Characterization of carbon nanostructures deposited on fibrillar Fe-Zr catalysts during Fischer-Tropsch synthesis with biomass gasification syngas

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Introduction

Fischer-Tropsch synthesis (FTS) is becoming an interesting alternative way to produce different fuels and chemicals from renewable origin, replacing crude oil as feedstock. The net CO_2 emissions can be zero when biomass is used as syngas source. The gasification of lignocellulosic biomass (preferably waste) usually generates a syngas with a low H_2 to CO ratio. In this sense, iron catalysts are preferred over cobalt ones because metallic iron is also active for the Water Gas Shift reaction, increasing the H_2/CO ratio in situ. On the other hand, when using syngas with low H_2 concentration, the formation of different carbonaceous deposits on the catalytic metallic phase takes place.

In this work, the effect of iron loading on the carbonaceous deposits produced on nanofibrillar iron-zirconia catalysts during the Fischer-Tropsch process have been studied.

Experimental

The fibrillar iron-zirconia catalysts were obtained in a one-step procedure by the electrospinning technique. A polymeric solution was prepared with zirconium acetate, polyvinylpyrrolidone and iron nitrate nonahydrate. The iron salt mass was adjusted to achieve iron loadings on the catalysts of 20, 25 and 30 % (w/w). The materials were calcined in a muffle furnace at 500 °C for 5 h. The used nomenclature was as follow: *FZrXXFe*, where *XX* was related to the final iron loading.

The materials were characterized before and after being used as catalysts in the FTS reaction by different techniques such as electronic microscopy, X-ray diffraction, Raman spectroscopy or thermogravimetric analysis. The catalytic tests were performed under High Temperature Fischer-Tropsch conditions: 340 °C, 20 bar and 10 m^3_{syngas} h^{-1} kg_{Fe}^{-1} and H_2/CO=1. The catalysts were reduced with H_2 at 450 °C prior the reaction.

Results

The three fibrillar catalysts were tested in the FTS reaction for 9 h of time on stream. Under the same FTS conditions, FZr20Fe showed a CO conversion of c.a. 40 % while the other two catalysts reached steady conversion values over 90 %. The main products generated in this process were CO_2 (c.a. 40 %), CH_4 (c.a. 10 %), C2-C4 hydrocarbons (c.a 26 %) and C5+ hydrocarbons (c.a. 24 %). The last components were calculated by difference, coke was also included.

