Efficient catalysts with fibrillar morphology for the Fischer-Tropsch reaction with synthesis gas from residual biomass

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Objectives and novelty

Biorefineries are a promising alternative to fossil fuels as they allow to obtain fuels but also substitutes for petrochemicals (e.g. olefins). In this sense the Fischer-Tropsch synthesis with synthesis gas -syngas- (H_2 and CO) produced from biomass waste represents an interesting route. However, this process present unsolved problems such as the heat evacuation from the reactor, the high pressure drop in fixed bed reactors and the necessity of catalysts active with syngas with low H_2/CO ratio.

The objective here is to study the preparation and use in reaction a catalyst that can amend the aforementioned problems. In this sense, the catalysts were structured with fibrillar morphology with the aid of the electrospinning technique. This morphology enhances the mass and heat transference, reducing the limitations in the reactor. They are also active for low H_2/CO ratio syngas. Two kinds of materials were studied: inorganic fibers based on ZrO_2 and Fe and carbon fibers prepared from a solution of Alcell® lignin and iron. The Figure 1 summarizes the objectives and the process.

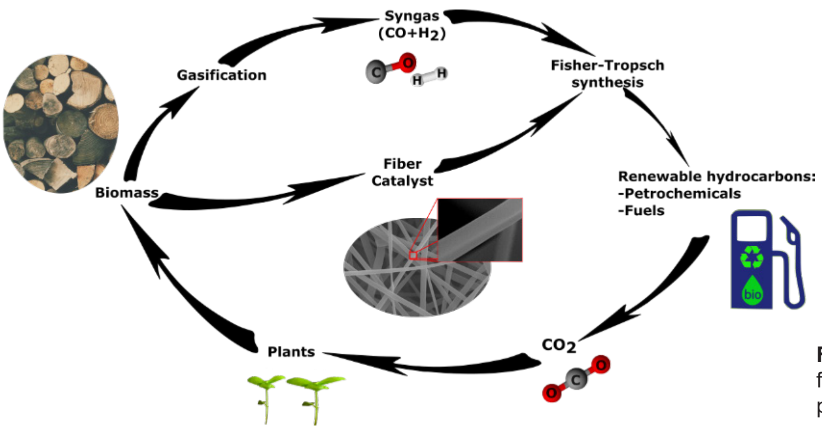

Figure 1. Overview of the overall process for Fischer-Tropsch synthesis and catalysts preparation from biomass.

Results

Two kinds of materials with fibrillar morphology were prepared, on the one hand with ZrO_2 and iron loadings from 20 to 30 (w/w) %; and on the other hand, carbon fibers with Alcell® lignin as precursor, carbonized at three different temperatures (500, 650 and 800 ºC). Both were used as catalysts for Fischer-Tropsch synthesis with a simulated syngas produced via biomass gasification (H_2/CO=1).

Study of the carbonaceous fraction in inorganic fibers catalysts

The catalysts with different loadings of Fe in ZrO_2 presented a high activity which was increased with the iron loading. The products were mainly gaseous products (from methane to butane), but liquids (up to C20) were also obtained in all the cases. The main product distribution is collected in Table 1. The C5+ compounds were calculated by difference between consumed reactants (CO) and products, so solid carbonaceous materials produced in the reaction, due to Boudouard process, was included.

The carbonaceous fraction was deeply analyzed by different techniques in this thesis work. First, the coke amount was quantified with thermogravimetric analyses (TGA) giving rise to a c.a. 17 (w/w) % of carbonaceous materials for the catalyst with 20 (w/w) % of Fe, and a c.a. 62 (w/w) % of burning material for the catalyst with 25 and 30 (w/w) % of iron. The higher production of coke could be related to the highest conversion or the later catalysts, however, the carbon productivity was also obtained with values 1 $g_C\ g_{cat}^{-1}\ mol_{CO}^{-1}$ for F20Fe@ZrO_2 and c.a. 3.2 $g_C\ g_{cat}^{-1}\ mol_{CO}^{-1}$ for F25Fe@ZrO_2 and F30Fe@ZrO_2.

