Carbon 2022

Fischer-Tropsch synthesis over lignin-derived cobalt-containing carbon fiber catalysts prepared in a single step by electrospinning

María José Valero-Romero[1], Francisco José García-Mateos[1], Xiaohui Sun[2], Freek Kapteijn[2], José Rodríguez-Mirasol[1] and Tomás Cordero[1]

Email: garciamateos@uma.es

[1]Departamento de Ingeniería Química, Escuela de Ingenierías, Universidad de Málaga, Andalucía Tech, Campus de Teatinos S/n, Málaga, 29071, Spain
[2] Catalysis Engineering, Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, Delft, 2629, HZ, Netherlands

Keywords
Fischer-Tropsch synthesis, lignin, electrospinning, Co-containing carbon fibers

INTRODUCTION

The growing concerns of greenhouse effects of using fossil resources have spurred worldwide interest in finding alternative feedstock for important petrochemical commodities and fuels. In this context, the development of efficient routes for the transformation of biomass into useful chemicals and fuels is of primary importance. Among possible options for the valorisation of biomass, gasification (followed by syngas cleaning) and Fischer-Tropsch synthesis (FTS) has received a renewed attention due to the growing attention to the use of sustainable energy and the implementation of more stringent environmental legislation on liquid fuels. In addition to this, biomass residues could be used to produce renewable FTS catalyst supports, and as a result both processes of biomass conversion have a positive environmental and economic impact (Valero-Romero, 2021).

In the present, work submicron-sized cobalt-containing lignin fibers have been prepared by the electrospinning technique, using Alcell lignin as carbon precursor, a low-cost co-product of the paper making industry. Carbon fibers were obtained by carbonization of Co-containing lignin fibers at different temperatures, yielding cobalt nanoparticles very well dispersed on the carbon fibers surface. These fibrillar catalysts were tested for Low-Temperature FTS using different H_2/CO ratios.

EXPERIMENTAL

Cobalt-containing lignin-based submicron-sized fibers were synthesized in one step by electrospinning, in a coaxial configuration (Lallave, 2007), and using a cobalt nitrate-lignin-ethanol solution with a weight ratio of 0.17:1:1 (Co:lignin:ethanol). The lignin fibers were later thermostabilized in air at 200 ºC for 1 h to prevent lignin fibers from fusion during the following carbonization process at 500, 650 or 800 ºC for 1 h in inert atmosphere to obtain lignin-based cobalt-containing porous carbon submicrometer sized fibers. The cobalt-containing carbon fibers were denoted as Co@CF-T, where T indicates the heat-treatment temperature. The FTS catalysts were tested in a six-flow fixed-bed microreactor setup (Sartipi, 2013). Prior to the FTS reaction the catalysts were reduced *in-situ* by H_2 at 350 ºC for 3 h. The reaction conditions were 220 and 240 ºC, H_2/CO molar ratios of 1 or 2 and space velocities of 3.3, 4, 5.3 and 8 $m^3_{STP}\ kg_{cat}^{-1}\ h^{-1}$.

RESULTS AND DISCUSSION

The Co-containing carbon fibers catalysts present a Co loading of 7, 8 and 12 *wt.* % for Co@CF-500, Co@CF-650 and Co@CF-800, respectively, due to the higher devolatilization of the Co-containing lignin fibers at higher heat-treatment temperatures. Furthermore, the catalysts present a well-developed

porosity (S_{BET} = 418-460 m^2 g^{-1}), attributed to a self-induced carbon oxidation during the carbonization stage by the oxygen retained on the surface of the lignin fibers from the stabilization process, which may be catalyzed by the presence of Co. Figure 1a evidences the high flexibility of this type of carbon fibers, which allows them to be adapted as a catalytic fixed bed in a tubular reactor. The cobalt containing fibers have diameter sizes ranging from 0.25 µm to 2.0 µm (Figure 1b and 1c), smaller than lignin-derived carbon fibers heat-treated at similar conditions but without cobalt (1-4 µm) (Lallave, 2007). TEM images (Figures 1c and 1d) evidence the high dispersion of Co on the carbon fiber, whose particle sizes increased with carbonization temperature. The samples carbonized at 500 and 650 ºC present narrow cobalt particle size distributions with average particles between 6 to 13 nm, within the optimal range of Co-particle size for FTS (Bezemer, 2006). The carbon selectivity to the different product ranges over Co@CF-500 and Co@CF-650 is compared in Figure 2 at iso-conversion conditions. Co@CF-500 presents a relatively high selectivity to long chain hydrocarbons (C5+) and a lower selectivity to methane (C1). Raman and HR-TEM showed that higher pyrolysis temperature (> 500 ºC) led to Co-containing carbon fibers catalysts with larger metallic cobalt nanoparticle sizes encapsulated in graphitic-type carbon. This rendered them inaccessible for the FTS reactants, decreasing the activity and selectivity to C5+ hydrocarbons on these materials.

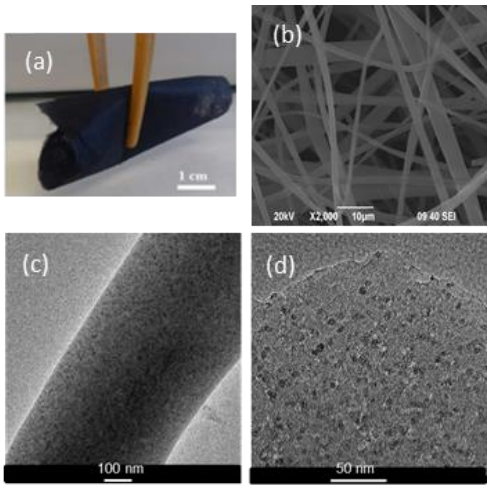

FIGURE 1: (a) photo of Co@CF-500 showing the catalyst flexibility, (b) SEM image, (c) TEM image and (d) HR-TEM image showing Co NPs for Co@CF-500.

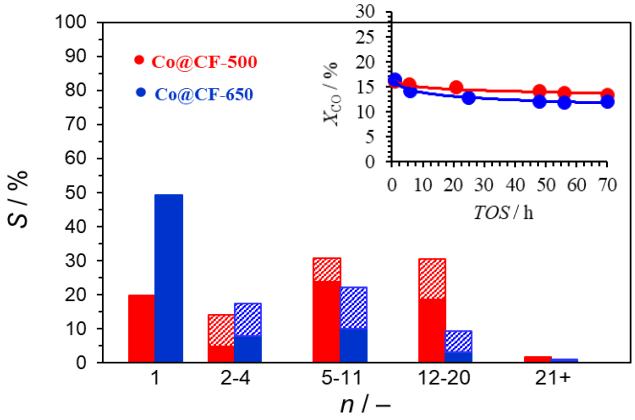

FIGURE 2: Carbon selectivity toward products of FTS at iso-conversion conditions after 70 h on stream; ▌: n-paraffins, ///: sum of isoparaffins and olefins. Reaction conditions: 513 K, 20 bar, H_2/CO = 1 y GHSV / m^3_{STP} kg^{-1}_{cat} h^{-1} = 4.5 and 6 for Co@CF-650 and Co@CF-500, respectively

Acknowledgements

The authors acknowledge the Spanish Ministry of Science, Innovation, and Universities (MICIU) and FEDER (Project RTI2018-097555-B-I00) and Junta de Andalucía (Project UMA18-FEDERJA-110 and P18-RT-4592).

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