

Electronic Supplementary Material(ESI) for RSC Advances.

The effect of pore size or iron particle size on formation of light olefins via Fischer–Tropsch synthesis

Yi Liu^a, *Jian-Feng Chen*^b, *Yi Zhang*^{a, b, *}

Experimental

Preparation of catalysts

Three manganese promoted catalysts with iron loadings of 10 wt% and Fe/Mn molar ratio of 20/1 were prepared by incipient wetness impregnation of aqueous solutions of ferric nitrate nonahydrate and manganese (II) nitrate tetrahydrate (Aldrich-sigma Co.) on commercially available silica gel with pore sizes varying from 5, 50 and 80 nm. After the impregnation, the precursor was dried in air at 393 K for 12 h, and then calcined in air from room temperature to 773 K in 3 h and maintained at 773 K for 2 h.

In addition, FeMn/S50-E and FeMn/S80-E catalysts with same composition (10 wt% Fe, Fe/Mn molar ratio of 20/1) were prepared by an ethylene glycol (EG) modified incipient wetness impregnation method to achieve the smaller Fe₂O₃ particle size compared with corresponding catalyst. The silica gel was treated with ethylene glycol (EG) for 1 h at room temperature by incipient-wetness impregnation method, in which the amount of EG was equal to the total pore volume of utilized silica gel. And then, the samples were dried in air at 373 K for 12 h. The details of EG pretreatment were reported elsewhere.^{1, 2} Then the aqueous solution of ferric nitrate nonahydrate and manganese (II) nitrate tetrahydrate was impregnated onto pretreated silica support by incipient-wetness impregnation method. After that, the sample was dried at 393 K for

12 h, following calcination at 773 K for 2 h. The number in the sample code indicates the average pore size of silica gel. To differentiate between nonpretreated and EG-pretreated samples, a letter E was added to the sample code of EG-pretreated catalyst.

Catalyst characterization

The BET surface area, pore volume, and pore size distributions of the mesopore samples were obtained via nitrogen physisorption at 77 K using a Micrometrics ASAP 2010 analyzer. Macropore intrusion volumes, total surface area, and macropore size distributions were recorded by mercury intrusion porosimetry using a Quantachrome PoreMaster 60GT porosimeter over a pressure range of 20 psi to 60 000 psi. All samples were degassed at 473 K for 6 h prior to the measurement.

An X-ray diffractometer (XRD, Shimadzu XRD-6000) was used to detect crystalline size of the fresh catalysts. The crystalline average size was calculated by $L = K\lambda / \Delta (2\theta) \cos \theta_0$, where L is the crystalline size, K is a constant (K=0.9), λ is the wavelength of X-ray (Cu K α =0.154 nm), and $\Delta (2\theta)$ is the width of the peak at half height.

The particle size distribution on the support was obtained by the analysis of transmission electron microscopy (TEM) micrographs. The images of the catalysts were determined by JEM-2200FS and JEM-2100 microscope. The specimen was prepared by ultrasonically suspending the catalyst powder in ethanol. A drop of the suspension was deposited on carbon-coated copper grids and dried in air. Iron particle and iron carbide size were calculated from the statistical TEM data over 100 particles.

Transmission ^{57}Fe Mossbauer spectra were collected at room temperature on an VIS-1170-MO constant-acceleration Mössbauer spectrometer (Cryodynamics, USA), using a 25 mCi ^{57}Co in

Pd matrix. The spectrometer was operated in the symmetric constant acceleration mode. Data analysis was performed using a nonlinear least-squares fitting routine that models the spectra as a combination of singlets, quadruple doublets, and magnetic sextuplets based on a Lorentzian line shape profile.

H₂-Temperature programmed reduction (H₂-TPR) experiments were carried out in a quartz tube reactor using 0.05 g calcined catalysts. The reducing gas, a mixture of 10% H₂ diluted by Ar, was fed via a mass flow controller at 30 ml/min and the temperature was increased from 303 K until 1073 K at a rate of 8 K/min. The effluent of reactor passed through a 5 Å molecular sieve trap to remove produced water, before reaching TCD. The hydrogen consumption was calibrated using the H₂-TPR of CuO (Aldrich, 99.99+%) as the standard sample under the same conditions.

