



Flame Spray Pyrolysis as fine preparation technique for stable Co and Co/Ru based catalysts for FT process



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ABSTRACT

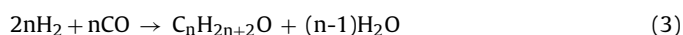
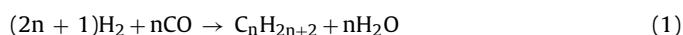
Flame spray pyrolysis (FSP) is an innovative and scalable technique, used to synthesize monometallic and bimetallic Co-Ru catalysts with 5% wt. Co, 10% wt. Co and 0.4% wt. Ru supported on SiO₂ active in the Gas-to-Liquids (GTL)-Fischer-Tropsch (FT) process, which converts syngas to hydrocarbons. The catalysts were characterized by TEM, FE-SEM-EDX, TPR, XRD and N₂ adsorption/desorption. All the three samples have been tested in a fixed bed FT-bench scale plant. Results demonstrated that the 5% wt. Co catalyst was not active toward FT synthesis, while samples containing 10% wt. Co and 10% wt. Co - 0.4% wt. Ru were suitable candidates for the GTL-FT process. With an increase in temperature, the CO conversion increased, the product selectivity remained unchanged, and the 10% wt. Co catalyst showed higher stability as a function of time-on-stream (TOS) with respect to traditionally prepared materials. The addition of 0.4% wt. of Ru improved the performance in terms of CO conversion and C₂₊ yield.

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1. Introduction

In recent years the necessity to develop processes which use alternative sources for fuel and chemicals production respect to the ones based on crude oil refinement and conversion became incumbent. Some of the issues concerning traditional fuels are the sulphur and aromatics compounds contents; these factors have increased, in addition to the necessity to find a fuel production process which allows a closed loop in terms of CO₂, the interest in the Gas-to-Liquid (GTL) – Fischer Tropsch (FT) process which allows the synthesis of ultra clean fuels with the FT reaction starting from the production of syngas (i.e. a mixture of H₂ and CO with a molar ratio equal to 2) [1–3]. Syngas can be produced from coal, natural gas and biomass; using this last feedstock the syngas is called bio-syngas and is characterized by a H₂/CO ratio lower than 2.

The FT process is an array of strongly exothermic reaction ($\Delta H \approx -200 \text{ kJ mol}^{-1}$) that forms alkanes, alkenes and some oxygenated compounds; all the main reactions of the FT process are reported in the following Eqs. (1–4) [1]



Moreover, if Fe-based catalysts are used, the water-gas-shift (WGS) reaction occurs simultaneously with the main FT one.

The FT reaction requires catalysts based on iron or cobalt; in particular, in the industrial FT process, massive iron or supported Co catalysts are traditionally used. Fe has lower price compared to Co, and in addition iron based samples could be used if bio-syngas is feeding the reactor; this advantage is due to the activity towards the WGS reaction which can raise the H₂/CO ratio to 2. On the other hand, Co based catalysts offer a good catalytic activity, high stability in function of time and better selectivity to linear paraffins [4].

All of the common catalyst preparation techniques used in research laboratories and industries are composed by several steps and as one of them varies, significant alterations of the chemical physical and morphological properties in the final products occur [5].

Flame spray pyrolysis (FSP) offers an alternative synthetic route, which is not affected by some of the limitations of traditional synthetic techniques and proved suitable for large scale production of catalytic materials [6,7]. FSP has been successfully applied for high-temperature applications where suitable thermal resistance

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is imparted by the flash calcination at $T > 1300\text{ }^\circ\text{C}$ [8,9]. Furthermore, FSP is able to achieve peculiar and thermally stable metal dispersions in the case of Ni-based catalysts for ethanol and glycerol steam reforming [10,11] and for V-based catalysts for the oxidative dehydrogenation of paraffins to olefins [12]. Both these applications share with FT the non-negligible issue of coking. For steam reforming of organic compounds, coking activity can be tuned and limited by selecting proper surface acidity (mainly through a right choice of the support) and by improving metal dispersion. Indeed, small metal particle size can inhibit the growth of carbon nanofilaments and nanofibers. In addition, it was also demonstrated that the FSP synthesis was able to strength the metal-support interaction, further improving metal dispersion and stabilizing it over prolonged operation at high temperatures [13–15].

FSP has been successfully employed in many different application fields, as extensively reviewed by many authors [16–20]. However, at the moment, this preparation approach has been studied in a very limited way in the field of Fischer Tropsch synthesis. For example Minnermann et al. [21] proposed a study where a monometallic 10%wt Co-based catalyst supported on Al_2O_3 has been synthesized and tested in this reaction. A deep preparation and characterization study was reported concerning different operative procedures in the FSP synthesis, although few activity tests on FT were proposed. In the present work, differently, we prepared monometallic 5–10% wt Co and bimetallic 10%wt Co-0.4%wt Ru by an already optimized [13] FSP technique; moreover several reaction tests were performed. A detailed study concerning the optimized quantity of cobalt and promoter supported on silica-supported catalysts and a primary evaluation of the catalytic activity as a function of temperature is reported in a previous paper [22]. Here the attention is focused on the effect of the preparation method on catalyst properties, activity and, above all, stability. The addition of the promoter (Ru) allows to improve the reduction of the Co oxide species, from Co_3O_4 to CoO and then to metallic Co [23].

The samples were characterized by TEM, FE-SEM-EDX, TPR and XRD to check metal dispersion, the nanostructure and size of the metal particles, the cobalt phases and the amount of the active metal present in the catalysts and then a detailed study regarding the BET surface area and pores volume in order to evaluate the effect of the metal loading and the FSP synthetic procedure.

