Supporting Information

Hierarchical structured α-Al_2O_3 supported S-promoted Fe catalysts for direct conversion of syngas to lower olefins

Xiangping Zhou,[a] Jian Ji,[a] Di Wang,[a] Xuezhi Duan,[a,*] Gang Qian,[a] De Chen[b] and Xinggui Zhou[a]

[a] *State Key Laboratory of Chemical Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China*

[b] *Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim 7491, Norway*

**Corresponding author: xzduan@ecust.edu.cn; Fax: +86-21-64253528.*

1. Catalyst preparation

Hierarchical structured boehmite was prepared by a two-step solvothermal method described earlier (*Chin. J. Inorg. Chem.* **2011**, 27: 251-258), and then calcined at 1300 ^{o}C (heating rate, 5 $^{o}C\cdot min^{-1}$) for 4 h to obtain hierarchical structured α-Al_2O_3 (i.e., α-Al_2O_3-H). The α-Al_2O_3-H and commercial α-Al_2O_3 (α-Al_2O_3-C, Nuoda Chemical Co. Ltd., China) were used to support iron species without S promoter using ammonium iron citrate (J.T. Baker, 14.5-16.0 wt% Fe) by incipient wetness impregnation method. The two impregnated samples were dried at ambient temperature for 12 h and then at 120 ^{o}C for 12 h and calcined at 500 ^{o}C for 2 h. The as-obtained two samples were donated as Fe/α-Al_2O_3-H and Fe/α-Al_2O_3-C, respectively. Similarly, Fe/α-Al_2O_3-H catalysts with different content of S promoter (Fe/α-Al_2O_3-H-xS, x representing the nominal loading of S (10^{-2} wt%)) were prepared using ammonium iron citrate and ferrous sulfate heptahydrate (Sinopharm Chemical Reagent Co. Ltd., China) precursors, where the amount of ferrous sulphate heptahydrate precursor is determined by the nominal S content. In addition, bulk α-Fe_2O_3 was obtained from the calcination of ammonium iron citrate at 500 ^{o}C for 2 h.

ICP results of two kinds of iron precursors and properties of iron catalysts with or without S promoter were listed in Table S1 and Table S2, respectively. As shown in Table S1, the S content in ammonium iron citrate precursor is very low, which can be ignored in our work. Because the S contents of our prepared S-promoted Fe catalysts are in the range of 0.03-0.08 wt%, the amount of ferrous sulfate precursor is much lower than that of ammonium iron citrate precursor. Therefore, different Fe-based catalysts contain comparable Na contents, and thus the effects of S concentration are apparent in the current work.

2. Characterization

The microstructures and elemental analysis of supports were characterized by field emission scanning electron microscopy (FESEM, FEI NOVA Nano SEM 450, Netherlands) fitted with an energy dispersive X-ray spectroscopy (EDS, EDAX). X-ray diffraction (XRD) was carried out using a Rigaku D/Max2550VB/PC X-ray diffractometer (Rigaku, Japan) with Cu K_α radiation (λ=1.54056 Å). The surface areas of α-Al_2O_3 supports were measured on ASAP 2020 (Micromeritics, USA) at 77 K after out-gassing the samples at 190 ^oC and 1 mmHg for 6 h. The elemental content of iron precursors were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Agilent 725ES, USA). H_2 temperature-programmed reduction (H_2-TPR) was performed using an Autochem 2920 (Micromeritics, USA) with 50 mg sample and 10% H_2/Ar (30 mL·min^{-1}) as reducing gas. The temperature was increased from room temperature to 900 ^oC at a heating rate of 10 ^oC·min^{-1}. The microstructures and elemental mappings of catalysts were characterized by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100, Japan) fitted with an energy dispersive X-ray spectroscopy (EDS, Oxford-INCA). Thermal gravimetric-differential thermal analysis (TG-DTA) was conducted with a flow of air in the temperature range 30-800 ^oC (heating rate: 10 ^oC·min^{-1}) carried out on a TA SDT-Q600 thermobalance.

