

Direct use of H₂-poor syngas in the Fischer-Tropsch synthesis

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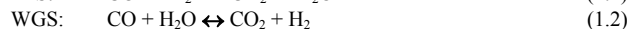
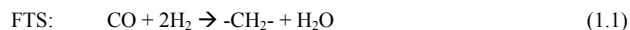
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Introduction

The depletion of fossil energy sources and the need for reduction of greenhouse gas emissions make renewable energy sources very attractive. Conversion of biomass into liquid fuels has a great potential for reducing CO₂-emissions in the transport sector. An option for the production of renewable automotive fuels from gasified biomass is the Fischer-Tropsch synthesis (FTS), in which syngas (H₂ + CO) is converted to long chains hydrocarbons (HCs) mainly over Co- or Fe-based catalysts according to reaction (1.1). Syngas obtained upon gasification of biomass or coal typically has a ratio of hydrogen to carbon monoxide (H₂/CO) lower than that in syngas produced from natural gas [1-2]. Utilization of this H₂-poor syngas in the Fischer-Tropsch synthesis is usually performed after adjusting the ratio to a value close to the stoichiometric one required by reaction 1.1 (i.e. approx. 2.1), in an external water-gas-shift (WGS) unit (see reaction 1.2). Direct employment of this H₂-poor bio-syngas via a one-pass through the FT-reactor is possible either using unconverted syngas in a gas turbine for co-production of electricity [3] or by performing the WGS reaction simultaneously inside the FT reactor, increasing the molar H₂/CO ratio of the syngas. The water needed in the WGS reaction (1.2) is produced in the FT reaction (1.1) or can be added externally.



In the current study, several alternative catalysts are considered in order to perform the FTS with a H₂-poor syngas with molar H₂/CO = 1.0. The aim of the current study is to screen possible catalysts and catalyst mixtures that could achieve high activity and selectivity to C₅+ together with a high conversion per pass. Fe- and Co-based catalysts as well as mechanical mixtures of such, and mechanical mixtures of a Co-catalyst and WGS-catalysts, are investigated.

Materials and Methods

Bulk iron catalysts are prepared by a conventional precipitation method. Cu and K are added as promoters to increase the reducibility of the iron oxide [4], and the WGS activity and S_{C5+} [5]. Cu is co-precipitated with Fe, while K with different atomic ratio is added to Fe (or FeCu) following the incipient wetness technique. A standard Co-catalyst (12wt.% Co/γ-Al₂O₃) is prepared by the incipient wetness impregnation technique. Since Co-catalysts have much lower WGS activity, compared to Fe-based catalysts, but can reach higher conversion per pass [1], Cu is added to the Co-catalyst (impregnated 12% Co/γ-Al₂O₃) to increase the WGS-activity by co-impregnation. Another investigated option, also considered in the literature [6], is a mechanical mixture of Co/γ-Al₂O₃ with a Cu-based WGS-catalyst. Two co-

precipitated Cu/ZnO/Al₂O₃ with different methods (one alkali-free) and a co-impregnated Cu/ZnO/γ-Al₂O₃ are tested. Finally, a mechanical mixture of a bulk iron catalyst and the Co-catalyst is tested. The catalysts are tested in a fixed-bed reactor at different GHSVs at 230 °C and 20 bar with an inlet H₂/CO ratio of 1.0.

Results and Discussion

Defining the usage ratio (u.r.) as $\frac{3xS_{CH_4} + 2.1xS_{C_2-C_4} + 2xS_{C_5+} - S_{CO_2}}{100}$, it can be seen from

Fig. 1 that it is possible to achieve the desired value of the u.r. (= 1.0) only when the Fe-based catalyst is promoted with potassium while Cu increase the WGS activity only through a synergy effect with K. It is possible to achieve the same effect with the mechanical mixture of a Co-catalyst and a Cu-based WGS catalyst or a K-promoted Fe-catalyst; however, a decrease in HC formation rate was observed, as compared to the pure Co-catalyst. Probably the presence of alkali metals either as a promoter (K in Fe) or from the preparation (Na in co-precipitated Cu/ZnO/Al₂O₃) poisons the Co [5].

Results for mechanical mixture of alkali-free WGS will be presented. Effect of the mixture presence on the product distribution will be also presented and discussed.

The catalysts are characterized with several techniques including XRD, BET, TPR, chemisorption etc.

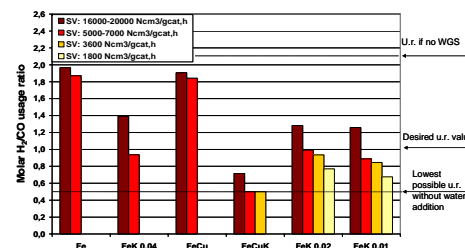


Figure 1. Usage ratios at different space velocities (SVs)

Significance

The possibility of direct use of H₂-poor bio-syngas in the Fischer-Tropsch synthesis with internal shifting could allow for a reduction of the investment cost since the external WGS and CO₂ removal units are not needed, together with a higher efficiency of the process. Moreover, the lower water pressure in the reactor, as result of the WGS reaction, could extend the life-time of the catalyst.

References

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