Influence of precursor porosity on sodium and sulfur promoted iron/carbon Fischer-Tropsch catalysts derived from metal- organic frameworks

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Electronic Supplementary Information (ESI†)

Supplementary Figures

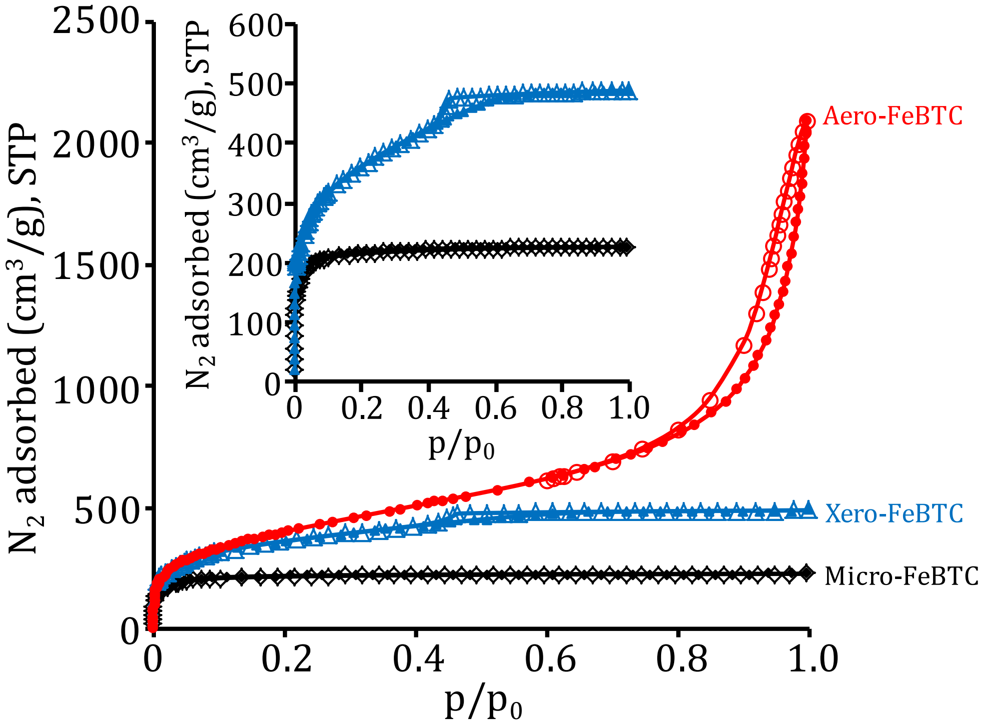

Figure S1. Nitrogen physisorption isotherms measured at -196°C of the MOF precursors Micro-FeBTC (black, diamonds), Xero-FeBTC (blue, triangles), and Aero-FeBTC (red, circles).

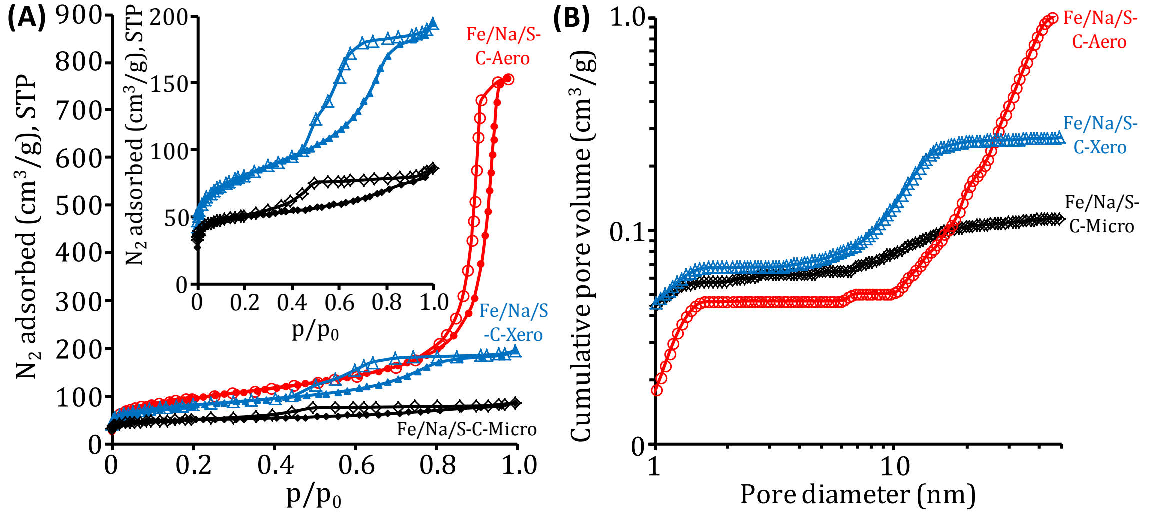

Figure S2. (A) Nitrogen physisorption isotherms measured at -196°C and (B) corresponding cumulative QSDFT pore size distributions of the Fe/Na/S-C-Micro (black, diamonds), Fe/Na/S-C-Xero (blue, triangles), and Fe/Na/S-C-Aero (red, circles) catalysts.