3. Catalytic testing

FTO reaction was carried out on a fixed-bed quartz reactor under 1 bar. Typically, 100 mg catalyst was first reduced in H_2 (15 mL·min^{-1}) at 350 ^{o}C for 2 h (heating rate, 5 ^{o}C·min^{-1}). After reduction, syngas (CO/H_2=1/1 v/v, 15 mL·min^{-1}) was introduced to the reactor. The outlet products were analyzed on-line using a gas chromatograph (GCA90, Echrom). A capillary column (MEGA-1) connected to a flame ionization detector (FID) was used to analyze hydrocarbons, while a packed column (Porapak Q) connected to a thermal conductivity detector (TCD) to analyze CO, CO_2 and H_2. Calculation of CO conversion and product selectivity can refer to our recent work (*J. Mater. Chem. A* **2015**, 3: 4560-4567). In addition, the selectivity to oxygenates was below 1%C and therefore excluded.

Table S1 ICP results of two kinds of iron precursors.

Iron precursor	Content (wt%)		
	Fe	S	Na
Ammonium iron citrate	15.0	0.0028	0.063
Ferrous sulphate heptahydrate	20.1	11.40	0.046

Table S2 Elemental loading of iron catalysts with or without S promoter.

Sample	Nominal loading (wt %)		
	Fe	S	Na
Fe/α-Al_2O_3-C[a]	10.0	~0	0.042
Fe/α-Al_2O_3-H[a]	10.0	~0	0.042
Fe/α-Al_2O_3-H-3S[b]	10.0	0.03	~0.042
Fe/α-Al_2O_3-H-5S[b]	10.0	0.05	~0.042
Fe/α-Al_2O_3-H-8S[b]	10.0	0.08	~0.042

[a] Using ammonium iron citrate precursor.

[b] Using ammonium iron citrate and ferrous sulfate precursors, and the amount of ferrous sulphate determined by the S content.

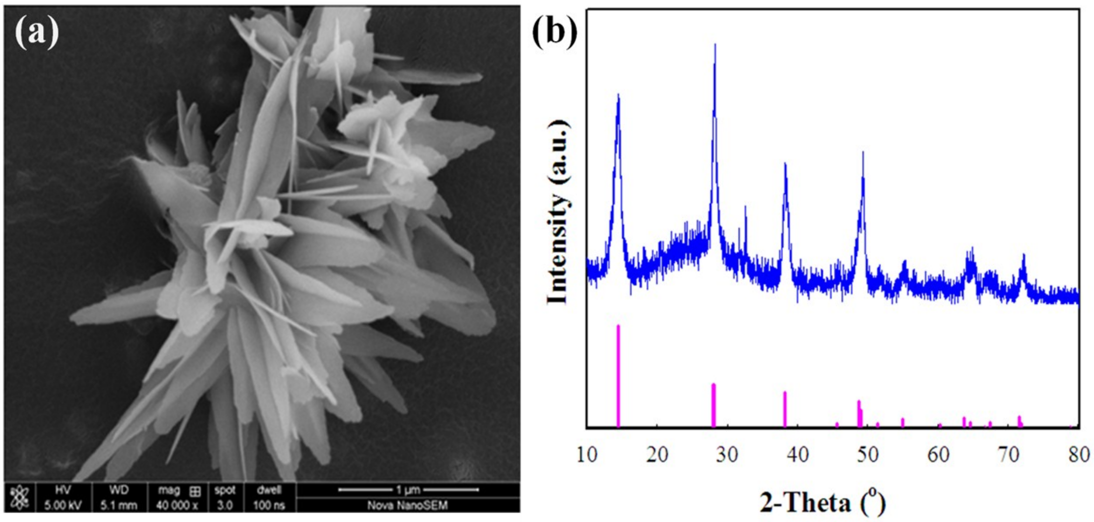

Figure S1 Typical FESEM image (a) and XRD pattern (b) of hierarchical structured boehmite. Standard pattern of boehmite (JCPDS No. 88-2112) was also presented for comparison.

