

Supplementary Information

The facile fabrication of magnetite nanoparticles and their enhanced catalytic performance in Fischer–Tropsch synthesis

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Electronic Supplementary Information (ESI)

Experimental Section

Synthesis of iron based nanoparticles

Iron(III) acetylacetonate ($\text{Fe}(\text{acac})_3$, 98%) were purchased from Aladdin Reagent Inc. Benzyl alcohol (BA, 99 %), benzaldehyde (BD, 98.5 %) were obtained from Sinopharm Chemical Reagent Co., Ltd. All of the chemical reagents were used without further purification.

The synthesis procedure was based on solvothermal synthesis, to be more specific, the benzyl alcohol route.¹ The original method is convenient to fabricate crystalline magnetite nanoparticles (NPs) with high purity. However, its protocol has been restricted to carry out in autoclaves under inert gas protection, and limitations are encountered to obtain magnetite NPs with size below 10 nm. Therefore, we made a partial modification on the original method in order to tune the particle size and enhance size uniformity.

The synthesis solutions both before and after fabrication was examined using GC-MS (Fig. S1). Before heating, the contents of the mixture solution are tiny BD [impurity, retention time (tR)≈6.75 min] and BA (tR≈8.38 min), to be the same of BA as received (Fig. S1a-b). However, after heating whether under argon protection or directly under air atmosphere, the peak of BD is remarkably enlarged, indicating the gradual and inevitable oxidation of BA to BD (Fig. S1c-d). The new peak (tR ≈ 10.25) is assigned to benzyl acetate, produced from the alcoholysis reaction of intermediate (formed by nucleophilical reaction between BA and acetylacetonate ligand).² No benzoic acid can be traced in all samples (Fig. S1). Fortunately, it was noticed that the iron oxide NPs are apparently smaller (Fig. 1d, e) with more BD appears under the exposure of air instead of inert gas, and further verified that the size of NPs continued to shrink if a certain amount of BD was added to the mixed

solution before heating (Table S1). On the basis of this, we tentatively assumed BD to be the key function agent in the synthesis system which efficiently regulated the size and size distribution of NPs by slowing down the particle growth rate.

To fabricate magnetite NPs with diameters of about 2.5 nm, Fe(acac)₃ (4 g) was dissolved in the mixture solution of BA (140 ml) and BD (20 ml) preloaded in a continuous stirred tank reactor (CSTR, 1 L in volume) and magnetically stirred at the speed of 800 rpm in atmosphere. After that, the solution was bubbled with purified air at the flow rate of 100 ml/min and heated to 190 °C at a rate of 5 °C/min under ambient pressure and kept for 2 h. Finally, the resultant dark colloidal solution was cooled to room temperature. The average particle size of the obtained NPs was 2.5 nm (Table S1 and Fig. 1b). Uniform NPs of different size ranging from 4 nm to 10 nm were fabricated respectively according to the corresponding additive amount of reagents and type of gases listed in Table S1.

Fischer-Tropsch reaction

The evaluation of catalyst was conducted directly after the fabrication of magnetite NPs. Poly- α -olefin (INEOS Durasyn 164, 200 ml) was added to the CSTR as the reaction medium. The NPs were activated *in-situ* in 65 % Ar/35 % CO (v/v) at 250 °C under ambient pressure for 20 h with a gas hourly space velocity (GHSV) of 5 L/h/g_{cata.}, during which BA distilled in temperature range from 205 °C to 220 °C and condensed in a stream trap for recycling. After that, the reactor was cooled down to room temperature and the pass through gas was switched to synthesis gas composed of H₂/CO at molar ratio of 2.0, then gradually pressurized to 2.0 MPa and increased the temperature to 250 °C at 1 °C/min with GHSV at 10 L/h/g_{cata.}. The composition of the reactants and tail gas were analyzed by an online gas chromatography equipped with three columns, two thermal conductivity detectors (TCD) and one flame ionization detector (FID). The selectivity of hydrocarbon product was calculated based on a carbon atom basis, and average 3% and maximum 5% mass balance errors were calculated for the run. After reaction, the catalysts particles were easily separated from the residues, mainly composed of poly- α -olefin and long chain hydrocarbons produced during reaction, within two minutes under an external magnetic field (Fig. S2). Generally, it takes about 3 h to obtain the magnetite NPs, followed by activation for 20 h, and then ready for subsequent FTS reaction. It was quite convenient for prompt running of experiments. The FTS performance of NP catalyst with an average size of 7 nm along with other iron based NP catalysts reported in the literatures was listed in Table S2 for comparison. Magnetite NPs with an average size of 10 nm was also evaluated under the same reaction conditions for stability comparison (Fig. S7).