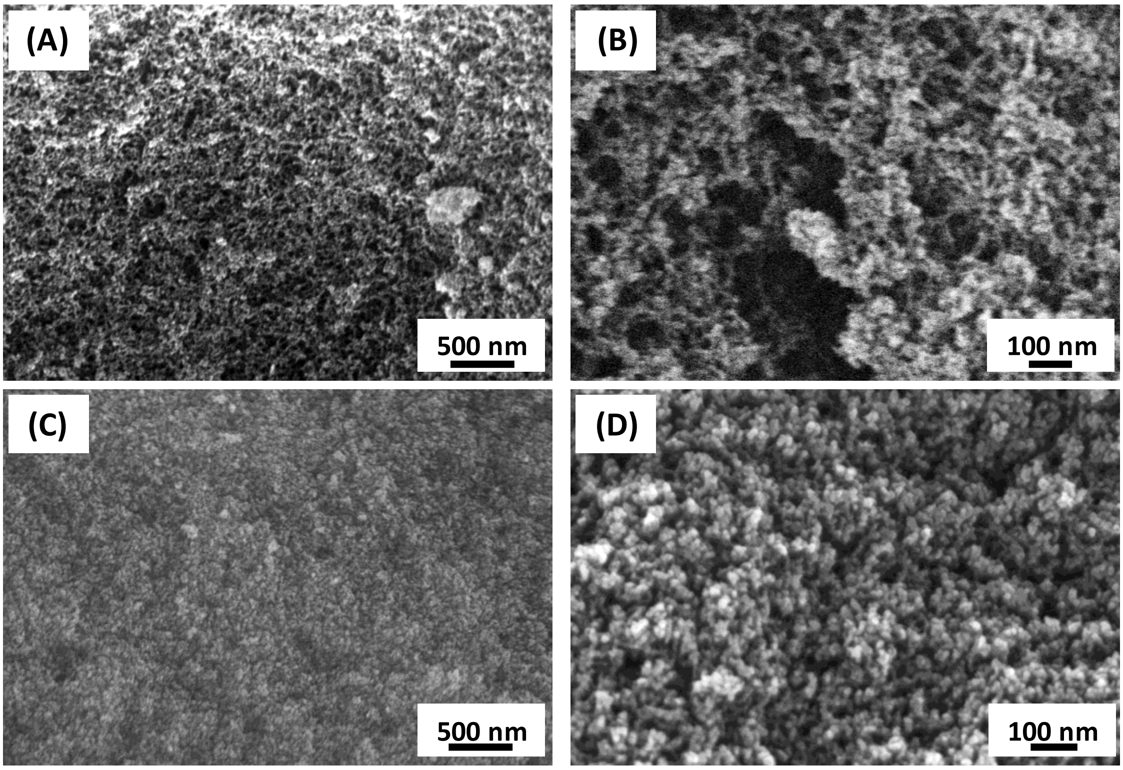

Figure S3. Scanning electron microscopy images of (A,B) Aero-FeBTC and (C,D) Fe/Na/S-C-Aero.