The used catalysts were also analyzed by scanning and transmission electronic microscopy, SEM and TEM respectively. The images can be observed on Figure 2. The catalyst with 20 (w/w) % of iron showed the original fibrillar morphology with low carbonaceous deposits, on the other hand, the catalysts with 25 and 30 (w/w) % presented a high accumulation of carbonaceous materials. However, in the former, the fibrillar morphology was maintained while in the later it was difficult to differentiate the catalysts from the deposits. Thanks to TEM images, it was possible to observe that the fibers with 30 (w/w) % were broken due to the carbon deposits (Figure 2.c).

Table 1. CO conversion and selectivity of the Fischer-Tropsch synthesis with the catalysts with 20, 25 and 30 (w/w) of iron on ZrO_2 at 340 ºC, 20 bar and 150 ml/min of syngas H_2/CO=1.

	Conversion (%)	Selectivity (%)			
	CO	CO_2	CH_4	C2-C4	C5+
F20Fe@ZrO_2	38.5	31.6	11.1	25.9	31.4
F25Fe@ZrO_2	92.7	42.5	9.9	23.5	24.1
F30Fe@ZrO_2	95.9	41.2	8.1	20.9	29.7

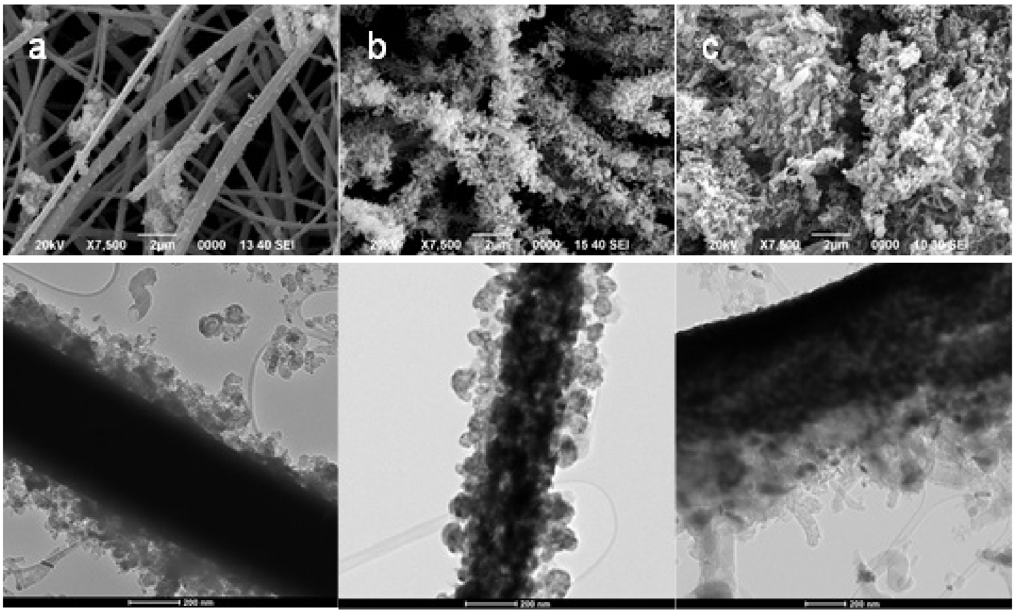

Figure 2. Up: SEM and down: TEM micrographs of the used catalyst a) F20Fe@ZrO_2, b) F25Fe@ZrO_2 and c) F30Fe@ZrO_2

The catalysts were also analyzed by Raman spectroscopy. The D and G bands were detected in the three used catalysts, evidencing low structured carbonaceous deposits. However, in the case of F25Fe@ZrO_2 and F30Fe@ZrO_2 catalysts, the radial breathing modes were also detected, which means that single or doble walled carbon nanotubes were also formed on these two catalysts.