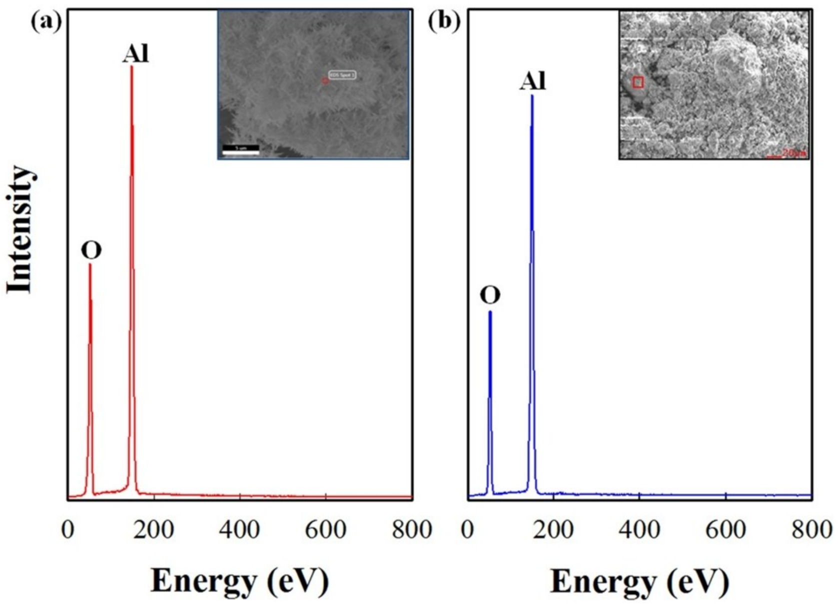

Figure S2 EDS spectra and FESEM images of α-Al_2O_3-H (a) and α-Al_2O_3-C (b).

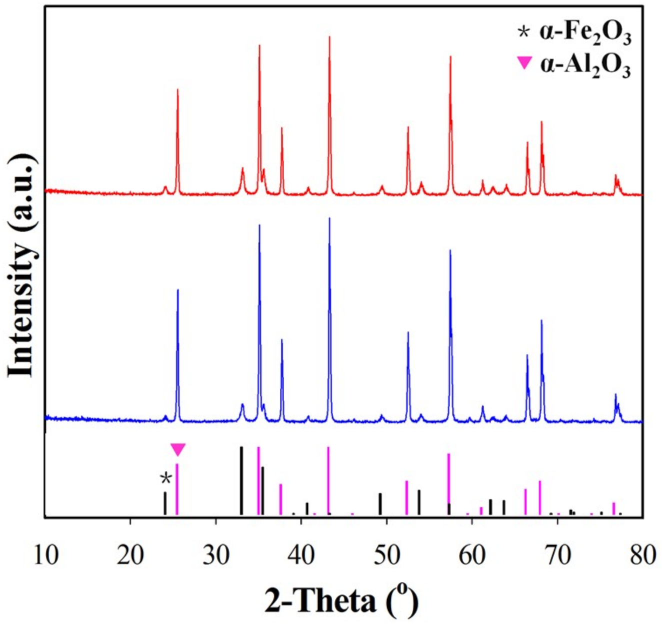

Figure S3 XRD patterns of calcined Fe/α-Al_2O_3-H (red) and Fe/α-Al_2O_3-C (blue) samples. Standard patterns of α-Fe_2O_3 (JCPDS No. 33-0664) and α-Al_2O_3 (JCPDS No. 46-1212) were also presented for comparison.