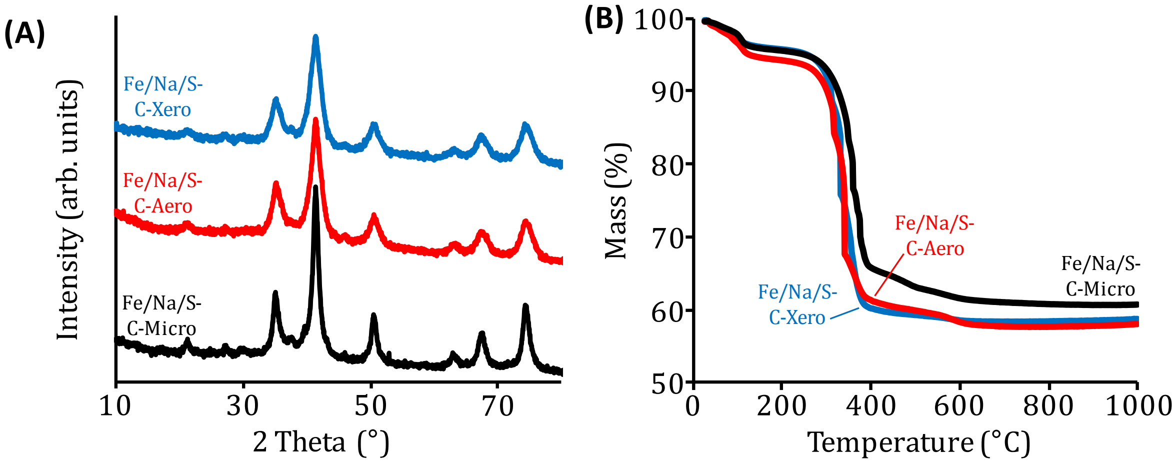

Figure S4. (A) X-ray diffraction patterns, and (B) thermogravimetric analysis under synthetic air atmosphere of the Fe/Na/S-C-Micro (black), Fe/Na/S-C-Xero (blue), and Fe/Na/S-C-Aero (red) catalysts.

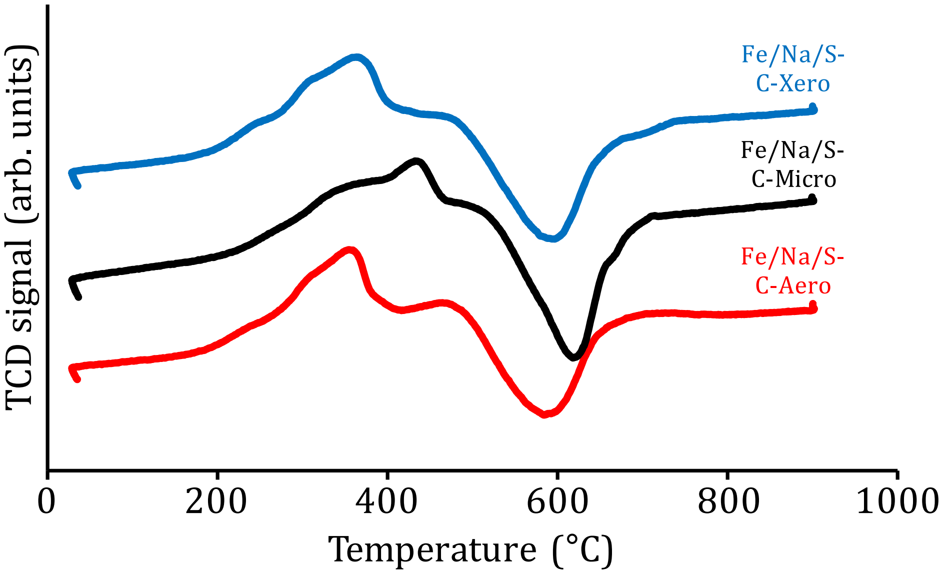

Figure S5. Hydrogen temperature programmed reduction (H_2-TPR) profiles of the calcined catalysts.

