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## Effect of the calcination temperatures of the Fe-based catalysts supported on polystyrene mesoporous carbon for FTS Synthesis

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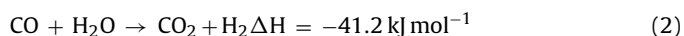
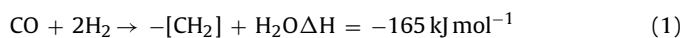
### ABSTRACT

The porous Fe-based catalysts supported on polystyrene mesoporous carbon were studied in the Fischer-Tropsch Synthesis. The solids were pretreated at different calcination temperatures and their characterizations were examined by X-ray diffraction (XRD), Raman spectroscopy, Scanning and Transmission electron microcopies (SEM and TEM), textural properties, elemental composition by X-ray dispersive spectroscopy (EDS), temperature programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS). It was shown that the preexistent carbides phases, obtained upon using elevated temperatures of calcinations procedure, were not completely reoxidized during the reaction, while the formation of carbides through the polymeric carbon reaction with magnetite and/or metallic iron resulted in highly active catalyst for FTS.

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### 1. Introduction

The synthesis gas conversion to hydrocarbons from Fischer–Tropsch synthesis (FTS) has been a sustained hot topic because of the high-value production of chemicals and clean fuels. Fischer–Tropsch synthesis reaction is schematically represented as follows [1,2].



The formation of water in the Reaction (1) can be responsible for the WGS Reaction (2), adjusting the initial H<sub>2</sub>/CO ratio and further affecting the FTS performances. Over the last decades, that is to say for more than 50 years ago, the exploitation of syngas via FTS may continue to be used as an important means of producing oxygenates, olefins, waxes, hydrogen and diesel from gasified renewable [1–7]. Interestingly, it is worth noting that the route

of transforming syngas into C<sub>2</sub>–C<sub>4</sub> olefins through cracking and upgrading have been reported by using traditional FTS petrochemical process, besides that of Texaco and Dow Chemical Company [2].

A major challenge of FTS process itself is the use of a catalyst in a practicable manner. Numerous supported metal catalysts have been tested for FTS [1–12], among which Co, Ru or Fe dispersed on carrier give promising catalytic performance in terms of syngas conversion and selectivity to parafins, olefins and alcohols [12–21]. It is argued that cobalt is of particular importance for the FTS activity, in reason of its ability to obtain increased CO conversion with high yield of heavy hydrocarbon products [13–15]. Ruthenium is known to be a highly selective catalyst for the production of C<sub>10</sub>–C<sub>20</sub> hydrocarbons (diesel fuel). On iron based-catalysts, high olefin and oxygenates contents are produced, in contrast with the lesser methane selectivity and reactivity to secondary hydrogenation observed upon using this metal [16–18].

Concerning the supports, clays, oxides, molecular sieves and carbonaceous materials have shown high stability, serving as a mechanical anchor that maintains separation of the active centers, avoiding the formation of clusters and particle growth in FTS [1–3].

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Specifically, carbons have been widely used as carrier for FTS by virtue of their relative chemical inertness to suppress the irreversible interaction between active species and support, such as forming non-reducible metal complex and interfacial electronic interaction [2,3,11–13,22]. The additional advantage of using carbon materials as support in FTS is their chemical reactivity in terms of forming the surface carbide species, surface functionalities, textural properties and low cost [2,11–13]. In particular, mesoporous carbon has been demonstrated to be advantageous due to its large specific surface area and pore volumes, high porosity, excellent accessibility to promote diffusion and material flux for both gases and liquids [18–21,23]. Additionally, the graded porosity of the carbons featuring a continuous reduction of mass transport resistance to either liquids or gases as well as the increase catalyst utilization and power density in catalytic reactions make carbons advantageous compared to other supports [18,23,24].

Therefore, many types of carbonaceous supports, such as nanoporous, carbon nanotubes, active carbons, nanofiber, sphere and graphene structures have been obtained by distinct methods ([18–25] and references herewith). These carbons can be potential supports for FTS in the presence of an active metal for specific chemical interactions with the reactants. Moreover, the unique intrinsic properties and the multifunctionality of metal/carbon have been proved to have an important role on the formation of special products for FTS.

In a previous work, we have shown the remarkable properties of Fe-based catalysts supported on polystyrene mesoporous carbon [3]. It is clearly suggested that combining the effect of polystyrene-based carbon carrier with the Fe could be an effective strategy to prepare efficient catalysts for FTS. Meanwhile, the structure, texture and morphology Fe/C-based catalysts could be easily regulated owing to the final treatments after the syntheses, i.e. the calcinations. As a continuation of the previous work, the effect of the calcination temperature has been studied to test the activity of Fe/C-based catalysts in FTS.