Finally, a regeneration study was carried out with a used catalyst with a 25 (w/w) % of iron. An isothermal gasification study at 300, 325, 350, 375 and 400 ºC, with air was performed in a thermobalance in order to develop a kinetic model. After trying to adjust different simple models a dual model was proposed with a very good fitting to the experimental data. The model includes a volumetric and a shrinking core model. There was a fraction of c.a. 70 % that reacted through the first model type. The two gasification models could be related with the different types of carbon detected by Raman spectroscopy.

Carbon fibers catalysts

An important section of this thesis work was a review article about different carbonaceous supports (powder, fibers, nanotubes, spheres, graphene oxide, etc.) as catalysts for the Fischer-Tropsch synthesis. Three of the main conclusions of this review paper were that carbon materials presented a low metal-support interaction; a high thermal conductivity, that enhances the heat evacuation; and finally, the possibility of recovering the metals from the deactivated catalyst by gasifying the support. On the other hand, most of the carbon fibers used nowadays as catalysts supports are obtained from fossil fuel (e.g. oil). For that reason, an important objective of this thesis was the preparation of carbon fibers from a more sustainable source, in this case it was the lignin.

Carbon fibers were obtained with the electrospinning technique from a solution of lignin, iron nitrate and ethanol. Once the fibers were stabilized the effect of the carbonization temperature was studied carrying out the process at 500, 650 and 800 ºC. The materials treated at high temperature showed an important development of the mesoporosity compared to the rest of the materials treated at lower temperatures. This phenomenon was attributed to an interaction between the iron and de carbon support, which was confirmed with X-ray diffraction. In the case of the fibers carbonized at 800 ºC iron carbides were detected, while in the rest of the materials iron oxides were present.

These materials were used as Fischer-Tropsch catalysts with the same conditions than the inorganic fibers (340 ºC, 20 bar). The catalyst treated at the highest temperature showed the best result in terms of conversion (c.a. 10 %) but also the product distribution was the most interesting. A higher quantity of hydrocarbons longer than methane was obtained with a lower selectivity to CH_4 and CO_2 than the catalysts treated at lower temperatures. In the case of these last catalysts the narrow microporosity hindered the chain growing of the hydrocarbons promoting methane and carbon dioxide. Furthermore, in the case of the catalyst treated at 800 ºC a high selectivity to olefins was obtained with a ratio of propene to propane of 4.

Conclusions

In this thesis work the electrospinning technique was proved as a feasible procedure to generate inorganic but also lignin fibers in just one step with the active phase already loaded. These catalysts showed a good activity in terms of conversion and an interesting product distribution such as olefins. In the case of the inorganic catalyst, a relationship between the carbon production and the iron loading was found, provoking in the worst case the damage of the fibrillar morphology due to coke production. That coke was of two kinds, including carbon nanotubes. On the other hand, it was also proved that the use of lignin is a useful carbon source to prepare carbon fibers loaded with iron as catalysts for the Fischer-Tropsch process. The temperature of carbonization was an important matter due to the porosity development which conditioned the conversion and product distribution.

Related Publications

[1] Cordero-Lanzac T, Rodríguez-Cano MA, Palomo J, Valero-Romero MJ, Aguayo AT, Bilbao J, et al. Binderless ZrO_2/HZSM-5 fibrillar composites by electrospinning as catalysts for the dimethyl ether-to-olefins process. Microporous Mesoporous Mater 2022;342:1–11. doi:10.1016/j.micromeso.2022.112102.

[2] Valero-Romero MJ, Rodríguez-Cano MÁ, Palomo J, Rodríguez-Mirasol J, Cordero T. Carbon-Based Materials as Catalyst Supports for Fischer–Tropsch Synthesis: A Review. Front Mater 2021;7:1–27. doi:10.3389/fmats.2020.617432.

Full Thesis can be downloaded from: *https://hdl.handle.net/10630/30788*