The samples were tested in a bench-scale FT plant at different temperature in the range $T = 220\text{--}260\text{ }^\circ\text{C}$ at 2.0 MPa and using a syngas with an H_2/CO ratio equal to 2. The kinetic tests allowed the estimation of the catalytic activity in terms of CO conversion, selectivity toward various reaction products (i.e. CH_4 , CO_2 , light and heavy hydrocarbons) and the stability for prolonged time-on-stream (TOS). Furthermore, on the basis of the collected data, the comparison between the Ru-promoted and the un-promoted catalysts allows to evaluate the effect of Ru on catalytic activity. The experimental data also show the benefits of the FSP technique with respect to other traditional synthetic methods.

2. Experimental

All the catalysts synthesized were supported on SiO_2 . Samples compositions are on a weight (%) basis. The percentages for CO conversion, product selectivity, and hydrocarbon yield are expressed on a molar basis. The Co-based catalysts are named as 5Co, 10Co and 10Co-0.4Ru, where the numbers represent the wt% of each metal present in the catalysts.

2.1. Catalysts preparation and characterization

2.1.1. Catalysts synthesis

The catalysts were prepared according to the FSP method [24–26]. A burner was specifically designed for this application,

allowing the injection of 4.4 ml min^{-1} of an organic solution containing the catalyst precursors into a nozzle. The latter is co-fed with oxygen at high flow rate (5 NL min^{-1}). The mixture is ignited by external flamelets supported by feeding $0.5\text{ NL min}^{-1}\text{ CH}_4 + 1\text{ NL min}^{-1}\text{ O}_2$.

The precursors solution was prepared by dissolving proper amounts of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (Fluka) and $\text{Si}(\text{OC}_2\text{H}_5)_4$ (Sigma Aldrich) in a 1/1 mixture of $\text{CH}_3\text{CH}_2\text{COOH}$ (Aldrich)/*p*-xylene (Aldrich) in order to obtain a molar concentration equal to 0.73 M. The pressure drop across the nozzle was adjusted to 0.7 bar, as optimised elsewhere [8,9,27]. The amount of metal present in the catalyst was easily varied by adjusting its concentration in the solution.

Ru was added by wet impregnation using $\text{Ru}_3(\text{CO})_{12}$ (Sigma Aldrich) as a precursor. A $3.00 \cdot 10^{-3}\text{ mol/L}$ solution of Ru carbonyl in *n*-decane (Sigma Aldrich) was prepared and then added to the sample made by FSP. The catalyst was then placed in a rotary evaporator at $T = 40\text{ }^\circ\text{C}$ at 36 rpm for 24 h. At the end of the impregnation step the sample was heated in air at $T = 100\text{ }^\circ\text{C}$ for 12 h and calcined at $T = 200\text{ }^\circ\text{C}$ for 4 h.

2.1.2. Catalysts characterization

SEM-EDX images were obtained using a Philips XL-30CP with backscattered electron detector. SEM images were obtained using a Field Emission Gun Electron Scanning Microscopy LEO 1525 (ZEISS). The samples were investigated by In lens detector and elemental composition was determined using a Bruker Quantax EDS.

The morphology of the catalyst particles was studied using a Philips 208 Transmission Electron Microscope (TEM). The conventional temperature-programmed reduction experiments (TPR) were performed using a Thermoquest Mod. TPR/D/O 1100 (TCD detector) by feeding 30 ml/min of a 5.1% v/v H_2 in Ar gas mixture while heating by $8\text{ }^\circ\text{C/min}$ from $T = 50\text{ }^\circ\text{C}$ up to $T = 900\text{ }^\circ\text{C}$. X-ray powder diffraction (XRPD) patterns were taken with a Philips X'PERT PRO MPD diffractometer.

The catalyst's surface area and porosity distribution were determined by low temperature ($T = -196\text{ }^\circ\text{C}$) N_2 adsorption using a Micromeritics ASAP 2020 instrument. Surface area was calculated on the basis of the Brunauer, Emmet and Teller equation (BET), while the pores size distribution was determined by the BJH method, applied to the N_2 desorption branch of the isotherm. Prior to the analysis the samples were outgassed at $T = 300\text{ }^\circ\text{C}$ for 24 h.

2.2. Apparatus for FT runs

Fischer–Tropsch reaction activity tests were carried out in a bench-scale fixed-bed tubular reactor with an internal diameter of 6 mm. 1 g of fresh catalyst was mixed with 1 g of $\alpha\text{-Al}_2\text{O}_3$ (Fluka) which act as diluting material. The entire bench scale experimental FT plant is already described by the authors in previous works [22,28,29]. Liquid products were collected, during the complete reaction cycle, in a cold trap ($V = 400\text{ mL}$), operating at $T = 5\text{ }^\circ\text{C}$ and at the same pressure of the reactor ($P = 2.0\text{ MPa}$), then analyzed by a gas chromatograph (Fisons-8000 series) equipped with a Porapack-Q column (this being able to separate the $\text{C}_7\text{--C}_{30}$ hydrocarbon fraction). The column temperature was maintained at $60\text{ }^\circ\text{C}$ for 1 min and then heated up to $T = 300\text{ }^\circ\text{C}$ at $8\text{ }^\circ\text{C min}^{-1}$. The aqueous phase collected in the cold trap was analyzed by a TOC (Shimadzu 5000A) to identify the quantity of carbonaceous species dissolved in water. The analysis of the gas-phase products (the fraction $\text{C}_1\text{--C}_6$ not condensed in the cold trap) was performed with an on-line micro-gas chromatograph (Agilent 3000A) equipped with two different columns: the first, a molsieves module, which can separate CO , N_2 and CH_4 at a column temperature of $T = 100\text{ }^\circ\text{C}$, and the second, a OV-1 module (stationary phase of polydimethylsiloxilane),

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