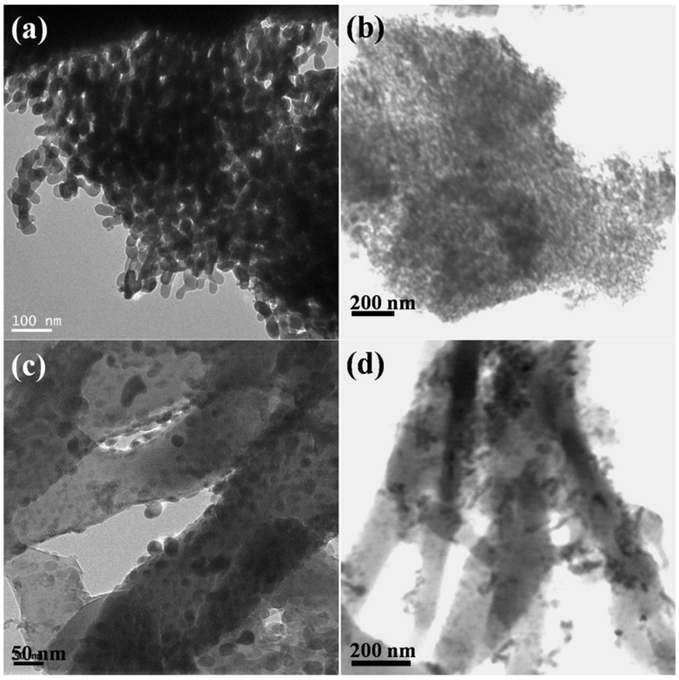

Figure S4 Typical HRTEM images of calcined Fe/α-Al_2O_3-C (a and b) and calcined Fe/α-Al_2O_3-H (c and d).

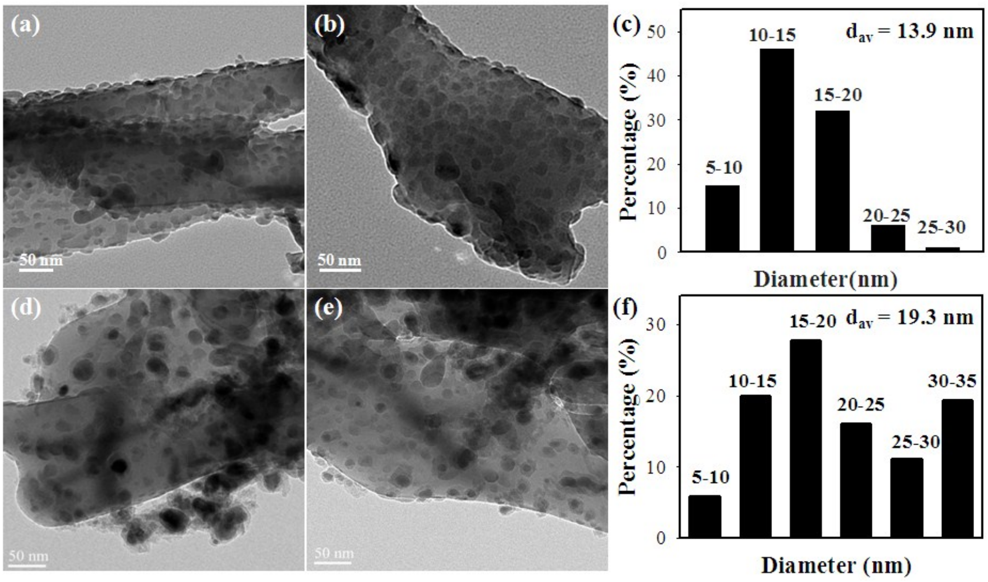

Figure S5 Typical HRTEM images and corresponding particle size distributions of fresh (a, b and c) and used (d, e and f) Fe/α-Al_2O_3-H catalysts. Reduction conditions: in H_2 (15 mL·min^{-1}) at 350 ^{o}C for 2 h (heating rate, 5 ^{o}C·min^{-1}). Reaction conditions: 350 ^{o}C, 1 bar, TOS=19 h and H_2/CO=1 with a GHSV=9000 mL·h^{-1}·$g_{cat}$$^{-1}$.

