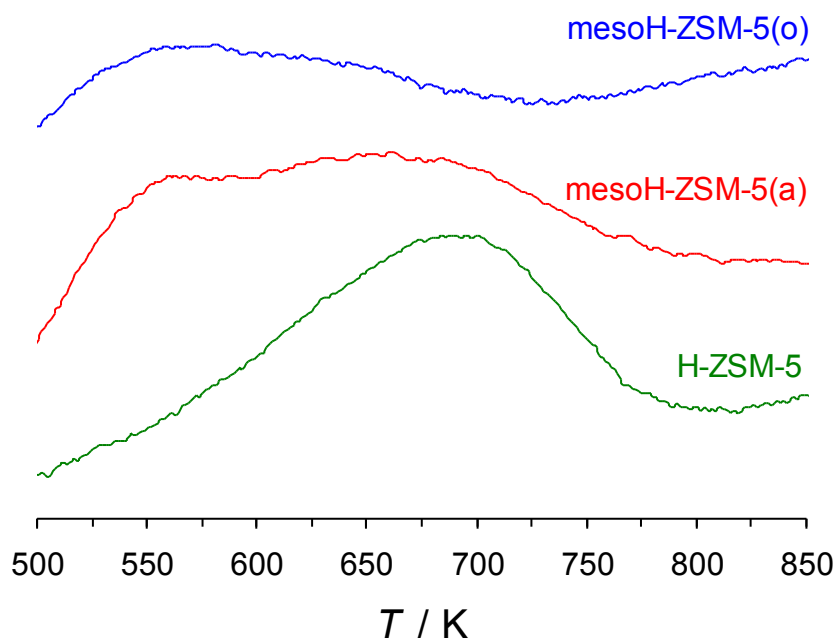


Fig. S3 Temperature programmed NH₃ desorption profiles of zeolite supports.

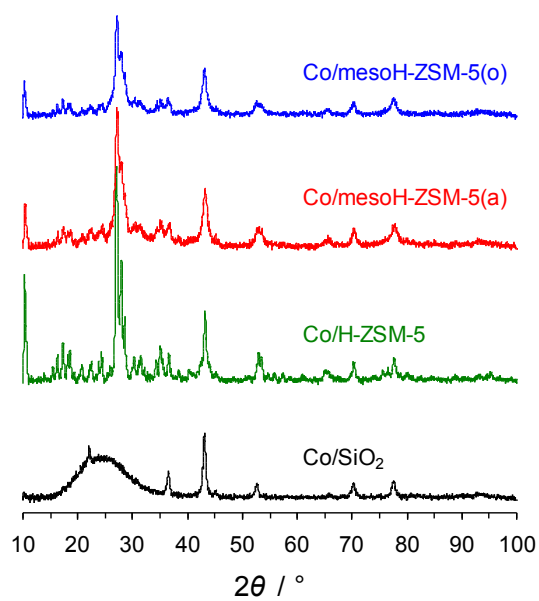


Fig. S4 XRD patterns of the catalysts.

