

EXPERIMENTAL STUDY OF FISCHER-TROPSCH SYNTHESIS OF ORGANICS USING CHONDRITE SAMPLES. V. Cabedo^{1,2,3}, J.M. Trigo-Rodríguez², A. Rimola³ and J. Llorca¹, ¹Institute of Energy Technologies, Department of Chemical Engineering and Barcelona Research Center in Multiscale Science and Engineering, Universitat Politècnica de Catalunya-BarcelonaTECH, Catalonia, Spain (jordi.llerca@upc.edu), ²Institute of Space Sciences (IEEC-CSIC), Campus UAB, 08193 Cerdanyola del Vallés (Barcelona), Catalonia, Spain, ³Department of Chemistry, Universitat Autònoma de Barcelona, 08193 Bellaterra, Catalonia, Spain.

Introduction: Organic compounds found in meteorites are believed to mostly originate in both the solar nebula and by hydrothermal processing of parent bodies [1]. One of the mechanisms that accounts for their formation in the solar nebula is the Fischer-Tropsch synthesis (FT), which consists on the reaction between hydrogen and carbon monoxide on a catalytic surface. Metals are good catalysts for FT processes through the formation of metal carbides. Iron and nickel are among the most active metals and yield hydrocarbons and oxygenated organic compounds depending on the reaction conditions, in addition to carbonaceous deposits as secondary products. Also, iron and nickel oxides can act as catalyst precursors and can activate during reaction to yield active catalysts as well. For that reason, metal phases in meteorites have been proposed as catalysts for FT processes in the solar nebula that originated organic molecules in meteorites [2-4]. In addition, the catalytic properties of chondritic components under the presence of hot water and formamide have been demonstrated [5]. Several works have been published showing the capability of Fe and Ni to catalyze FT processes under nebular environments [6,7] but, to the best of our knowledge, there are no studies reporting the direct use of meteorites as catalytic materials for FT. Here we have used Allende (CV3), NWA 801 (CR2) and KG 007 (H6) to study their ability to catalyze the FT reaction.

Methods: The meteorite samples were first studied by X-ray absorption tomography to determine the amount of metal phases present in order to normalize the catalytic results (Figure 1). Then, the samples were crushed and sieved and mixed with inert SiC (0.5 g of meteorite and 2.5 g of SiC) to ensure a constant gas hourly space velocity value in a plug flow reactor (GHSV=3000 h⁻¹), which was placed inside an oven (± 0.5 K). The catalytic tests were carried out at atmospheric pressure in the temperature range 200-600 °C and the H₂:CO ratio was set at 4:1 (molar basis; total flow 40 ml min⁻¹, contact time $\tau=1.2$ s). The analysis of the reaction products was performed by on-line gas chromatography.

Results and discussion: The catalytic tests demonstrate that KG 007 (H6) and NWA 801 (CR2) are active in the FT synthesis, whereas Allende (CV3)

it is not. This is ascribed to the abundance of metal phases in the different meteorite types: ~0.1% vol. for Allende, ~6% vol. for NWA 801 and ~8% vol. for KG 007. For the most active samples, KG 007 and NWA 801, CO conversion at 400 °C was about 12 and 18%, respectively.

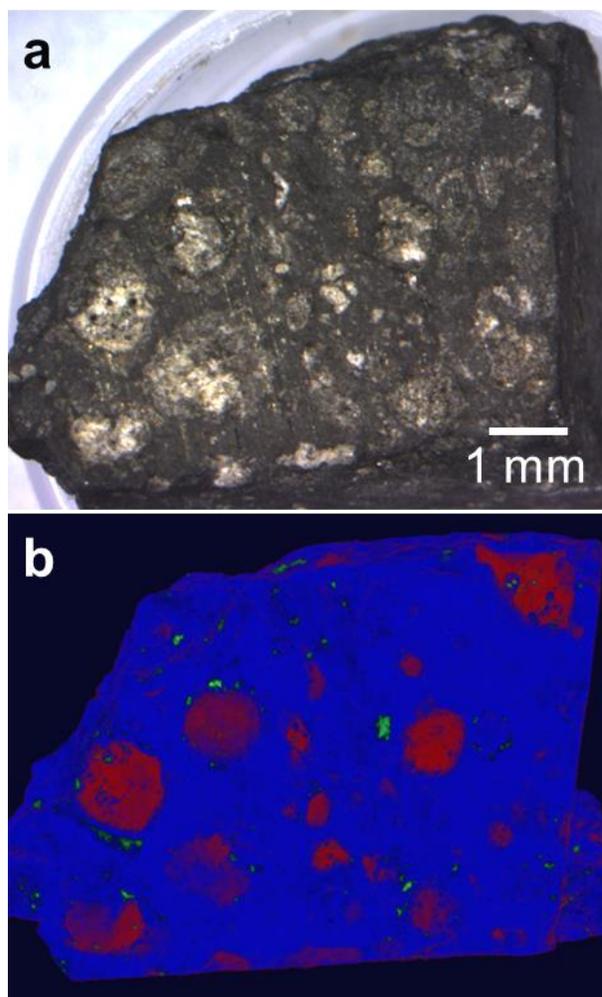


Figure 1. Allende chip used for the FT experiments under the optical microscope (a) and X-ray tomography (b).