Characterization Techniques

NPs were characterized using chromogenic reaction, H₂ temperature-programmed reduction (H₂-TPR), X-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and the selected area electron diffraction (SAED).

Chemical composition verification

Fe²⁺ in acid solution can coordinate with 1,10-phenanthroline to form a soluble, dark red complex while Fe³⁺ does not react under these conditions. To verify the chemical phase of the as-synthesized NPs, the chromogenic reaction was performed for the as-synthesized NPs and pure Fe₂O₃ powder. We observed a dark red color for the as-synthesized NPs, while a colorless solution was observed for pure Fe₂O₃ powder.

H₂-TPR was performed on a Quantachrome ChemBET Pulsar multi-absorption instrument. About 0.15 g of NPs after vacuum drying was treated in 5 % H₂/95 % Ar (v/v) (flow rate 30 ml/min), and the reduction temperature was increased from room temperature to 900 °C at a heating rate of 10 °C min⁻¹ and the hydrogen consumption was recorded using a TCD. The H₂-TPR profiles of the as-synthesized NPs and pure Fe₂O₃ powder are shown in Fig. S3. For Fe₂O₃ powder sample, two distinguishable reduction peaks are observed. The first reduction peak at temperatures of 300-450 °C is assigned the reduction of Fe₂O₃ to Fe₃O₄, while the second reduction peak at temperatures of 450–800 °C corresponds to the transformation of Fe₃O₄ to FeO, combined with the reduction of FeO to α-Fe which occurs in the nearly same temperature range. However, as for the as-synthesized NPs sample, only one broad peak appears in the temperature range 300–800 °C, indicating that no transformation of Fe₂O₃ to Fe₃O₄ take place in the reduction process.

In conclusion, the results of the chromogenic reaction and H₂-TPR results provide solid evidences that the chemical phase of as-synthesized sample is Fe₃O₄.

Structural characterization

XRD analysis were carried out with a Bruker AXS-D8 diffractometer, equipped with Cu Kα radiation ($k = 1.54 \text{ \AA}$) in the 2θ range from 20 ° to 80 ° with a scanning rate of 2 ° min⁻¹. The X-ray source was operated at 40 kV and 100 mA. ASTM powder diffraction files were used to identify the phase of the sample.

The size and morphology of as-synthesized NPs and catalyst particles were characterized by means of TEM, HRTEM and SAED on a JEM 2010 microscope. The samples were prepared by dipping a colloidal suspension of NPs dispersed in n-hexane and mounted on a carbon foil supported on a copper grid.

Table S1 List of reagents usage amount and corresponding particle size of Fe₃O₄ NPs

Entry	Fe(acac) ₃	BA	BD	Gas Type	Particle Size
1	4 g	140 ml	20 ml	Air	~2.5 nm
2	4 g	148 ml	12 ml	Air	~4 nm
3	4 g	160 ml	0 ml	Air	~7 nm
4	4 g	160 ml	0 ml	Argon	~10 nm

Table S2 The catalytic performance of iron based unpromoted NPs catalysts in FTS

Catalysts	Current Study	Commercial Fe ₂ O ₃ NPs ³	Fe-Al ₂ O ₃ nanocomposites ⁴	Fe ₃ C NPs ⁵	Fe ₅ C ₂ /SiO ₂ ⁶	Fe ₃ O ₄ NPs ⁷
Particle size (nm)	7	3	4.5	5-25	5-30	50
Catalyst Type	Unsupported	Unsupported	Unsupported	Unsupported	Supported	Unsupported
Reactor	CSTR	CSTR	FBR	CSTR	FBR	FBR
Temperature (°C)	250	260	260	250	270	280
Pressure (MPa)	2.0	0.8	2.0	3.0	3.0	2.0
GHSV (Lg ⁻¹ h ⁻¹)	10	5.57		1.8	15	3
Methane selectivity (Cmol %)	2.5	6.4	22.9	6	13	7.7
C ₂ -C ₄ selectivity (Cmol %)	12.3	4.5	40.9	--	30	28.1
C ₅₊ selectivity (Cmol %)	85.2	89.1	36.2	--	57	64.2
Activity (mol _{comol} Fe ⁻¹ h ⁻¹)	2.90	1.9	2.7	0.74	--	2.3
Partial oxidation during reaction	No	Yes	Yes	Yes	Yes	Unknown*