The XPS analysis of the fresh catalysts was performed on a ThermoFisher Scientific ESCALAB 250 spectrometer. The spectra were excited by the monochromatized Al K α source (1486.6 eV). The analyzer operated in the constant analyzer energy (CAE) mode. Survey spectra were measured at 30 eV pass energy. The peak positions were corrected for sample charging by setting the C 1 s binding energy at 284.8 eV.

Catalytic reaction

The FTS reaction was carried out in a fixed-bed reactor (SUS 316L, 8 mm i.d.). The reaction conditions were P (total) = 1.0 MPa, CO/H₂ = 1, W/F(CO+H₂+Ar) = 5 g-cat. h mol⁻¹, T = 573 K. The reactor temperature was measured with a K-type thermocouple buried in the catalytic bed. Flow rates were controlled using a Brooks 5850 TR Series mass flow controller. The feed gas consisted of Ar (4.99%), CO (47.5%) and H₂ (47.6%). 0.5 g catalyst (20-40 mesh) mixed with 1.0 g quartz sand was placed in the reactor tube and reduced in situ at 593 K for 10 h in the flow of feed gas at

0.1 MPa, followed by cooling down to 353 K in N₂. When the reaction temperature was reached, pressurized syngas was introduced and the reaction was carried on continuously for 30 h.

The effluent gas from the reactor was analyzed by on-line gas chromatography (GC). A thermal conductivity detector (TCD) was used to analyze gaseous products (CO, CO₂ and CH₄). Light hydrocarbons (C₁–C₅) were on-line analyzed by another GC with flame ionization detector (FID) using a Porapak-Q column. The analyses of hydrocarbons dissolved in the solvent and cooled in the trap were carried out with GC-FID using silicone SE-30 column. The mass balance of various reactions were calculated, which were almost 95% based on carbon mole for all reactions.

Table S1 Mössbauer parameters of the fresh iron-based catalysts.

Catalysts	Phases	Mössbauer parameters ^a				
		IS (mm/s)	QS (mm/s)	Line Width (mm/s)	Hhf (kOe)	Area (%)
FeMn/S50	Fe ³⁺ (spm)	0.32	0.79	0.49	-	37.2
	α-Fe ₂ O ₃	0.35	-	0.48	502	62.8
FeMn/S5	Fe ³⁺ (spm in bulk)	0.34	0.67	0.47	-	69.1
	Fe ³⁺ (spm in surface)	0.34	1.35	0.43	-	30.9
FeMn/S50-E	Fe ³⁺ (spm in bulk)	0.34	0.76	0.47	-	71.6
	Fe ³⁺ (spm in surface)	0.35	1.42	0.43	-	28.4

^a Measured at room temperature.

