



## Support effects in high temperature Fischer-Tropsch synthesis on iron catalysts



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### ARTICLE INFO

#### Article history:

Received 2 May 2014

Received in revised form

17 September 2014

Accepted 19 September 2014

Available online 30 September 2014

#### Keywords:

Syngas

Fischer-Tropsch synthesis

Iron

Carbon materials

### ABSTRACT

The paper addresses the effects of silica and carbon supports on the structure and catalytic performance of iron catalysts for high temperature Fischer-Tropsch synthesis. Iron phase composition and dispersion in both calcined and activated catalysts were strongly affected by the support. Hematite was the major iron phase in calcined silica supported catalysts, while carbon supported counterparts contain magnetite. Catalyst activation in carbon monoxide leads to carbidisation of iron oxides to principally Haag iron carbide. Higher Fischer-Tropsch reaction rates were observed on carbon supported iron catalysts compared to silica supported counterparts. The catalytic performance principally depended on iron phase composition rather than on iron dispersion. Iron catalysts supported on carbon nanotubes and activated carbon showed highest activity in Fischer-Tropsch, which could be attributed to the formation of composites of iron carbide and residual magnetite.

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## 1. Introduction

Light olefins (C<sub>2</sub>–C<sub>4</sub>) are important building blocks for petrochemical industry. They are usually produced by thermal or catalytic cracking of petroleum fractions. The interest to alternative methods of olefins synthesis has been constantly growing due to the rapid depletion of oil resources. One of the most interesting alternative methods for olefin manufacturing is Fischer-Tropsch (FT) synthesis, which converts syngas into a mixture of hydrocarbons [1–3]. Syngas is an important intermediate, which can be produced from natural gas, coal or biomass. Both cobalt and iron catalysts are used for this reaction [4–6]. Cobalt catalysts are principally used in low temperature FT synthesis ( $T=220$ – $240$  °C) for production of middle distillates and waxes, while iron catalysts have more interesting properties for synthesis of olefins and oxygenates in high temperature FT operating mode ( $T=300$ – $330$  °C). Supporting iron species on a porous support leads to a more efficient use of active phase and could result in a better catalytic performance. It usually considered that high temperature FT

synthesis on iron catalysts occurs on iron carbide species which form during catalyst activation or the reaction. Indeed, the Fe–C–O diagram calculated by Audier et al. [7] suggests that bulk iron carbide is the most stable iron phase in the presence of carbon monoxide at the reaction temperatures.

Several problems currently restrict application of high temperature FT reaction for direct olefin synthesis: insufficient activity, water-gas-shift activity (WGS), broad hydrocarbon distribution and catalyst deactivation (e.g. sintering, carbon deposition, iron oxidation). The WGS activity of Fe based catalysts results in CO conversion into CO<sub>2</sub>, which coincides with a decrease in the selectivity to hydrocarbons. Another problem is broad and unselective Anderson-Schulz-Flory (ASF) distribution, which limits selectivity to the desired hydrocarbon fraction [6]. Numerous efforts have been made in the past to enhance the activity and olefin selectivity of the Fe based catalysts by tuning the support [5,6,8], catalyst promotion [9–11] and optimizing catalytic reactor and reaction conditions [12].

Silica, alumina and titania are the most common supports for FT catalysts [13–15]. Carbon materials such as activated carbon, carbon nanotubes, carbon spheres, glassy carbon and carbon nanofibres have also been recently applied for supporting iron catalysts [5,6,8–11]. Carbon materials exhibit several advantages as supports. They have high surface area, which could lead to higher

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iron dispersion. They also have versatile surface chemistry, which makes it possible to add new functional surface groups and to vary their density by activation and post-treatments. The presence of oxygen containing groups in carbon materials allows tuning support acidity, which could affect interaction between the support and Fe species and thus, hydrocarbon selectivity in FT reaction [16]. Close contact between Fe nanoparticles and carbon support may facilitate formation of iron carbide, which is often considered as active phase for FT synthesis [17,18]. The porous texture and morphology could lead to encapsulation of Fe inside of the carbon support. It was found that the confinement of Fe within carbon nanotubes (CNTs) modified the redox properties of encapsulated iron oxides and led to a significant increase in the activity of iron catalysts for FT synthesis [19,20]. The catalyst stability towards sintering can be also improved by isolating metal nanoparticles within the carbon matrix.

Most of the previous works have reported characterization and catalytic data obtained with iron catalysts prepared using only one support. This makes difficult a direct comparison between iron catalysts supported on different materials. This paper is aimed at clarifying this point. In this work, iron catalysts for FT synthesis on carbon supports (active carbon, CMK-3 and carbon nanotubes) at different stages of preparation and activation are compared with silica supported counterparts (amorphous silica and SBA-15). Iron species before and after activation and catalytic reaction have been characterized by a wide range of techniques (X-ray diffraction, FTIR, TEM, *in situ* magnetic method, transmission Mössbauer spectrometry and XPS) in order to elucidate the correlations between the catalytic performance in FT synthesis and catalyst structure.

## 2. Experimental

### 2.1. Catalyst preparation

Commercial amorphous silica (CARIACT Q-10, Fuji Silysia), SBA-15, activated carbon, mesoporous CMK-3 carbon [21] and carbon nanotubes were used as catalytic supports. SBA-15 was obtained following procedure reported in Ref. [22] and using block copolymer (P123) poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol), average  $M_n$  ca. 5800 (Aldrich, 43546-5) as a template. First, 6 g of P123 copolymer was dispersed in 45 g of water and 180 g of 2 M HCl under stirring. After complete dissolving P123, 12.75 g of tetraethylorthosilicate (TEOS) were added to the solution. The mixture was kept at 40 °C under stirring for 24 h to obtain a uniform solution. Then the solution was transferred into a hermetically closed polypropylene flask and kept in an oven at 100 °C for 48 h. The gel was washed with distilled water, dried at room temperature for 24 h, and subsequently calcined with flow air at 550 °C for 6 h. The rate of temperature ramping was 1 °C/min.