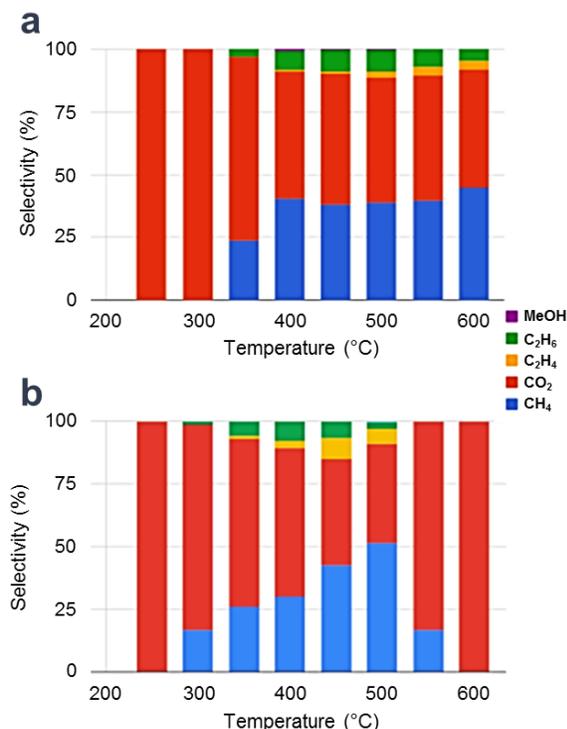


Figure 2. Product selectivity obtained at different temperature over KG 007 (a) and NWA 801 (b).

Figure 2 shows the selectivity of the products obtained over KG 007 and NWA 801 at different temperatures. In both cases, the main products obtained are carbon dioxide and methane, according to the Boudard (equation 1) and methanation reactions (equation 2) and, according to thermodynamics, the disproportionation of CO is favored at low temperatures. A blank run (without any meteorite sample) yielded methane only at temperatures higher than 500 °C.



In addition to the main products, ethylene and ethane are also formed through C-C coupling, especially at temperatures higher than 350 °C. Oxygenated compounds are also identified particularly at 400 °C, but at much lower yield. These are methanol (equation 3), and trace amounts of ethanol, formaldehyde and dimethyl ketone.



Interestingly, the distribution of products obtained over KG 007 and NWA 801 differs significantly. In particular, the CR2 carbonaceous chondrite is active for FT processes at lower temperature with respect to the H6 ordinary chondrite, even if the metal content of the former is lower. In addition, the selectivity to C₂ is higher in NWA 801. This suggests that other character-

istics in addition to the presence and abundance of metal phases participate in FT processes. This has been demonstrated by separating the metal fraction from KG 007 (by disaggregation and magnetic separation) and testing it as catalyst for FT. Over FeNi, a higher catalytic activity is attained, but exactly the same selectivity is obtained.

Taking into account that CR2 carbonaceous chondrites experienced extensive aqueous alteration that originated phyllosilicates, and that phyllosilicates exhibit catalytic properties and are indeed associated with organics in carbonaceous chondrites [8], it is likely that simple organic molecules formed through FT processes over metal phases further evolved over phyllosilicates to more complex molecules. In fact, NWA 801 contains organic globules dispersed in the matrix with isotopic compositions and morphologies which suggest that they were formed in the early solar nebula [9]. Concerning the apparent non-reactivity of CV3 Allende for FT processes, it should be taken into account that the amount of Fe associated with sulfides and metal phases is minor, as most appears as oxide (FeO) in ferromagnesian minerals forming the chondrules [10].

In conclusion, the results obtained demonstrate that FeNi metal in chondrites catalyzes FT-type processes and produce hydrocarbons and oxygenated organic compounds at short contact times ($\tau=1.2$ s) at temperatures higher than 300 °C, suggesting that simple organic molecules in meteorites could be easily originate in hot events in nebular environments. CR carbonaceous chondrites appear to be particularly active in C-C coupling and formation of oxygenated compounds with respect to ordinary chondrites.

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