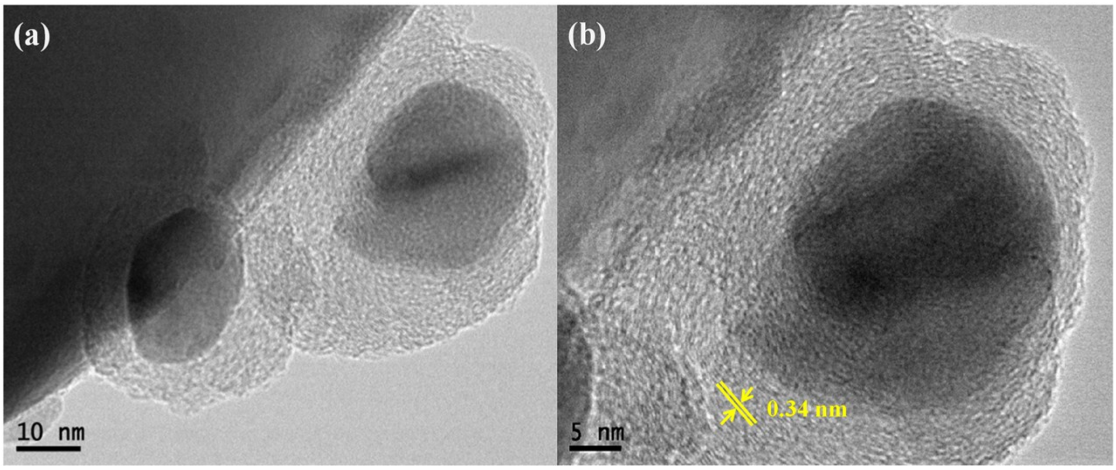

Figure S6 Typical HRTEM images of used Fe/α-Al_2O_3-H. Reaction conditions: 350 ^oC, 1 bar, TOS=19 h and H_2/CO=1 with a GHSV=9000 mL·h^{-1}·g_{cat}^{-1}.

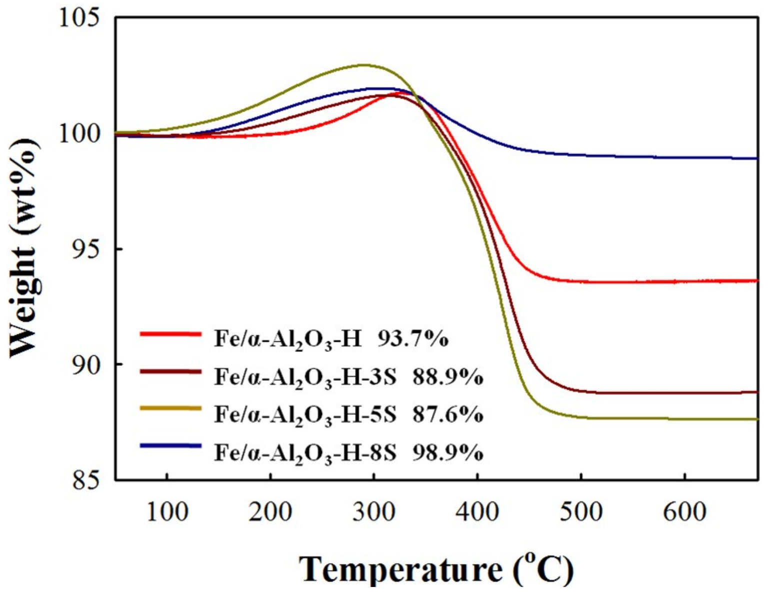

Figure S7 TGA curves of the used catalysts. Reaction conditions: 350 ^{o}C, 1 bar, TOS=19 h and H_2/CO=1 with a GHSV=9000 mL·h^{-1}·g$_{cat}^{-1}$.