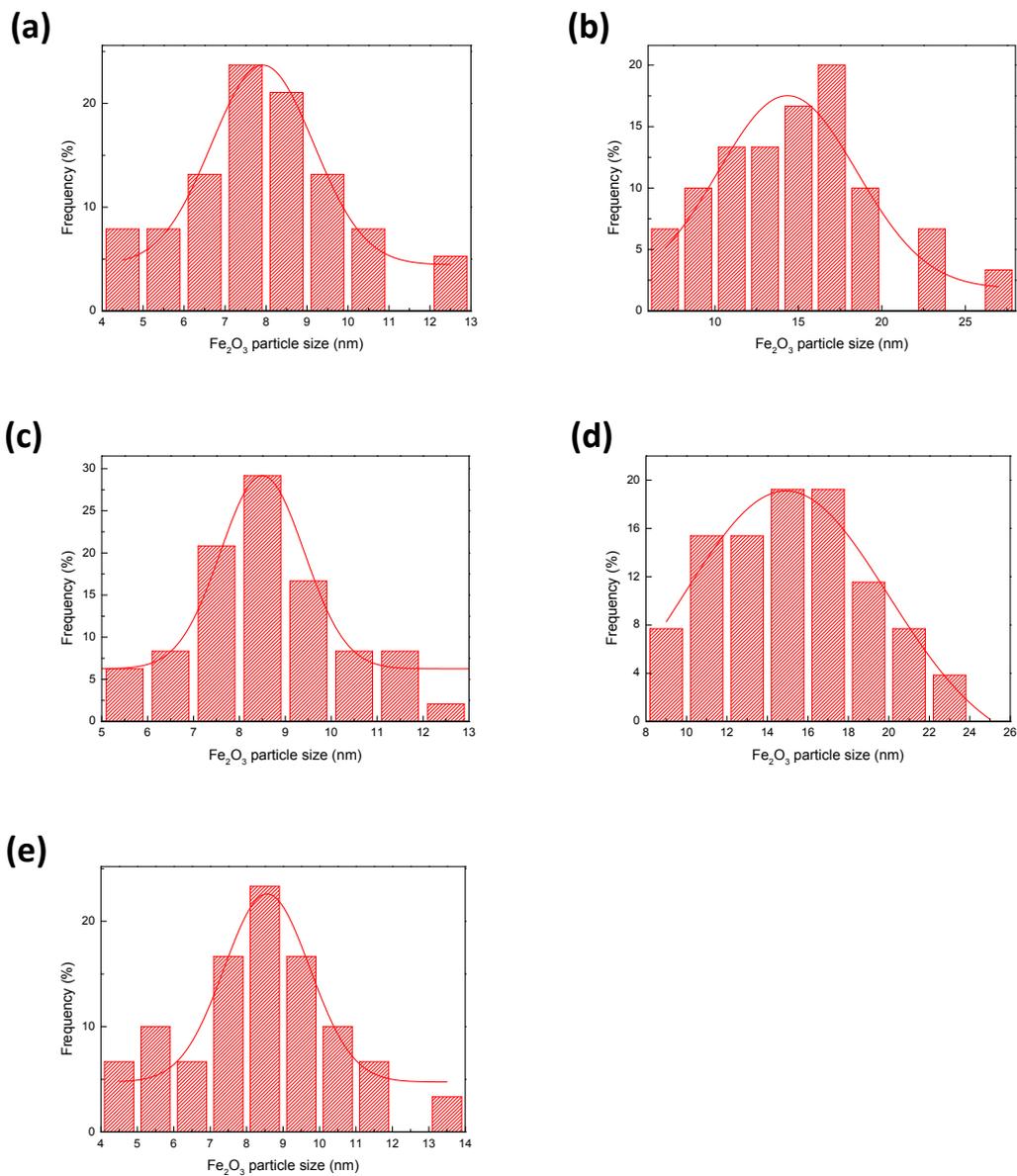


Fig. S1 The Fe_2O_3 particle size histograms from corresponding TEM micrographs for silica supported iron-based catalysts on (a) FeMn/S5, (b) FeMn/S50, (c) FeMn/S50-E, (d) FeMn/S80 and (e) FeMn/S80-E as prepared.