Activated carbon (AC) was provided by CEKA S.A. and was washed with 1 M nitric acid solution at 50 °C for 2 h. The synthesis of CMK-3 was carried out according to Ref. [21]. Briefly, 5 g of above-mentioned SBA-15 was added to a solution obtained by dissolving 6.25 g of sucrose and 0.7 g of H<sub>2</sub>SO<sub>4</sub> in 25 g of H<sub>2</sub>O. The mixture was transferred to a drying oven for 6 h at 100 °C, and followed by increasing the oven temperature to 160 °C for 6 h. After dissolving additional 4 g of sucrose, 0.45 g of H<sub>2</sub>SO<sub>4</sub> and 25 g of H<sub>2</sub>O, the mixture was treated again at 100 and 160 °C using the same drying oven. The carbonization was completed by pyrolysis with heating to typically 900 °C under N<sub>2</sub>. The obtained carbon-silica composite was washed twice with 1 M NaOH solution (solid-to-liquid ratio 1:100) at 95 °C to remove the silica template. The template-free carbon material was filtered, washed with deionized water and dried at 120 °C overnight. The synthesized CMK-3 was treated with

1 M nitric acid solution at 50 °C for 2 h to remove residual sodium ions.

Multi-wall carbon nanotubes (CNT, purity  $\geq$  95%, outer diameter 20–30 nm) prepared by chemical vapor deposition (CVD) were purchased from the Chengdu Company of Organic Chemistry (CCOC) in China. Before using, raw CNTs were refluxed for 16 h in concentrated HNO<sub>3</sub> (65 wt.%) at 120 °C in an oil bath. Then, the mixture was filtered and washed with distilled water thoroughly until neutral pH was reached, followed by drying at 100 °C overnight.

The Fe/SiO<sub>2</sub>, Fe/SBA-15, Fe/AC, Fe/CNT, Fe/CMK-3L catalysts were prepared by incipient wetness impregnation of the relevant supports with aqueous solutions of hydrous iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O). Ethanol solution was used for preparation of Fe/CMK-3S. The concentrations of the impregnating solutions were calculated to obtain 10 wt.% iron in the final catalysts. After the impregnation, the catalysts were dried overnight in an oven at 100 °C. Then they were calcined in air (Fe/SiO<sub>2</sub> and Fe/SBA-15 samples) or N<sub>2</sub> flow (Fe/SiO<sub>2</sub>-N<sub>2</sub>, Fe/CNT, Fe/CMK-3L, Fe/CMK-3S, Fe/AC) at 400 °C for 6 h with 1 °C/min temperature ramping. The catalysts were activated in a flow of carbon monoxide. A very small amount of O<sub>2</sub> was introduced in the flowing N<sub>2</sub> (1% O<sub>2</sub> in N<sub>2</sub>) for passivation of the catalysts activated in carbon monoxide before their removal from the reactor at room temperature for *ex situ* characterization.

### 2.2. Characterization

The BET surface area, pore volume and average pore diameter were determined by N<sub>2</sub> physisorption using a Micromeritics ASAP 2000 automated system. The samples were degassed under vacuum at <10 μm Hg in the Micromeritics ASAP 2000 at 300 °C for 4 h prior to N<sub>2</sub> physisorption.

*Ex situ* X-ray powder diffraction (XRD) experiments were conducted using a Bruker AXS D8 diffractometer using Cu(K $\alpha$ ) radiation ( $\lambda = 0.154$  nm). The XRD patterns were collected in 2 $\theta$  (2 $\theta$ ) range. The identification was carried out by comparison with JCPDF standard spectra software. The average crystallite size of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> or iron carbides was calculated using the diffraction peaks according to the Scherrer equation [23].

IR spectra of carbon supports and iron catalysts were recorded with a Nicolet Protégé 460 FT-IR spectrometer at 2 cm<sup>-1</sup> optical resolution. Prior to the measurements, the catalysts were pressed with KBr in the discs.

Decomposition of iron nitrate on CMK-3 was studied by temperature programmed reaction using an AUTOCHEM II (Micromeritics) with a MS detector. 50 mg of sample were loaded in the reactor and then heated in a flow of dry He in the range of 25–800 °C with a heating ramp of 10 °C/min.

The TEM analyses were carried out on a Jeol 2100F (field emission gun) microscope operating at 200 kV equipped with probe corrector for the spherical aberrations. Prior to the analysis, the sample was dispersed by ultrasound in ethanol solution for 5 min, and a drop of solution was deposited onto a carbon membrane onto a 300-mesh-copper grid.

The catalysts were also characterized by transmission Mössbauer spectrometry (TMS). TMS allows identification and quantification of iron based phases. Mössbauer spectra were recorded at room temperature, in the  $\pm 12$  mm s<sup>-1</sup> range, using a 1 GBq source of <sup>57</sup>Co in rhodium matrix, MR360 constant acceleration driving unit, DFG1200 digital function generator, a 1024 multichannel analyser and an NaI(Tl) scintillation detector. The experimental Mössbauer spectra were analysed using a least square computer fit assuming Lorentzian peak shapes. Hyperfine field (HF), isomer shift (IS) or quadrupole splitting (QS), which are the characteristics of each iron environment, were calculated with respect to  $\alpha$ -Fe reference [24]. These hyperfine parameters were compared to those of iron

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