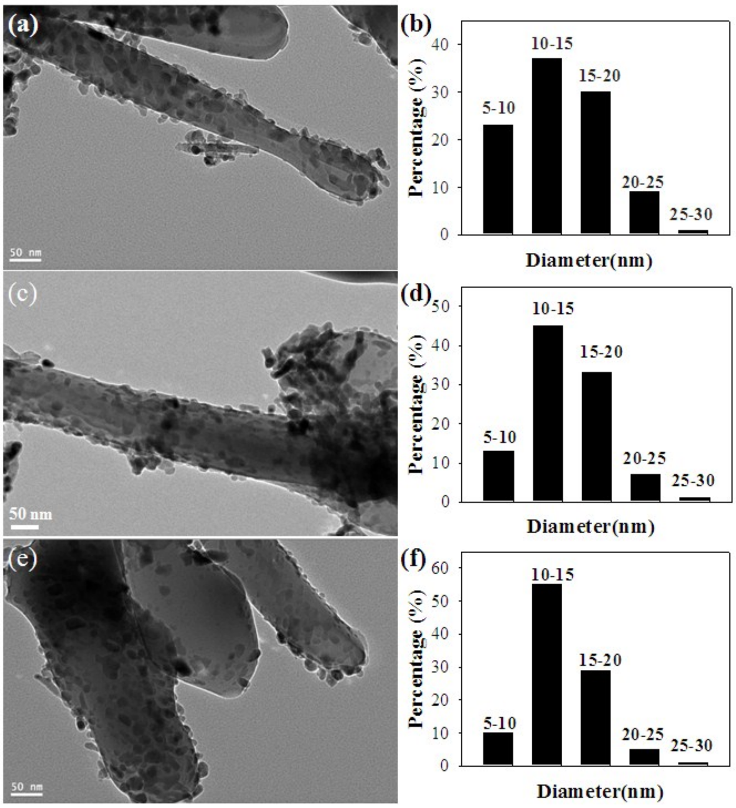

Figure S8 Typical HRTEM images and corresponding particle size distributions of fresh Fe/α-Al_2O_3-H-3S (a and b), Fe/α-Al_2O_3-H-5S (c and d) and Fe/α-Al_2O_3-H-8S (e and f) catalysts. Reduction conditions: in H_2 (15 mL·min^{-1}) at 350 ^{o}C for 2 h (heating rate, 5 ^{o}C·min^{-1}). The mean iron particles sizes on the three fresh catalysts are 14.0, 14.1 and 13.9 nm, respectively.

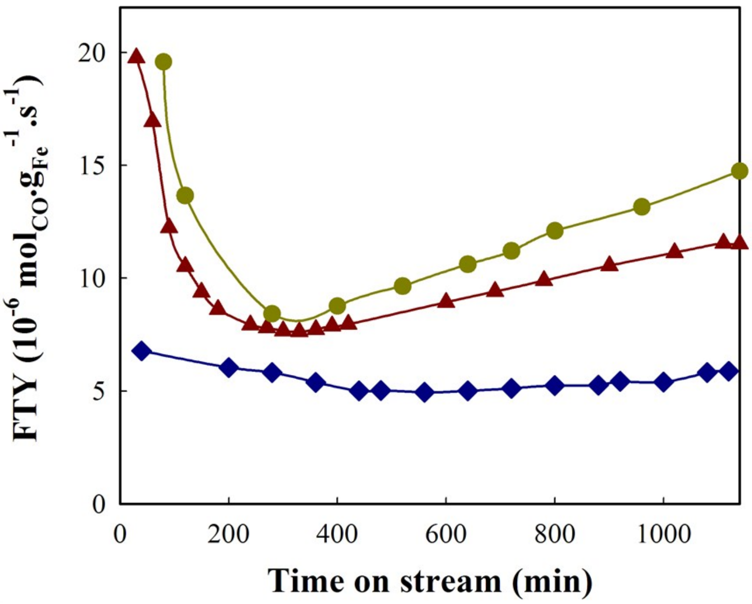

Figure S9 FTY as a function of time on stream over Fe/α-Al_2O_3-H-3S (▲), Fe/α-Al_2O_3-H-5S (●) and Fe/α-Al_2O_3-H-8S (◆) catalysts. The reaction was performed at 350 ^oC, 1 bar and $H_2/CO=1$ with a GHSV=9000 $mL \cdot h^{-1} \cdot g_{cat}^{-1}$.