Cobalt and iron supported on carbon nanofibers as catalysts for Fischer–Tropsch synthesis

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ABSTRACT

Cobalt and/or iron supported on carbon nanofibers were prepared and used as monometallic or bimetallic catalysts for Fischer–Tropsch synthesis at 523 K and 20 bar. Catalysts were characterized by ICP, N_2 adsorption–desorption, TPR, XRD and XPS. Characterization results revealed that cobalt and iron had a synergetic effect: cobalt particles were better dispersed in presence of iron, and the latter was reduced to Fe^0 in a higher extent due to the presence of the former. Catalytic results revealed that cobalt content played an important role in the catalytic conversion of CO. This way, the higher the content in cobalt, the higher the CO conversions were observed. Thus, sample **15**Co/CNF presented the highest CO conversion. However, the presence of iron in bimetallic catalysts avoided an excessive production of CH_4. The bimetallic sample with the highest Co loading (**10**Co**5**Fe/CNF) was the most active catalyst for the FTS reaction, because it led to the highest yield of long-chained hydrocarbons.

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1. Introduction

The Fischer–Tropsch synthesis (FTS) is a heterogeneously catalyzed polymerization process that converts syngas (CO and H_2) into a wide variety of hydrocarbons, which constitutes a promising route for the production of clean liquid fuels. The product distribution in the FTS is very broad. Consequently, many studies have been carried out with the aim of controlling and limiting the product selectivity. Nickel-, ruthenium-, iron- and cobalt-based catalysts have been actually used in this process, but the latter (Co- and Fe-based catalysts) are the most widely studied. Although Ni is relatively inexpensive, it produces short-chain alkanes. Ru shows good catalytic properties but its annual world supply cannot even fulfill the requirements of an average plant [1]. Under the same experimental conditions, Fe-based catalysts lead to the formation of light hydrocarbons and small amounts of CH_4 in comparison to Co-based ones. On the other hand, Co-based catalysts show high catalytic activity and are suitable for the production of middle distillates and waxes, but they are more expensive.

In recent years, the preparation of bimetallic Co:Fe catalysts to be used in FTS has gained increased interest. It has been reported that the simultaneous use of Fe and Co gives rise to a synergistic effect between the two active phases [2–4].

Co:Fe metal mixtures have traditionally been supported on typical FTS supports such as silica [3,5,6], titania [7,8] and alumina [4]. However, several studies related to the preparation of bimetallic catalysts supported on carbonaceous materials and their use in FTS can be found in the literature [9].

Carbon materials have shown special properties (high mechanical strength, chemical inertness, and possibility of being used with both acidic and basic solutions) that allow them to be used as catalyst supports [10–13]. Among these materials, amorphous ones have proven to be ill-defined and thus they are not appropriate as FTS catalysts [14]. Among carbon materials, structured ones such as carbon nanofibers (CNF), which are based on ordered parallel graphene layers arranged in a specific conformation, could be good candidates to be used as catalyst supports in this process. CNF are believed to be less prone than inorganic supports to coke formation and, in case of deactivation, the active phase would be relatively easy to recover [15]. Moreover, CNF presented some defects in their structure, leading to higher porosity than that observed in other structured carbon materials such as carbon nanotubes (CNT).

Very few studies related to the use of CNF as a catalyst support in the FTS processes have been reported in the literature. Den Breejen et al. [16] and Bezemer et al. [14] compared CNF and SiO_2 as cobalt catalyst

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supports in the FTS at 493 K and 1 bar. In both cases, Co/SiO₂ showed a slightly lower FTS activity and higher selectivity for long-chain hydrocarbons (C_{5+}) than Co/CNF. Yu et al. [17] compared *Platelet* and *Fishbone* type CNF-based catalysts with Al₂O₃ systems at 493 K and 20 bar. It was confirmed that *Platelet* type CNF-based catalysts had high activity and selectivity, the catalytic activity being comparable to that of Al₂O₃-based ones. Finally, Bezemer et al. [18] studied the influence of different promoters present in CNF-supported catalysts. They found that the presence of MnO in the catalysts led to positive effects on both activity and selectivity.

In this work, catalysts with different contents in Co and Fe supported on CNF were prepared. The influence of the Co:Fe ratio in the resulting catalysts on their catalytic activities was studied in order to maximize fuel production in the FTS. To the best of our knowledge, no study related to the use of bimetallic catalysts supported on CNF for the FTS has been reported until now.

2. Experimental

CNF were prepared by the catalytic decomposition of ethylene over a Ni/SiO₂ catalyst at 873 K according to the procedure described elsewhere [19]. Once CNF were synthesized, they were subjected to a demineralization treatment with HF (48% v/v) for 15 h with vigorous stirring, to remove any residual metal that could contribute to the subsequent reaction. CNF-supported cobalt and iron catalysts with ca. 15 wt.% of metal (namely **15**Co/CNF and **15**Fe/CNF, respectively) were prepared by the incipient wetness impregnation method using aqueous solutions of Co(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O (Merck), respectively. Three bimetallic Co–Fe catalysts, containing different amounts of both metals (namely **10**Co**5**Fe/CNF, **7**Co**7**Fe/CNF and **5**Co**10**Fe/CNF) were also prepared using the same procedure. The total amount of metal in each catalyst was close to 15 wt.%.

