Supporting Information

Liquid-Phase Fischer-Tropsch Synthesis over Fe Nanoparticles Dispersed in Polyethylene glycol (PEG)

Xiao-Bing Fan, Zhi-Yuan Tao, Chao-Xian Xiao, Fang Liu, and Yuan Kou*

PKU Green Chemistry Center, Beijing National Laboratory for Molecular Sciences,
College of Chemistry and Molecular Engineering, Peking University, Beijing 100871,
China
Email address: yuankou@pku.edu.cn

Materials and Methods

CO (99.9%), H_2 (99.999%), $FeCl_2{\cdot}4H_2O$ (AR grade), $Co(CH_3COO)_2{\cdot}4H_2O$ (AR grade), ethylene glycol (AR grade), Polyethylene glycol (PEG 200, PEG 400; AR grade), poly(N-vinyl-2-pyrrolidone) (PVP, K30), and other chemicals were commercially available locally and used without further purification. [BMIM][BF_4] were prepared according literature.[1]

Transmission electron microscopy (TEM) measurements were carried out on JEM-2010 transmission electron microscope. IR spectra were recorded on a Fourier transform infrared spectrophotometer (Tensor 27, Bruker) with a resolution of 1 cm^{-1}. GC analyses were carried out on an Agilent Chrompack HP-6820 equipped with an HP-INNOWax capillary column (30 m, 0.25 mm, using nitrogen as carrier gas), and a Fuli 9790 equipped with an OV-101 capillary column (30 m, 0.25 mm, using nitrogen as carrier gas). GC-MS analyses were carried out on a DSQ GC-MS system (Thermo Fisher). XRD patterns were recorded on a Rigaku D/MAX-PC 2500 diffractometer.

Preparation and characterization of metal catalysts

1) Preparation of Fe nanoparticle catalyst

$NaBH_4$ solution (500 mg $NaBH_4$, 4.0 ml EG, 1.0 ml water) was quickly adding into a conical flask containing $FeCl_2$ solution (400 mg $FeCl_2{\cdot}4H_2O$, 10.0 ml EG) under stirring. The color of the solvent rapidly became dark accompanied with the release of hydrogen. The Fe nanoparticles prepared were gathered on the bottom of the flask by using a strong magnet. The colorless, transparent solvent was discarded. The Fe nanoparticles were immediately washed three times with deoxygenated water and then by PEG to remove water. All the procedures were carried out under the protection of N_2 (99.99 %).

2) Preparation of Co catalyst

$NaBH_4$ solution (800 mg, 2.0 mL water) was quickly added into a conical flask containing $Co(CH_3COO)_2{\cdot}4H_2O$ solution (500 mg $Co(CH_3COO)_2{\cdot}4H_2O$, 10.0 mL H_2O, 400 mg CH_3COOH) under stirring. Black Co metal particles were rapidly generated accompanied by release of hydrogen. The black Co nanoparticles were separated by centrifugation (4000 round/min) and washed three times with water and/or by PEG to remove water.

Characterization of the iron/cobalt catalyst

For transmission electron microscopy (TEM), one drop of the suspension of Fe nanoparticles in PEG was dispersed in isopropanol under ultrasonication for 1 h, and then one drop of solution was placed on a copper grid coated by a polymer or carbon film which was further dried under vacuum. All the manipulations were conducted under N_2. For powder X-ray diffraction (XRD), the Fe nanoparticles before and after reaction were washed with ethanol and acetone then dried under nitrogen atmosphere. The sample was sealed with a polyethylene film to avoid oxidation during the measurements. In order to crystallize the iron nanoparticles, the catalysts were treated at 600 ^{o}C for one hour in an nitrogen atmosphere. The XRD patterns were recorded at 40 kV and 100 mA, in the 2θ range from 28^{o} to 90^{o}. The characterization of Co catalyst was the same as that of Fe catalyst.

Catalytic performance testing

In a typical experiment, the freshly prepared metal catalyst (2.0 mmol, in 40.0 ml PEG 200) was placed in a 140 ml stainless steel autoclave. The reactor was purged three times with N_2 (99.99 %) and was then sealed at a CO (99.9 %) pressure of 1.0 MPa. An additional 2.0 MPa H_2 (99.999 %) was further added, providing a H_2/CO mole ratio equals to 2. The autoclave was kept at 150 °C, with stirring speed at 800 rpm until the total pressure decreased to ~2.5 MPa (or ~2.0 MPa at room temperature) indicating a CO conversion of about 30 %. Except for the cases of very slow reaction rates, the reaction time required was in the range of 3-12 h. After reaction, the autoclave was cooled to room temperature and the products were collected and analyzed.