* The activity gradually decreased during the first 50 h of reaction. However, after reaction, the bulk phase of catalyst was not characterized for chemical composition information.

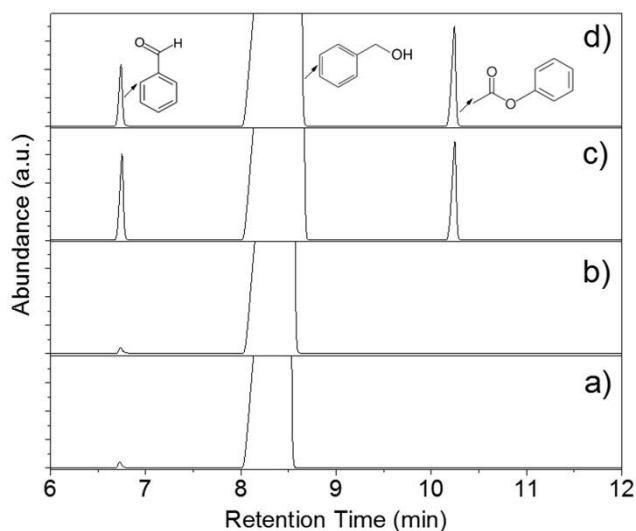


Fig. S1 GC-MS chromatograms obtained from the synthesis solutions: (a) benzyl alcohol as received; (b) before fabrication; (c) after fabrication under air atmosphere; (d) after fabrication in Ar protection.



Fig. S2 Photographs of the catalyst sample separated from reactor residues under an external magnetic field.

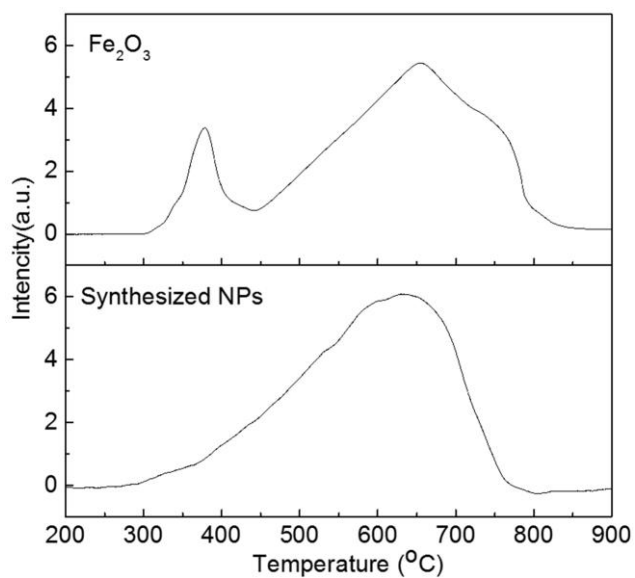


Fig. S3 Comparison of TPR profiles between as-synthesized NPs and Fe₂O₃.

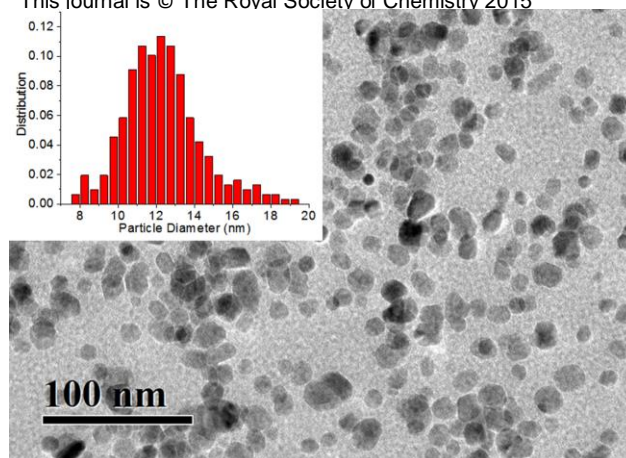


Fig. S4 TEM image of NP catalyst after pretreatment in CO/Ar for 20 h, the inset is the statistic size distribution over 200 particles.