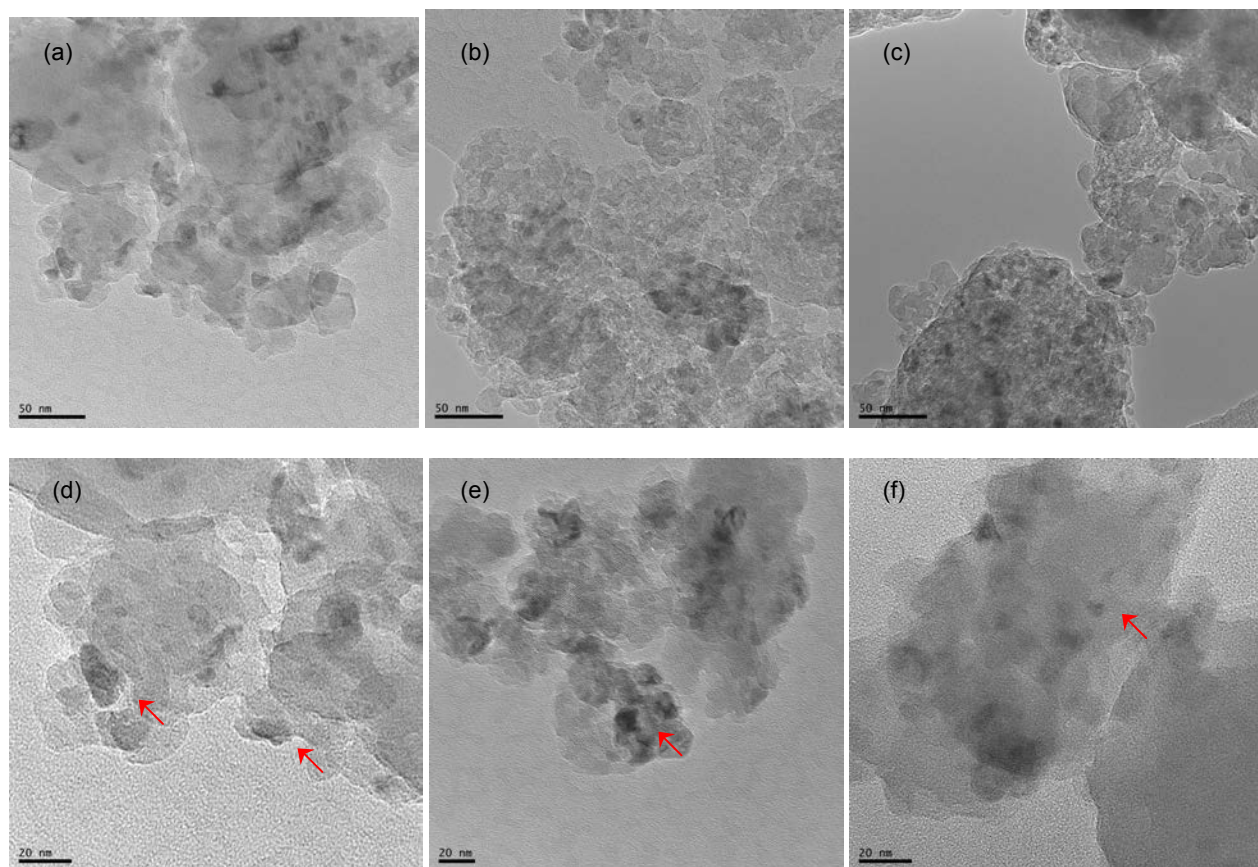


Fig. S5 TEM images of the zeolite supported Co catalysts (before activation); In each row from left to right: Co/H-ZSM-5 (a and d), Co/mesoH-ZSM-5(a) (b and e) and Co/mesoH-ZSM-5(o) (c and f); Arrows point to the position of some Co oxide clusters/particles; Scale bars correspond to 50 nm for the top row and 20 nm for the bottom row images.

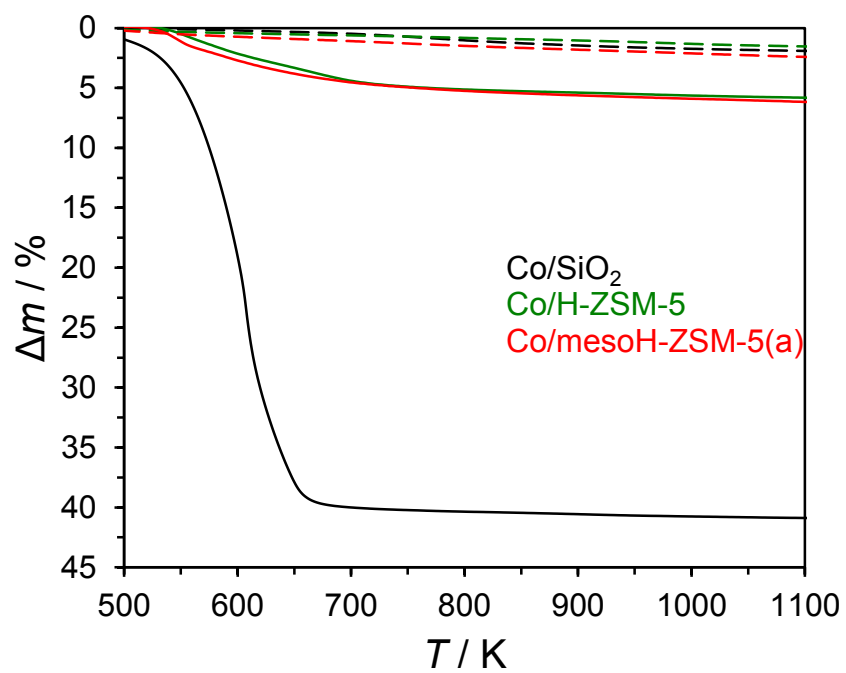


Fig. S6 TGA analysis of fresh (dashed lines) and spent (solid lines) catalysts after 30 h FTS reaction at 513 K, 15 bar, $\text{H}_2/\text{CO} = 2$ and $GHSV / \text{m}^3_{\text{STP}} \text{kg}^{-1}_{\text{cat}} \text{h}^{-1} = 2.4$.