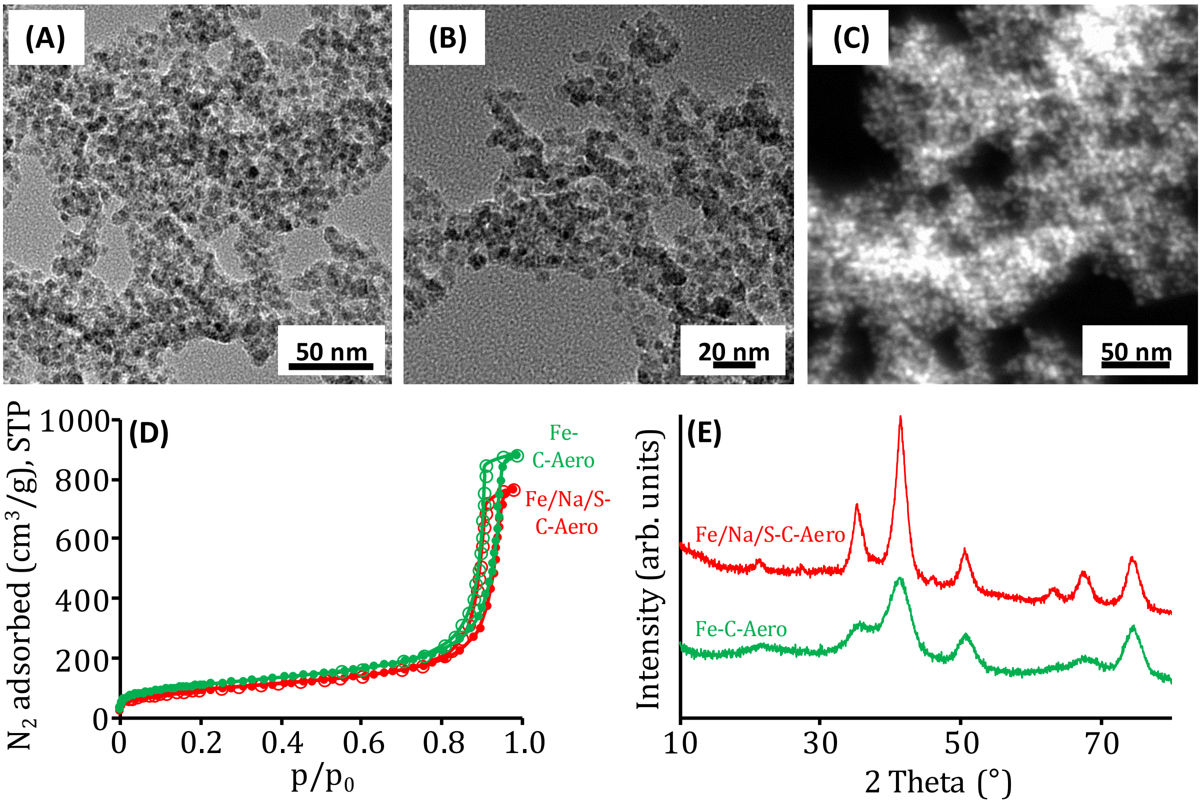

Figure S6. (A-C) TEM and HAADF-STEM images, (D) nitrogen physisorption isotherm measured at -196°C, and (E) X-ray diffraction patterns of the unpromoted Fe-C-Aero catalyst. The curves of the promoted Fe/Na/S-C-Aero catalyst are shown for comparison in (D) and (E).