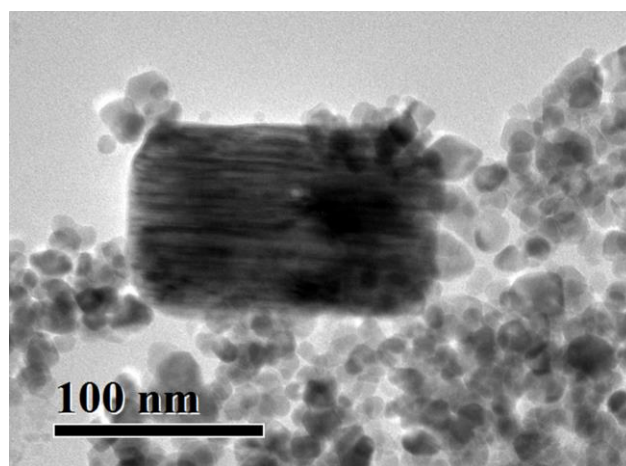


Fig. S5 TEM image of the large-sized particle surrounded by small ones for NP catalyst under reaction for 100 h. According to statistics, the proportion of these large-sized particles is less than 2 %.

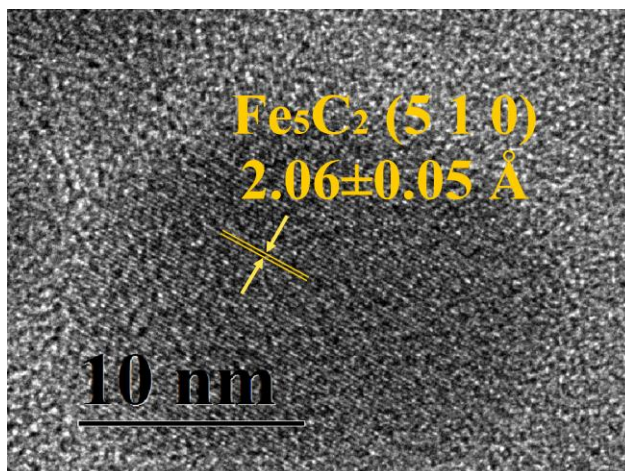


Fig. S6 Typical HRTEM image of a NP catalyst particle of normal size after reaction for 100 h

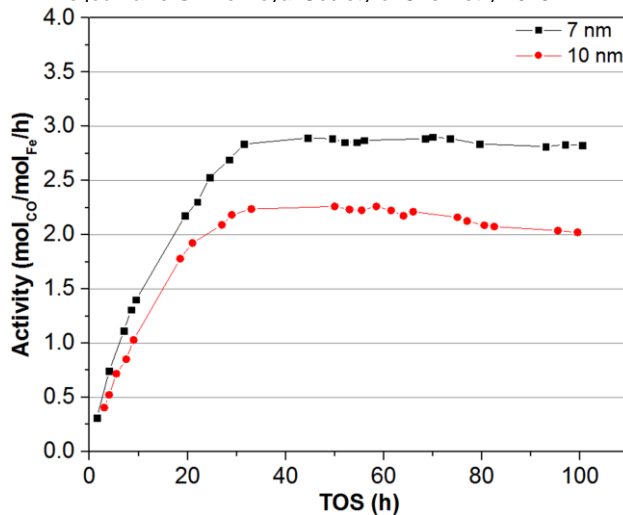


Fig. S7 Catalytic activity of NP catalysts of different size (7 nm versus 10 nm) with time-on-stream for stability comparison. Reaction conditions: 250 °C, 2.0 MPa, H₂/CO=2(v/v), gas hourly space velocity at 10 L/h/g_{cata.}. NP catalyst of 10 nm with broader PSD shows lower stability as its activity gradually decreases after 60 h of reaction. XRD patterns of the catalyst samples after reaction indicate no sign of re-oxidation.

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