

# Comparison of preparation methods of iron-based catalysts for enhancing Fischer-Tropsch synthesis performance

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## ARTICLE INFO

### Keywords:

Fischer-Tropsch synthesis  
Iron  
Carbon  
Catalyst preparation

## ABSTRACT

Carbon supported iron catalysts for Fischer-Tropsch synthesis, with the same iron loading of *ca.* 35 wt.%, were prepared by pyrolysis process and incipient wetness impregnation methods. The effect of the preparation methods on the catalyst structure, catalytic properties, and the direct conversion of syngas via Fischer-Tropsch synthesis was investigated. The iron species, iron particle size and iron reducibility depended on the preparation method. The pyrolysis of homogeneous fusion yielded a unique core-shell structure with dispersed iron species embedded in a matrix of porous carbon. The FeO<sub>x</sub>/AC catalyst obtained by incipient wetness impregnation contained Fe<sub>2</sub>O<sub>3</sub> species after calcination, while the core-shell structured catalyst obtained by pyrolysis process contained Fe<sub>3</sub>C species after calcination. The results show that the core-shell structure iron-based catalyst had higher extent of carburization and dispersion, which led to higher activity for Fischer-Tropsch reaction than that of other two catalysts obtained by different synthesis methods. Furthermore, the Fe<sub>3</sub>C@C catalyst promoted by alkali metals (Na, Mg, K, Ca) resulted in the increase of O/P ratio and low carbon olefin selectivity, and the decrease of methane selectivity.

## 1. Introduction

Along with the increased petroleum demand by emerging economics, there is currently worldwide interest in finding alternative feedstocks for fuels, chemicals and materials. Fischer-Tropsch synthesis (denoted as FTS) is a well-established catalytic process to produce clean liquid fuels and chemicals from syngas as a versatile intermediate [1–4]. Synthesis gas (syngas) is a mixture of hydrogen and carbon monoxide derived from various non-petroleum carbon resources, such as coal, natural gas or biomass. Fischer-Tropsch synthesis begins with the dissociation of CO and H<sub>2</sub> on transient metal surface, and then follows with the hydrogenation and polymerization process [5,6].

Both cobalt and iron-based catalysts are often preferred for industrial process, because of their high activity and selectivity toward hydrocarbons. Iron-based catalyst is more cost-effective and feedstock flexible over Co-based catalyst. The main drawback of iron-based FTS catalysts is the high deactivation rates because of sintering, carbon deposition and iron phases changes. To stabilized iron active phases from sintering,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and TiO<sub>2</sub> are often used as supports to disperse Fe particles [1,7,8]. However, these supports have a strong

interaction with iron precursors, and form hardly reducible mixed oxides which lead to low activity. Thus, the interaction between active component and support should be carefully adjusted.

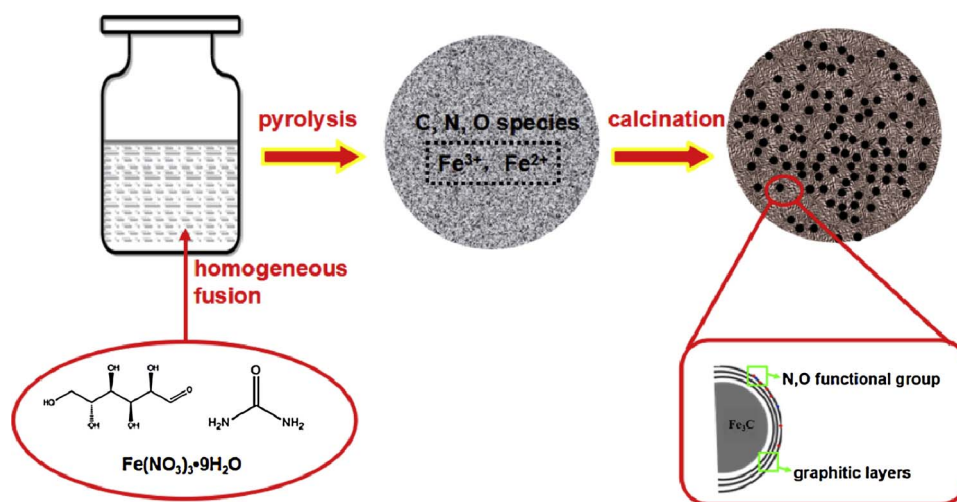
Due to the favorable chemical inertness, high specific surface area and surface chemistry, carbon supports in the form of activated carbon, carbon spheres, carbon nanotubes and carbon nanofibres are often employed as a carrier for iron-based FTS catalysts [9–11]. It has been claimed that iron catalysts supported on carbon have a higher activity as a consequence of higher dispersion and higher olefin selectivity. However, iron catalysts supported on carbon are usually prepared in a multistep process and the active component distribution on the carbon surface is frequently compromised during the calcined and reaction process, especially when high loadings are targeted.

Recently, metal organic frameworks (MOFs) have emerged as promising precursors for the synthesis of carbon-encapsulated metal nanoparticles, because of their unique structure and textural properties [12–14]. Carbon-encapsulated metal nanoparticles typically have a core-shell nanostructure of iron cores surrounded by a multilayer of carbon shells. Santos et al. have demonstrated that carbon-encapsulated iron carbides nanoparticles were achieved when Basolite F300 is used

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Scheme 1. The schematic representation of the formation process of  $\text{Fe}_3\text{C}@C$  catalyst.