The catalyst support was placed in a glass vessel and kept under vacuum at room temperature for 2 h to remove water and other impurities adsorbed on the structure. A known volume of an aqueous solution (the minimum amount required to wet the solid) was then poured over the sample. In the case of bimetallic samples, two aqueous solutions, one for each metal precursor, were prepared and poured simultaneously over the support. After 2 h, the solvent was removed by evaporation under vacuum at 363 K. The final catalysts were dried at 403 K overnight and sieved into a batch with an average diameter of 254 μm.

Surface area/porosity measurements were conducted using a Quantachrome Quadrasorb SI apparatus with N₂ as the sorbate at 77 K. All samples were outgassed prior to analysis at 453 K under vacuum ($1°10^{-2}$ Torr) for 12 h. Total specific surface areas and mesoporosities were determined by the multipoint BET and the Barret–Joyner–Halenda (BJH) methods, respectively. XRD analyses were conducted with a Philips X'Pert instrument using nickel-filtered Cu-Kα radiation. Samples were scanned at a rate of 0.02° step⁻¹ over the range $5° \leq 2\theta \leq 90°$ (scan time = 2 s·step⁻¹) and the

corresponding diffractograms were compared with those of the PDF-ICDD references. Temperature-programmed reduction (TPR) experiments were conducted in a commercial Micromeritics AutoChem 2950 HP unit with TCD detection. Samples (ca. 0.15 g) were loaded in a U-shaped quartz reactor and ramped from room temperature to 1173 K (5 K min⁻¹) under a reducing atmosphere (17.5% v/v H₂/Ar, 60 cm³ min⁻¹). X-ray photoelectron spectroscopy (XPS) analyses were performed in an AXIS Ultra DLD spectrometer with a monochromatized Al-Kα X-ray source (1486.6 eV) with pass energy of 40 eV and spot size aperture of 300 × 700 μm. C$_{1s}$ (binding energy of 284.6 eV) of adventitious carbon was used as the reference. In the case of reduced catalysts, samples were reduced in situ prior to analysis. Cobalt and/or iron content were measured by using an inductively coupled plasma spectrometer (ICP, model Liberty Sequential, Varian). Samples were diluted to 1:1 v/v using 4N HNO₃, in order to ensure the total solubility of the metal.

FTS catalytic activity was tested in a stainless steel fixed bed reactor (9 mm i.d. × 305 mm length) provided with a porous plate (2 μm pore size). Initially, the catalyst bed (2 g) was activated at 623 K (heating ramp of 5 K min⁻¹) for 5 h with a flow rate of 100 Nml min⁻¹ of ultrapure hydrogen. The reactor was then cooled and pressurized up to reaction conditions (523 K and 20 bar, respectively) under a N₂ atmosphere (100 Nml min⁻¹). A flow of a mixture of CO, H₂ and N₂ (CO:H₂:N₂ volume ratio of 3:6:1, N₂ used as the internal standard) was established through the reactor during 18 h, with a constant gas hourly space velocity (GHSV) of 3000 Nml g⁻¹ h⁻¹. The product stream was cooled in a wax trap (T ≈ 393 K) to retain the waxes and then in a liquid–liquid–gas separator, which consisted of a Peltier cell (T ≈ 278 K). Liquid hydrocarbon samples were analyzed off-line by capillary GC (VARIAN 430) equipped with a flame ionization detector (FID). C₁–C₃ hydrocarbons, unreacted CO and H₂, N₂ and CO₂ were analyzed on-line by GC (VARIAN 4900). Calibrations were performed with standard samples for data quantification. The CO reaction rate and the yield of long-chain hydrocarbons (C_{5+}) were calculated using the following equations:

$$rate = \frac{N_{CO,converted}(mol/min)}{(m_{cobalt+iron})(mol)}$$

$$yield_{C_{5+}} = \frac{N_{CO,converted}(mol/min)}{N_{CO,feed}(mol/min)} \cdot S_{C_{5+}}.$$

3. Results and discussion

3.1. Textural properties

The physicochemical properties of the supports and catalysts used in this work are listed in Table 1. Nitrogen adsorption–desorption

Table 1
Physicochemical properties of the carbonaceous support and prepared catalysts.

Sample	CNF	**15**Co/CNF	**10**Co**5**Fe/CNF	**7**Co**7**Fe/CNF	**5**Co**10**Fe/CNF	**15**Fe/CNF
Metal loading (% wt.) (Co/Fe)	−/−	15.0/−	8.9/5.5	6.5/6.7	5.2/9.4	−/15.8
BET surface area (m² g⁻¹)	275	231	217	260	257	300
Mesopore surface area (m² g⁻¹)	219	134	143	158	155	176
Total pore volume (cm³ g⁻¹)	0.46	0.30	0.29	0.30	0.30	0.37
Mesopore volume (cm³ g⁻¹)	0.43	0.26	0.25	0.25	0.25	0.31
Average pore diameter (nm)	6.7	5.3	5.3	4.7	4.7	4.8
XRD-average metal particle size (nm)[a]	–	25	–	–	–	60
TPR-T$_{max}$ (K)[b]	C: 864	Co: 573	Co: 605	Co: 612	Co: 619	Co: –
		Fe: –	Fe: –	Fe: 764	Fe: 762	Fe: 783
		C: 794	C: 834	C: 859	C: 877	C: 894

[a] Calculated from the XRD main peak in each case, only possible in monometallic samples.
[b] Maximum reduction temperatures of the following phases: Co: Co₃O₄ + CoO → Co⁰. Fe: Fe₃O₄ → Fe⁰. C: CNF gasification.