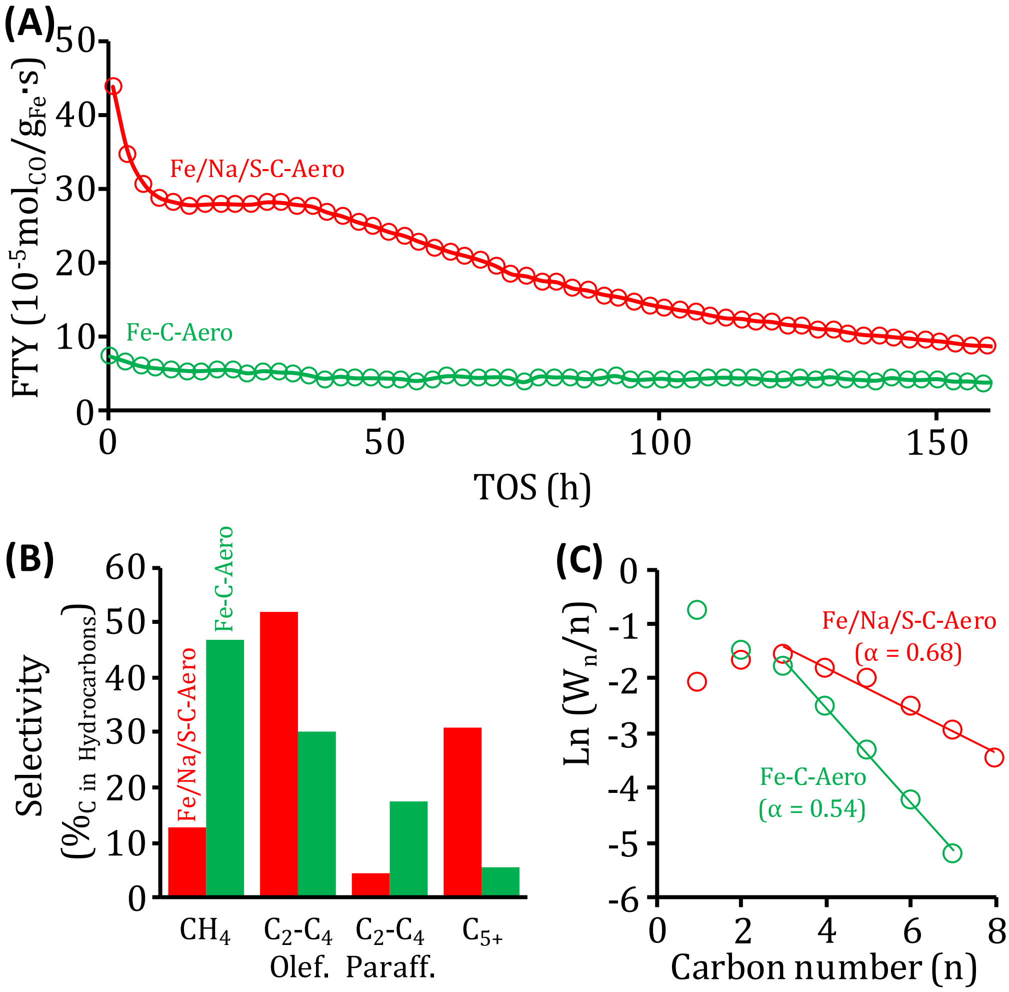

Figure S7. (A) Iron-weight based activity (FTY) over time on stream (TOS), (B) hydrocarbon product selectivity after 150 h TOS (CO conversion = 7.5 and 18 %; CO_2 selectivity = $43\%_C$ for both catalysts), and (C) corresponding Anderson–Schulz–Flory (ASF) plots of the C_1-C_8 product fractions with chain growth probability (α) based on the C_3-C_8 products of the Fe-C-Aero and Fe/Na/S-C-Aero catalysts.

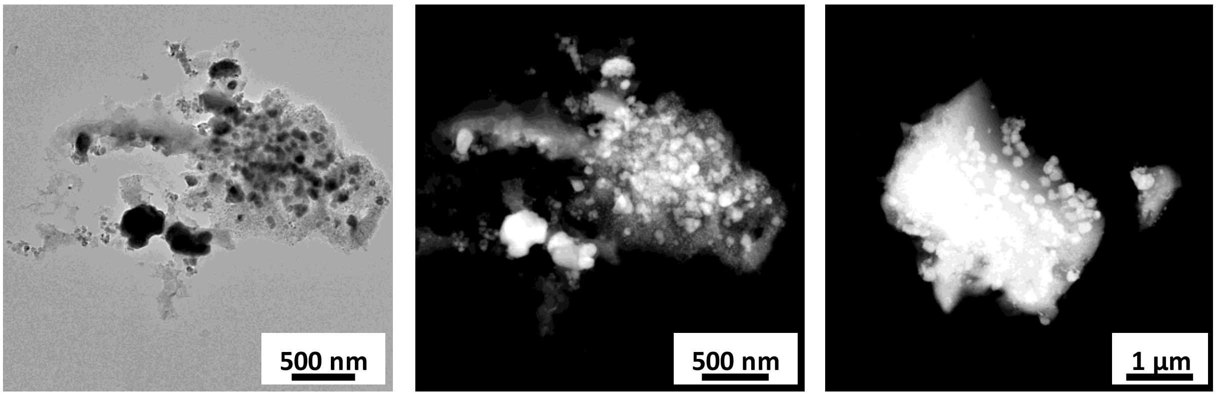

Figure S8. TEM and HAADF-STEM images of the catalyst "Fe-C-Aero-Preloaded" after pyrolysis.

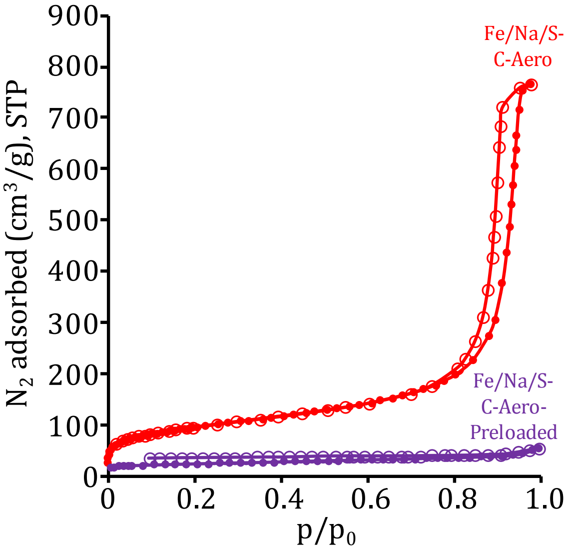

Figure S9. Nitrogen physisorption isotherms of the Fe/Na/S-C-Aero and Fe/Na/S-C-Aero-Preloaded catalysts measured at -196°C.

