Catalytic potential of natural minerals towards Fischer-Tropsch Type (FTT) synthesis of hydrocarbons

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Fischer-Tropsch synthesis is used in the industry for the production of methane and other light hydrocarbons, by reacting gas phase CO with H_2 in the presence of various synthetic catalysts. Fischer-Tropsch Type (FTT) reactions more largely include reactions involving CO_2 and aqueous phases. However, though those reactions have been widely studied, little is still known about the catalytic activity of natural minerals for FTT synthesis of hydrocarbons, in geological environments largely dominated by water. Recent studies [1],[2] have shown that some sulfides have the ability to activate the formation of C-H bonds. This reaction appears to be purely promoted by the mineral surface, where neither the metallic cation nor the sulfur participate as reactants. The aim of the present work is to understand the extent of abiogenic hydrocarbon production in natural environments by studying the catalytic potential of natural sphalerite (ZnS) and other sulfides (eg. marcasite, pyrite - polymorphs of FeS_2), by performing laboratory experiments on various mineral assemblages (eg. olivine, fayalite, chamosite).

First experiments were performed reacting an assemblage composed of 91 wt.% iron-rich olivine, $(Mg_{0.9}Fe_{0.1})_2SiO_4$, and 9 wt.% sulfides, with a 0.64M $NaHCO_3$ solution under hydrothermal conditions (T = 300 °C, P = 30 MPa). An experiment without the catalyst was used as the control to compare the effect. The first reaction, so-called "serpentinization reaction", produced H_2 by oxidizing iron from the silicate; H_2 then reacted with the dissolved CO_2 in the presence of the natural sulfide catalyst to form methane and other light hydrocarbons. Alkanes up to C4 were detected and quantified in the gas phase of the experimental run products. Serpentine, magnetite and sulfide catalyst were observed in the solid run product. Initially produced H_2 was quantified indirectly by conducting magnetic measurements on the solid run products, according to [3].

[1] Shipp et al. (2014) PNAS **111 (32)**: 11642-11645.
[2] Roldan et al. (2015) Chem. Commun **(51)**: 7501.
[3] Malvoisin et al. (2012) J. Geophys. Res **(117)**: B01104.