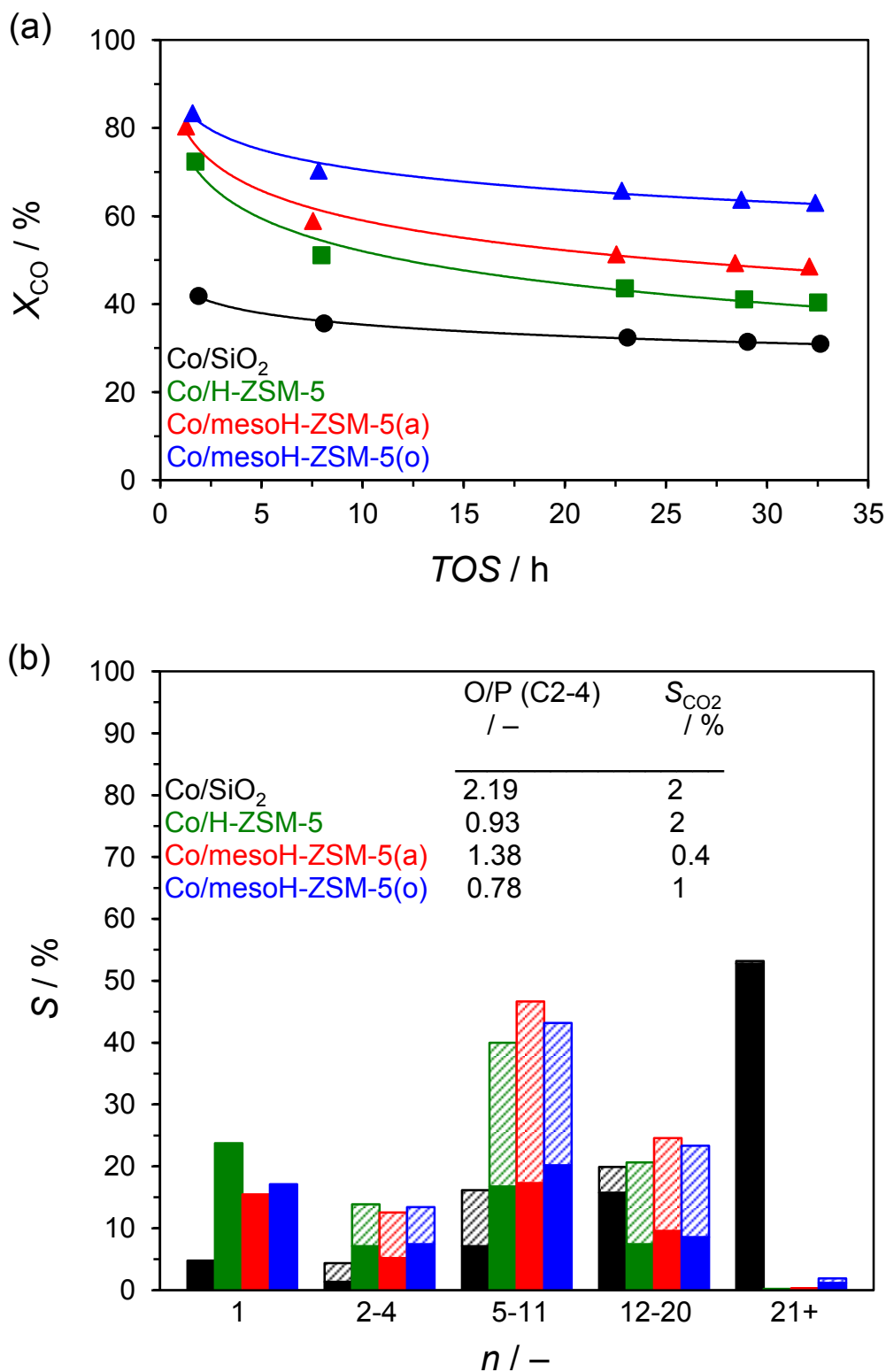


Fig. S7 Time-on-stream (*TOS*) evolution of CO conversion during FTS at 493 K, 15 bar, H₂/CO = 2 and $GHSV / m^3_{STP} kg^{-1} h^{-1} = 2.4$ (a). Carbon selectivity of FTS products after 20 h on-stream; ■: *n*-paraffins, ///: Sum of isoparaffins and olefins; O/P (C2-4): Olefin to *n*-paraffin ratio of C2–C4, S_{CO₂}: CO₂ selectivity.