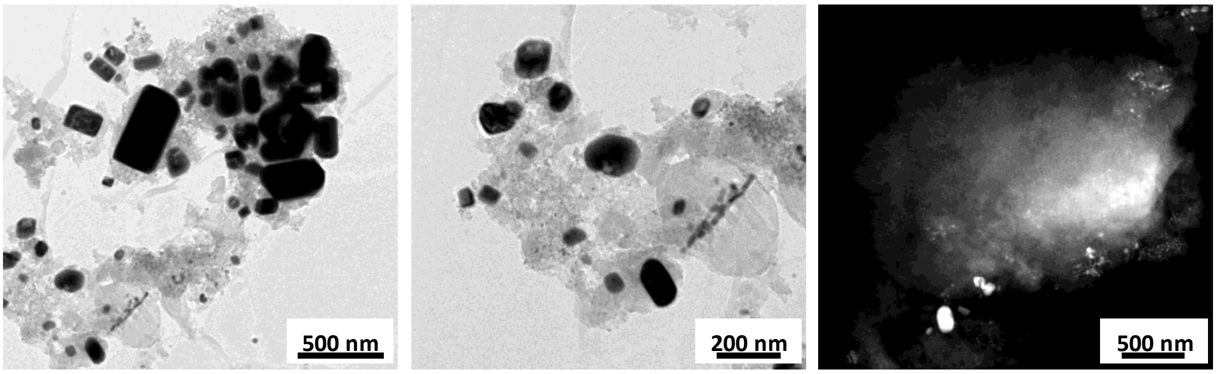

Figure S10. TEM and HAADF-STEM images of the spent Fe/Na/S-C-Micro catalyst after ~165 h TOS.

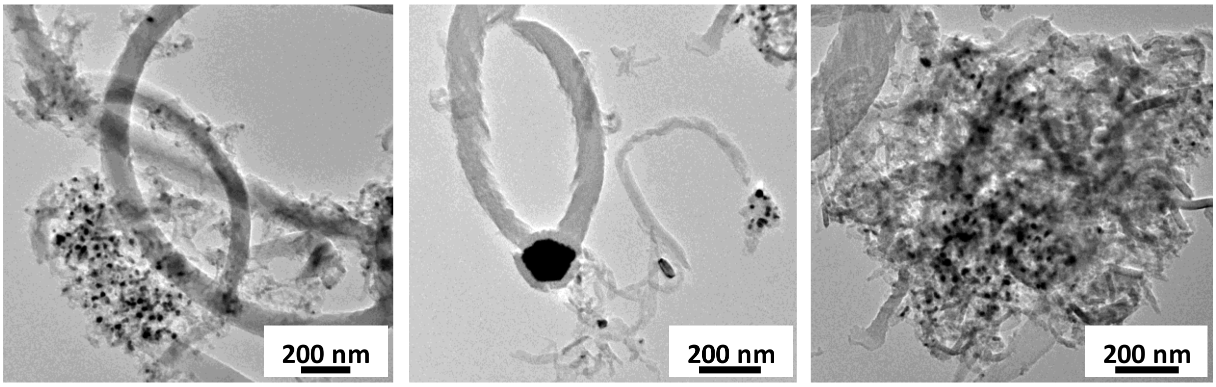

Figure S11. TEM images of the spent Fe/Na/S-C-Aero catalyst after ~165 h TOS.

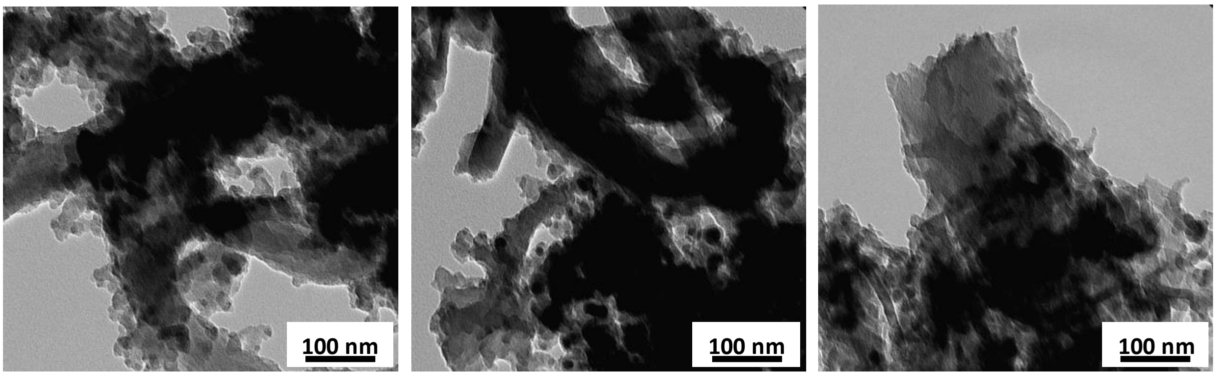

Figure S12. TEM images of the spent Fe/Na/S-C-Xero catalyst after ~165 h TOS.