Most of the research on an iron-based catalyst for FTS in the last 15 years has focused on carbide formation as a factor to deactivate the Co-based FTS catalyst [5,6,8]. Opposite trends have been shown by other researchers, which stated that the formation of iron carbide is necessary for the Fischer–Tropsch reaction, as it is recognized as the active phase [26,25]. Therefore, the presence of carbides in some materials will be a factor to be related with the catalytic performance of the materials. Thereby, the role played by the carbides will be also evaluated in this work.

## 2. Experimental

### 2.1. Preparation of the solids

The Fe-based catalysts supported on polystyrene mesoporous carbon were prepared by wet impregnation method with using an excess of iron(III) nitrate solution into the porous carbon support, according to the procedure described elsewhere [3]. Typically, 2.0 g of commercially available carbon support, namely CP (BLÜCHER GmbH Erkrath, German P25, Degussa) were dispersed in an aqueous solution of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Sigma-Aldrich) to obtain a weight nominal composition 50% of the iron precursor (w/w) supported on the carbon. After that, the previous mixture was stirred in a rotary evaporator at 60 °C and 100 mmHg, the water and volatile compounds were removed from the solid. The mixture was then repeatedly washed following completion by drying overnight and finally, thorough heated at 500 °C under nitrogen flow. The sample obtained was denoted as FeCP500.

Variations in the calcination temperatures e.g. 600 and 700 °C were performed to obtain other phases besides that of iron ones and the solids were labelled as FeCP600 and FeCP700.

### 2.2. Characterizations

The crystal phases of the samples were analyzed by X-ray powder diffraction (XRD) on a PANalytical X'PERT HighScore's diffractometer, which was equipped with a Cu-K $\alpha$  source. The data were collected for scattering angles ( $2\theta$ ) ranging between 5 and 80° with a step size of 0.02° and a counting time of 10 s per step at 40 kV and 40 mA. The Rietveld refinement method was used to give information about the phases present in the diffractograms. The (104) diffraction peak at  $2\theta = 34^\circ$ , was used to calculate the size of the crystals by using the Scherrer formula for FeCP500 and FeCP700. In case of FeCP600, the (311) diffraction peak at  $2\theta = 35.4^\circ$ , was used to determine the particle size. The diffractograms were compared to those of Inorganic Crystal Structure Database (ICSD) database.

Raman spectra were acquired on a LabRam spectrometer with a microscope over a range of 50–2200  $\text{cm}^{-1}$ . The laser emission line at 532 nm was used for the spectral excitation. For each sample, 16 accumulated spectra were collected at a resolution of 4  $\text{cm}^{-1}$ , with a power of 10 mW in the sample. The device was coupled to an Olympus confocal microscope and a 100 times objective lens was used for simultaneous illumination and collection.

Scanning Electron Microscopy micrographs coupled to Energy Dispersive X-ray (SEM-EDS) images were acquired by a TESCAN VEGA XMU electron microscope equipped with an EDS Bruker QUANTAX system coupled to the SEM microscope using an acceleration voltage of 20 kV. The solids were previously prepared by Au sputtering on the samples.

Transmission electron microscopy (TEM) measurements were carried out using a FEI Tecnai 20 G2 200 kV electron microscope. Initially, the samples were ultrasonically dispersed in ethanol and then dropped onto a carbon coated copper grid and afterwards allowed to air dry.

Temperature-programmed reduction ( $\text{H}_2$ -TPR) of the solids experiments were carried out with a Micromeritics TPR/TPD 2900 apparatus. The sample weight used was ca. 50 mg, which was placed in a quartz tubular reactor and heated in a furnace under argon flow at 150 °C for 1 h to drive off water or impurities. Then, the sample was cooled down to 70 °C. Afterward, the flowing gas e.g., 5%  $\text{H}_2/\text{Ar}$  (or 2%  $\text{CO}/\text{He}$ ) was put in the reactor and the temperature linearly increased from 50 up to 1000 °C at a heating rate of 10 °C  $\text{min}^{-1}$ . The  $\text{H}_2$  consumption rate was monitored by a thermal conductivity detector (TCD).

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Physical Electronics PHI 5700 spectrometer equipped with a non-monochromatized Mg K $\alpha$  source focused to a spot size of 720  $\mu\text{m}$ . All binding energies were calibrated using the C1s peak (284.8 eV).

The specific surface area, pore volume and pore size were determined by the Brunauer–Emmett–Teller (BET) method through the nitrogen adsorption-desorption at  $-196^\circ\text{C}$  in a BelSorp Mini II (Bel Japan INC.) equipment. The samples were degassed at 150 °C for 2 h, prior to measurements. The data were collected at a relative pressure ( $P/P_0$ ) ranging from 0.1 to 1.0. Both pore volume and average pore diameter were calculated by Barret–Joyner–Hallenda (BJH) method from the desorption branch of the isotherms.

### 2.3. Fischer–Tropsch synthesis catalytic tests

The catalytic assays of the solids were performed in the Fischer–Tropsch synthesis using a stainless steel (500 mL) Parr-type model 4571 semi-batch reactor at 240 °C. The hexadecane was used as solvent and stirring was carried out at 800 rpm. The reaction was

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