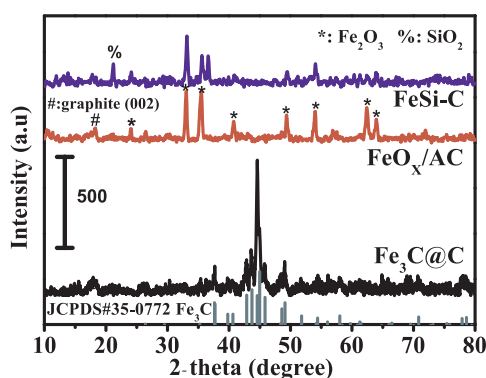


Fig. 1. XRD patterns of as-synthesized Fe-based samples obtained by different preparation methods.

as a precursor [12]. The optimal dispersion of the active iron carbide phase and unique iron spatial confinement minimize catalyst deactivation, resulting in high active and stable operation. However, these metal organic frameworks constructed out of iron and organic ligands were typically synthesized through a complex and expensive process and therefore not suitable for scale-up.

As is well known, the catalyst preparation methods play a major role in catalyst activity and deactivation. In this study, the physical characteristics of various carbon supported iron catalysts obtained by incipient wetness impregnation and one-pot synthesis process are compared and their performance in the Fischer-Tropsch synthesis is compared with that of a typical Fe-based catalyst. Compared with Fe/C catalysts obtained by impregnation process, the unique iron spatial confinement of Fe@C materials could effectively avoid the iron nanoparticles agglomerations and sintering. Therefore, it is interesting to introduce carbon-encapsulated metal nanoparticles structures as novel carbon support active phase in stable state for Fischer-Tropsch synthesis. The catalyst synthesis route is shown in Scheme 1. In the initial process, the precursors melt into a transparent liquid above  $160\text{ }^\circ\text{C}$  and iron species is homogeneously dispersed. When the calcined temperature increased to the  $750\text{ }^\circ\text{C}$ , the  $\text{Fe}_3\text{C}@C$  catalyst of highly dispersed iron carbides nanoparticles in the carbon matrix was obtained. The structure-activity and selectivity relationship of the various carbon supported iron catalysts is also discussed on the basis of characteristic studies. It was suggested that the highly dispersed iron carbides nanoparticles display outstanding Fischer-Tropsch synthesis performance, with high activity and stability.

## 2. Experimental

### 2.1. Catalysts preparation

Synthesis of  $\text{Fe}_3\text{C}@C$  catalyst: 3.0 g of  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  was mixed with 5.0 g urea and 3.0 g glucose at  $160\text{ }^\circ\text{C}$ , forming a transplant solution. After drying at  $200\text{ }^\circ\text{C}$  for 24 h and then calcined at  $750\text{ }^\circ\text{C}$  for 10 h under  $\text{N}_2$  atmosphere to carbonize the carbon precursor, black powders were obtained. The as-synthesized catalyst was denoted as  $\text{Fe}_3\text{C}@C$ .

Synthesis of  $\text{FeO}_x/\text{AC}$  catalyst: The activate carbon supported catalyst was obtained by the incipient wetness impregnation (IWI) method. In the IWI method, 3.0 g  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  was dissolved into  $18.0\text{ cm}^3$  of deionised water. The obtained aqueous solution was added drop-wise to 10.0 g of the active carbon support. The resulting slurry was dried in a rotavaporator at  $90\text{ }^\circ\text{C}$  for 60 min, and then calcined under nitrogen at  $450\text{ }^\circ\text{C}$  for 2 h. The as-synthesized sample was denoted as  $\text{FeO}_x/\text{AC}$ . For comparison purposes, a commercial iron-based catalyst denoted as FeSi-C has been applied in Fischer-Tropsch synthesis.

Synthesis of alkali on  $\text{Fe}_3\text{C}@C$  catalysts: Alkalies were added by wetness impregnation with an aqueous alkali nitrate to obtain an alkali/iron atomic ratio of 2:100. The mixture was re-slurried and spray-dried. The spray-dried powder was calcined at  $450\text{ }^\circ\text{C}$  for 5 h under  $\text{N}_2$  atmosphere. The catalysts were denoted as  $\text{Fe}_3\text{C}@C\text{-M}$  ( $\text{M} = \text{Na}, \text{Mg}, \text{K}, \text{Ca}$ ).

### 2.2. Catalysts characterizations

Powder X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 powder diffractometer using  $\text{Cu-K}\alpha$  radiation operated at 40 kV and 40 mA and a Vantec-1 detector. The size and morphology of samples were determined using a FEI Tecnai G20 transmission electron microscope (TEM) operated at 200 kV and SU8000 field emission scanning electron microscope (FESEM, Hitachi, Japan) at an accelerating voltage of 15 kV. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a VG Multilab 2000 (VG Inc.) photoelectron spectrometer using Al  $\text{K}\alpha$  radiation as the excitation source under vacuum at  $2 \times 10^{-6}$  Pa. All the binding energy (BE) values were calibrated by the C 1s peak at 284.6 eV of the surface adventitious carbon. The Fe content was calculated by elemental analysis (ICP).

Thermogravimetric analysis (TGA) was carried out on a NETZSCH TG 209F3 instrument. About 10 mg of the samples was placed in a ceramic crucible and heated from 30 to  $900\text{ }^\circ\text{C}$  with a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  using air as carrier gas at a flow rate of 50 mL/min. was

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