Product analysis

All the products were determined based on standard procedures established in our previous work.[2] After reaction, the gas was collected and analyzed by gas chromatography (GC), gas chromatograph-mass spectrometer (GC-MS) and fourier transform-infrared spectrometer. Then 10.0 ml of cyclohexane (HPLC grade) was injected into the autoclave with dodecane and naphthane as the internal standard. The autoclave was sealed and heated at 150 °C for 2 h. After the autoclave was cooled to room temperature, the upper phase containing hydrocarbon products was collected and analyzed immediately by GC and GC-MS. For the gas phase, the major components are

CO, H_2, CO_2 and C_1-C_5 products (mainly alkanes and alkenes). The amounts of CH_4, CO and CO_2 were determined by FT-IR spectroscopy (Bruker Vector 22 spectrometer) using appropriate calibration curves. The CO_2 concentration was rather small, typically only 0.3 v/v%. C_1-C_5 products were measured by GC (Fuli 9790, Porapak Q, FID). For the liquid phase: the major products in the cyclohexane phase are C_{3+} products (mainly alkanes and alkenes). Their amounts were determined by GC (Fuli 9790, 30 m×0.25 mm i.d OV-101, FID; Agilent 6820, 30 m×0.32 mm i.d HP-INNOWax, FID). A typical spectrum is shown in Figure S4. The bottom PEG phase was also analyzed by GC (Agilent 6820, 30 m×0.32 mm i.d HP-INNOWax, FID), using isobutyl alcohol as the internal standard.

Calculations of the activity

Activity = mol CO converted / (mol catalyst used * reaction time).

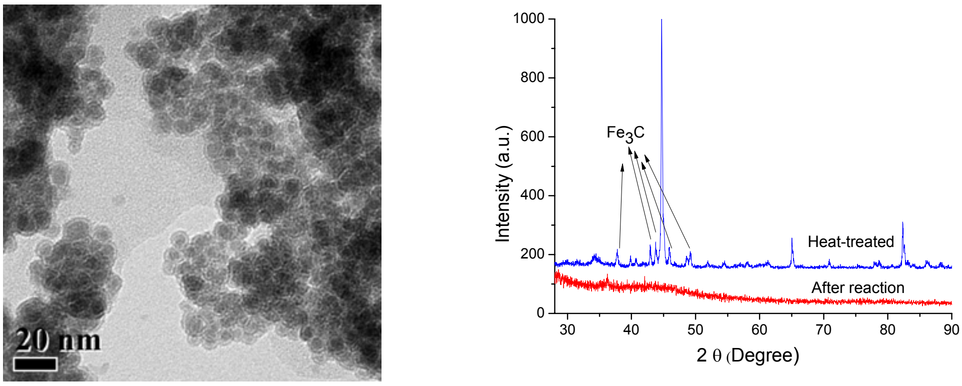

Fig. S1. TEM and XRD results of iron catalyst after reaction. Reaction conditions: 150 °C, 3.0 MPa H_2, 1.5 MPa CO, 2.0×10^{-3} mol Fe, 40 mL PEG 200, 5 hours.

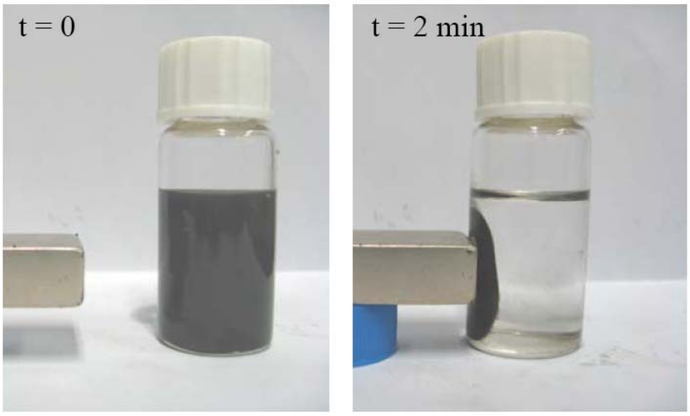

Fig. S2. Pictures for the demonstration of the convenient separation of the iron catalysts after reaction using an external magnetic.

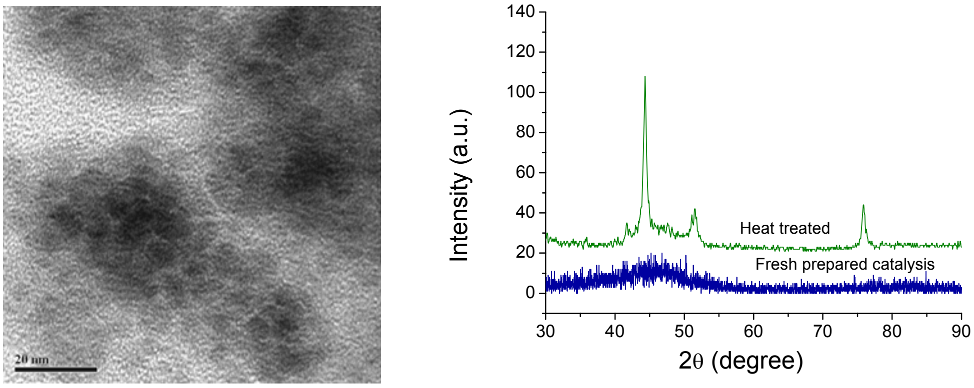

Fig. S3. TEM and XRD results of the fresh Cobalt catalyst.