Supplementary Tables

Table S1. Summary of nitrogen physisorption (-196°C) and thermogravimetric analysis data of the MOF precursors.

MOF	Specific surface area (m^2/g)	Total pore volume (cm^3/g)	Mean pore diameter (nm)	Residual mass after TGA under nitrogen (%)
Micro-FeBTC	863	0.35	1.62	46.4
Xero-FeBTC	1315	0.75	2.29	44.6
Aero-FeBTC	1474	2.98	8.08	43.7

Table S2. Summary of nitrogen physisorption (-196°C) data of the catalysts.

Catalyst	Specific surface area (m^2/g)	Total pore volume (cm^3/g)	Mean pore diameter (nm)
Fe/Na/S-C-Micro	190	0.13	2.78
Fe/Na/S-C-Xero	290	0.30	4.13
Fe/Na/S-C-Aero	344	1.18	13.7
Fe-C-Aero	405	1.36	13.4
Fe/Na/S-C-Aero-Preloaded	83	0.08	4.0

Table S3. ICP-OES data of the catalysts.

Catalyst	Fe (wt.%)	Na (wt.%)	S (wt.%)
Fe/Na/S-C-Micro	36.8	4.0	0.41
Fe/Na/S-C-Xero	34.6	2.7	0.26
Fe/Na/S-C-Aero	34.2	4.0	0.42
Fe-C-Aero	35.3	not detected	not detected

Experimental Section

MOF Synthesis. The synthesis of Iron-BTC gel was adopted from reference.[1] Solutions of trimesic acid (1.68 g in 40 ml ethanol) and iron(III) nitrate nonahydrate (4.84 g $Fe(NO_3)_3 \cdot 9 H_2O$ in 40 ml ethanol) were cooled to ca. -70 °C and mixed at the same temperature. The cold solution was slowly dropped in a 40 °C silicon oil bath. After 20 min the red droplets were filtered of and washed thoroughly with n-heptane to remove residual silicon oil and suspended in ethanol. The ethanol was then exchanged 5 times over 3 days at room temperature. The MOF gel was activated in three different ways to obtain a microporous powdered xerogel (Micro-Fe-BTC), a conventional xerogel (Xero-Fe-BTC), and a shaped aerogel (Aero-Fe-BTC). To obtain Xero-Fe-BTC, the ball shaped gel particles were thermally activated by removing the ethanol through filtration and subsequent treatment at 80 °C in an oven under ambient pressure for 12 h. The strongly shrunken balls were additionally activated in dynamic vacuum at 10^{-3} mbar and 80 °C for 5 h. A part of the Xero-Fe-BTC balls was milled in a mortar and sieved through a 1 mm sieve to obtain Micro-Fe-BTC. To obtain spherical Aero-Fe-BTC particles, supercritical activation in CO_2 as was applied to the spheres suspended in ethanol as described elsewhere.[1] After supercritical activation the ball shaped particles were additionally activated in dynamic vacuum at 10^{-3} mbar and 80 °C for 5 h.

Catalyst Synthesis. The MOFs with different porosity (0.588 g each) were loaded into an alumina boat and placed into a quartz tube into the isothermal zone of a horizontal tube furnace. The materials were heated to 500°C under nitrogen flow for 2 h (heating rate 120 °C/h). After cooling to room temperature (RT), the pyrolyzed MOFs are impregnated in multiple steps (drying at 120 °C under air in between) with an aqueous solution (0.4 ml) of 0.068 g sodium citrate dehydrate and 0.014 g iron(II)sulfate. After drying at 120 °C over night, the promoters were calcined under the same conditions as described above for the MOF precursors. Promoted catalysts obtained from Micro-Fe-BTC, Xero-Fe-BTC, and Aero-Fe-BTC are labelled as Fe/Na/S-C-Micro, Fe/Na/S-C-Xero, and Fe/Na/S-C-Aero, respectively. The unpromoted Fe-C-Aero catalyst was obtained by pyrolysis of the Aero-Fe-BTC without subsequent promoter loading.