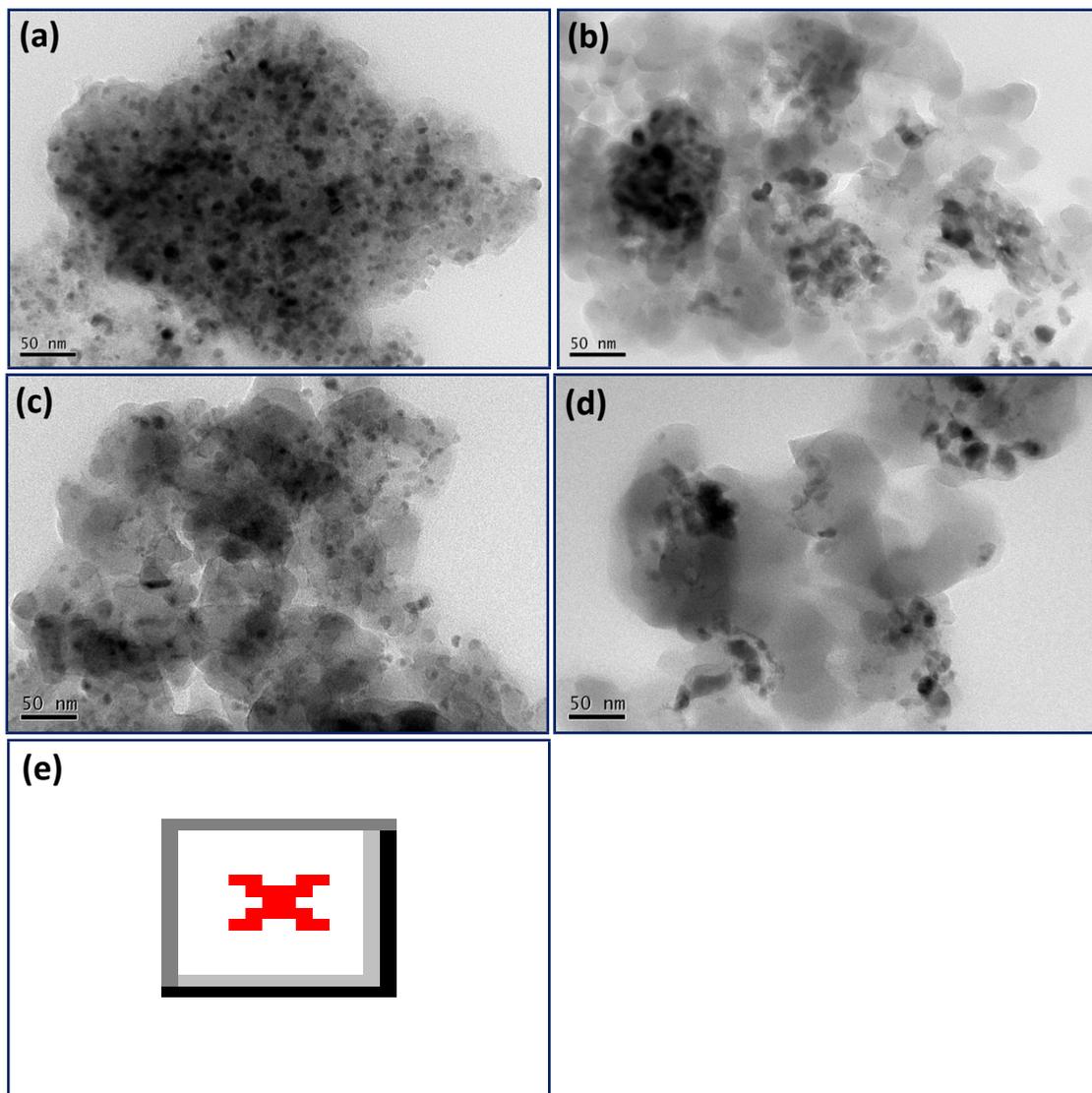


Fig. S2 TEM micrographs for silica supported Fe-Mn catalysts on (a) FeMn/S5, (b) FeMn/S50, (c) FeMn/S50-E, (d) FeMn/S80 and (e) FeMn/S80-E after reduced.

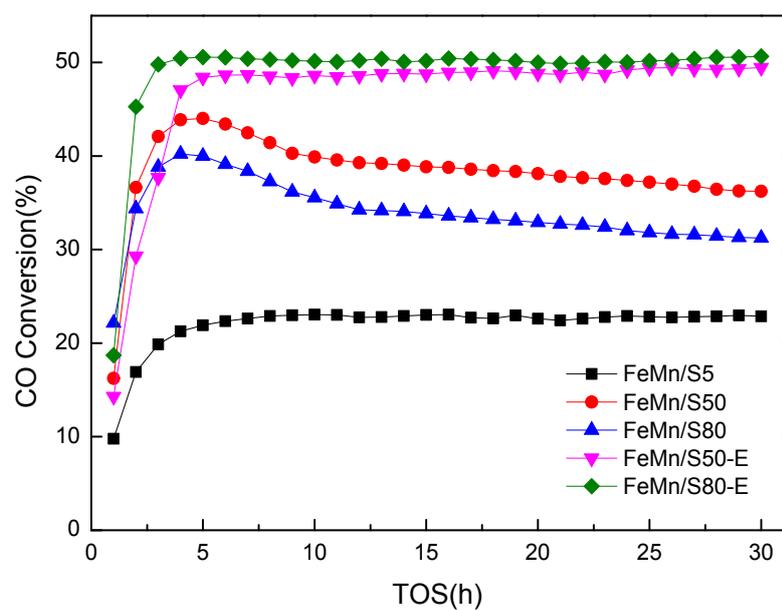


Fig. S3 CO conversion as a function of time on stream for various catalysts.

References

- 1 X. Lv, J. F. Chen, Y. Tan and Y. Zhang, *Catal. Commun.* 2012, **20**, 6.
- 2 J. F. Chen, Y.R. Zhang, L. Tan and Y. Zhang, *Ind. Eng. Chem. Res.* 2011, **50**, 4212.