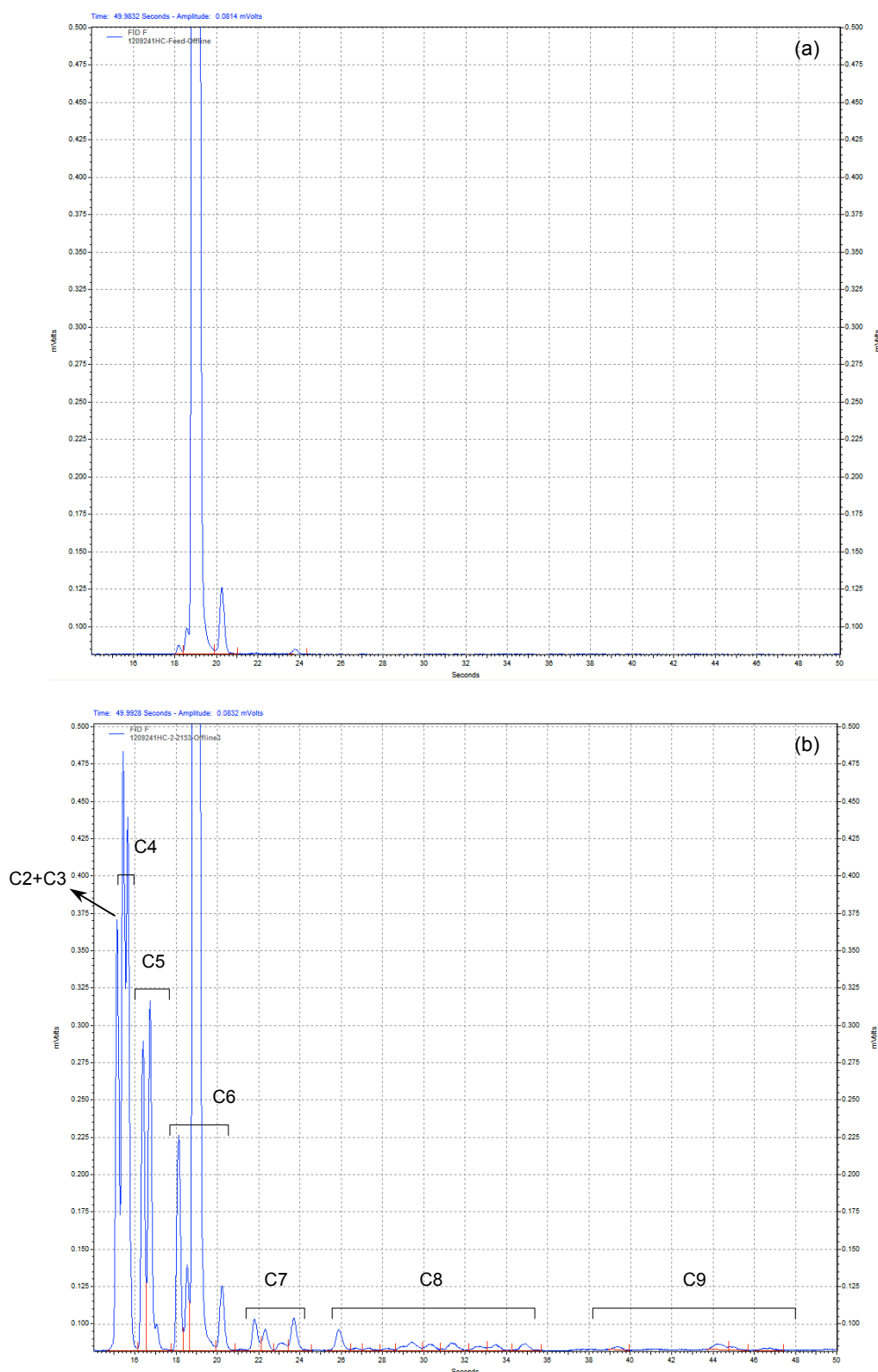


Fig. S8 GC analysis chromatograms of the hydrocarbon feed (a) and products (b) obtained from the *n*-C6 hydroprocessing experiments over mesoH-ZSM-5(a) at 513 K, 15 bar, $H_2/n\text{-C6} = 9.0$, $N_2/H_2 = 2.0$ and $WHSV = 359.7 \text{ mol kg}^{-1}_{\text{cat}} \text{ h}^{-1}$. Analysis was performed offline, by Compact GC (Interscience) equipped with an RTx-1 column at 353 K ($0.5\mu\text{m}$, $15 \text{ m} \times 0.32 \text{ mm}$) and FID as a supplement to the online analysis (see *n*-Hexane Hydroprocessing).