The synthesis of the Fe/Na/S-C-Aero-Preloaded catalyst was carried out by impregnation of 0.588 g Aero-Fe-BTC with an aqueous solution (0.5 ml) of 0.068 g sodium citrate dehydrate and 0.014 g iron(II)sulfate followed by drying at 120°C and subsequent pyrolysis as described above.

Catalyst Characterization. Nitrogen physisorption isotherms were measured at -196°C. Specific surface areas (SSAs) were calculated with the multi-point BET method and total pore volumes at $p/p_0 = 0.98$-0.99. The quenched solid density functional theory (QSDFT) pore size distributions were calculated from the adsorption branches of the isotherms with the ASiQwin 3.01 software (Quantachrome Instruments) for nitrogen on carbon with mixed slit/cylindrical/spherical pores.

X-ray diffraction measurements were performed by using a Bruker D2 PHASER with a $CoK_{\alpha 1}$ radiation source ($\lambda = 0.1788$ nm).

Thermogravimetric analysis (TGA) measurements were carried out on a thermo microbalance TG 209 F1 Libra (Netzsch) with a heating rate of 10 °C/min. For the measurements up to 600 °C a nitrogen flow of 40 ml/min was applied. The measurements up to 1000 °C were carried out under a flow of 40 ml/min nitrogen and 10 ml/min oxygen.

Scanning electron microscopy (SEM) images were taken with secondary electrons in a HITACHI SU8020 microscope using 1.0 kV acceleration voltage and 10.8 mm working distance. The powdered samples were prepared on a sticky carbon sample holder.

Transmission electron microscopy (TEM) and high-angle annular dark-field scanning electron microscopy (HAADF-STEM) investigations were carried out on a FEI Talos F200X transmission electron microscope and on a FEI Tecnai 20 FEG instrument operated at 200 kV. Both instruments were operated at 200 kV. Before the measurements, the samples were ground into fine powders, dispersed in ethanol, sonicated for 30 s, and drop-casted on a carbon-coated copper TEM grid.

Temperature programmed reduction (TPR) under hydrogen atmosphere was performed by heating 40 mg of the calcined catalysts up to 1000 °C with heating rate of 5 °C/min in a 50 ml/min flow of a gas mixture of 5% hydrogen in argon by using a Micromeritics Autochem II 2920 chemisorption analyzer.

ICP-OES was performed by using a SPECTRO ARCOS ICP-OES instrument after aqua regia extraction of the samples.

Catalytic testing. The FTO catalysts were tested under industrially relevant conditions by using a 16-reactor catalytic testing setup (Flowrence, Avantium) at 10 bar, 340 °C, and a H_2/CO ratio of 2 (by volume). 10 mg of the catalysts were diluted with ~150 mg silicon carbide (50 mL, 212–425 mm) and transferred to a tubular fixed bed reactor. Hence, there was nearly similar iron content in all reactors. The catalysts were dried in a He flow at 280 °C for 20 min at 3 bar followed by subsequent change to a flow of H_2/CO (2/1 by volume) at 280 °C and 3 bar for 10 min. Then, the temperature was increased to 340 °C (heating rate =

28 °C/min) and after 10 min the pressure was increased to 10 bar (TOS = 0 h). The products were analyzed by using online GC (Agilent 7890A). The permanent gases and CO_2 were separated on a ShinCarbon ST column and quantified against He as an internal standard using a thermal conductivity detector (TCD). CO conversions were calculated as $X_{CO} = (mol_{CO,in} - mol_{CO,out})/mol_{CO,in}$. Hydrocarbons ($C_1$-$C_9$) were separated on an Agilent J&W PoraBOND Q column, detected using a flame ionization detector (FID) and quantified against the TCD signal of the internal standard He. The activity of the catalysts is expressed as FTY in moles of converted CO per gram of Fe per second. The product selectivity in $\%_{Carbon}$ was calculated as the equivalent of carbon atoms present in a product fraction in relation to total carbon atoms present in the formed hydrocarbons. At the end of the catalytic testing experiment, the reactors were cooled to RT under a flow of He.

The initial CO conversions of the promoted catalysts were between ~85% (Fe/Na/S-C-Aero) and ~10% (Fe/Na/S-C-Micro). The weight hourly space velocity (WHSV) was ~800 $cm^3_{Syngas}/g_{Cat}\cdot min$ for all catalysts. Because all catalysts had different density, the gas hourly space velocity (GHSV) ranged from ~13700 h^{-1} (Aero-Fe-BTC) to ~22600 h^{-1} (Micro-Fe-BTC).

1 M. R. Lohe, M. Rose and S. Kaskel, *Chem. Commun.*, 2009, 6056.