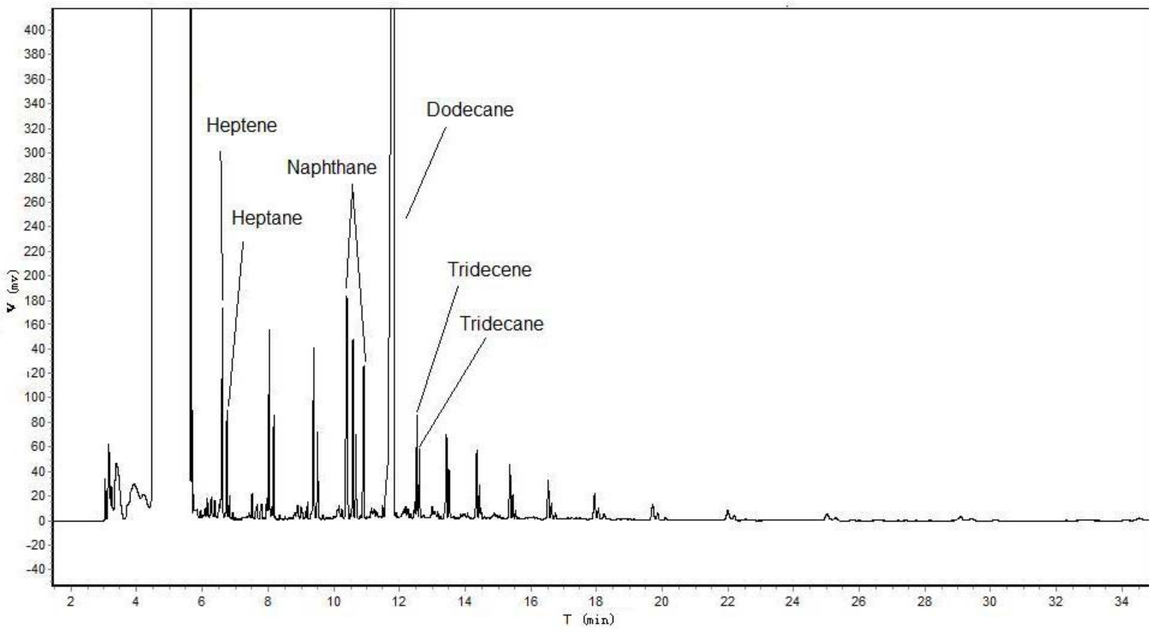

Fig. S4. A typical GC spectrum of products in the top layer obtained on Fe catalyst. The products were extracted by cyclohexane at 150 °C for 2 h, with dodecane and naphthane as the internal standard. Reaction conditions: 150 °C, 2.0 MPa H_2, 1.0 MPa CO, 2.0×10^{-3} mol Fe, 40 mL PEG 200.

Table S1. Products selectivity of Fe catalyst in PEG 200.[a]

Catalysis	Fe	Fe
Reaction condition	150 °C, 1.0 MPa CO, 2.0 MPa H_2	130 °C 1.0 MPa CO 2.0 MPa H_2
Solvent	PEG 200	PEG200
Activity / mol_{CO} mol_{meta}^{-1} h^{-1}	1.5	0.29
Products selectivities (wt %)		
Hydrocarbons	76.4	77.2
Oxygenates	23.6	22.8
Hydrocarbon products distribution (wt %)		
CH_4, wt%	5.6	7.7
C_2-C_4	38.3	40.3
C_5-C_{12}	46.5	41.6
C_{13}+	9.6	10.4
Olefin selectivity (by weight ratio)		
$C_2^=/C_2^o$	1.9	1.8
$C_3^=/C_3^o$	2.8	3.0
$C_4^=/C_4^o$	2.2	2.4
$C_{10}^=/C_{10}^o$	2.2	2.3

[a] The selectivity for CO_2 is lower than 3 mol %.

Table S2. Activities of Co nanoparticles in H_2O and PEG 200.[a]

Solvent	CO conversion (%)	Temperature / °C	Activity / mol_{CO} mol_{Co}^{-1} h^{-1}
H_2O	14.5	170	0.12
H_2O	10.6	150	0.09
H_2O	8.0	130	0.08
PEG 200	6.8	150	0.03

[a] Typical reaction conditions: 150 °C, 2.0 MPa H_2, 1.0 MPa CO, 2.0 × 10^{-3} mol Co, 40 mL solvent, PVP K30 was used when water was used as solvent (PVP : Co = 5 : 1).

References:

1. Handy, S. T. and X. Zhang, *Org. Lett.*, 2001, **3**, 233.
2. C. X. Xiao, Z. P. Cai, T. Wang, Y. Kou, N. Yan, *Angew. Chem. Int. Ed.*, **2008**, 47, 746.