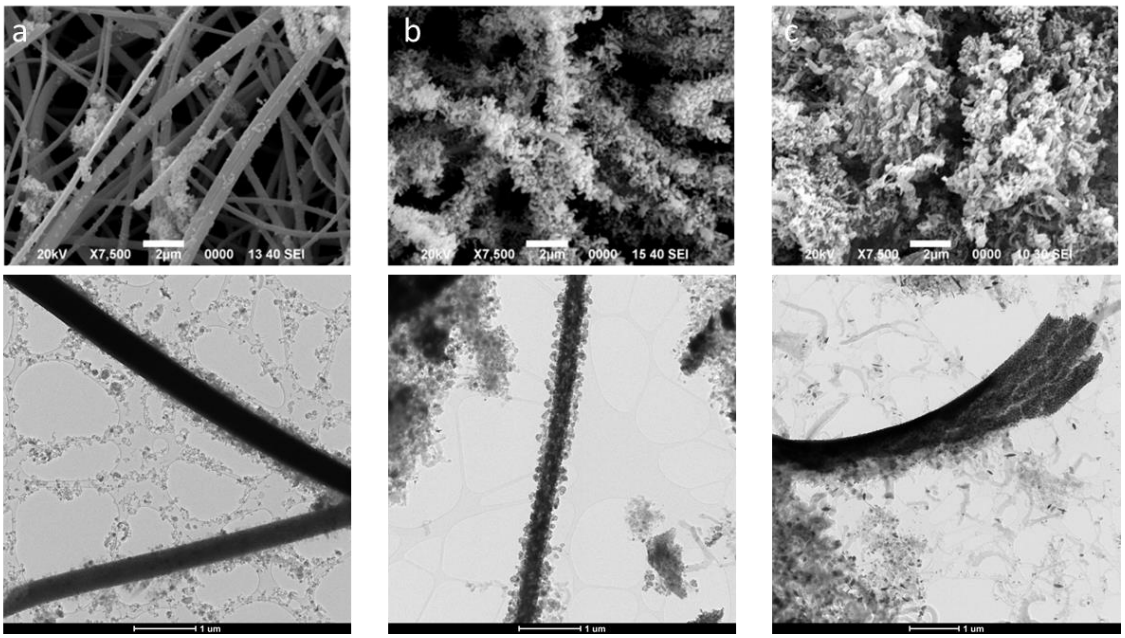

Figure 1. Scanning (up) and transmission (down) electron microscopy micrographs of iron-zirconia fibrillar catalysts used after reaction (340 ºC, 20 bar and 10 m^3_{syngas} h^{-1} kg_{Fe}^{-1}) for 10 h. a) FZr20Fe, b) FZr25Fe and c) FZr30Fe

The catalysts were characterized after reaction in order to study the carbonaceous deposition and their nature. The SEM micrographs after reaction are presented in Fig. 1. In accordance with the lower conversion, the carbon deposition on FZr20Fe were less abundant that those observed in the case of FZr25Fe and FZr30Fe. Moreover, in the case of FZr25Fe the fibrillar structure was maintained, while in FZr30Fe, the massive formation of carbon nanostructures from the core of the fibers teared them apart, destroying the fibrillar structure. This phenomenon was observed in more detail in the TEM micrographs (Fig. 1), were FZr20Fe and FZr25Fe maintained the fibrillar morphology but FZr30Fe was destroyed. However, the catalyst did not show any activity lost in terms of conversion.

Air thermogravimetric analyses were performed to calculate the coke deposited in the final fiber. The results can be observed in Fig. 2.a. As previously mentioned, the final amount of carbon was much lower for FZr20Fe, around 17 % (w/w), but it reached more than 60 % (w/w) in the case of FZr25Fe and FZr30Fe.

Additionally, the samples were also analyzed by Raman spectroscopy. The results are presented on Fig. 2.b. Both D and G bands were detected in all the catalysts, indicating the deposition of carbonaceous deposits with low structural order. Additionally, in the case of FZr25Fe and FZr30Fe the bands for the Radial Breathing Modes (RBM) were also detected, indicating the presence of single or double walled carbon nanotubes (CNT). The higher iron loading produced nanoparticles with a proper size to obtain CNT. However, the high activity maintained during the catalytic experiment evidenced that the CNT formed are also active for the FTS.

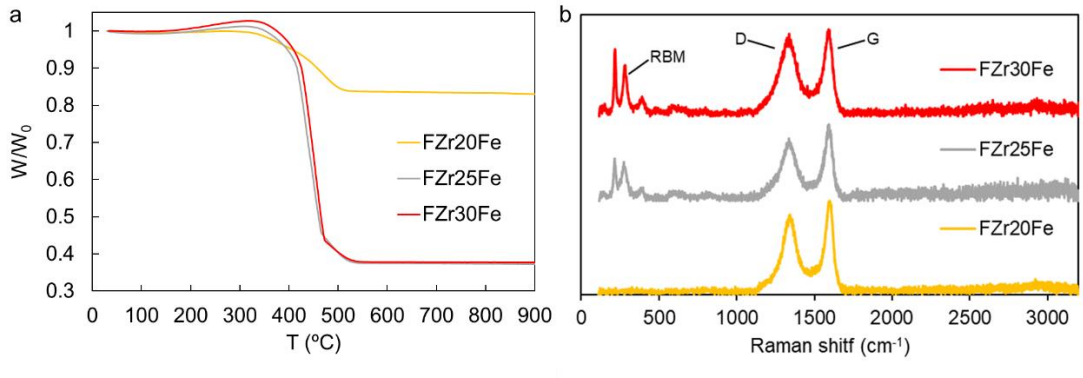

Figure 2. a) Thermogravimetric analysis in air, heating rate 10 °C/min and b) Raman spectroscopy (532 nm) of iron-zirconia fibrillar catalysts used after reaction (340 °C, 20 bar, 10 m^3_{syngas} h^{-1} kg_{Fe}^{-1} and H_2/CO=1) for 10 h.

Acknowledgement

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