

## CO<sub>2</sub> Conversion by Low-Temperature Fischer-Tropsch

**Authors :** Pauline Bredy, Yves Schuurman, David Farrusseng

**Abstract :** To fulfill climate objectives, the production of synthetic e-fuels using CO<sub>2</sub> as a raw material appears as part of the solution. In particular, Power-to-Liquid (PtL) concept combines CO<sub>2</sub> with hydrogen supplied from water electrolysis, powered by renewable sources, which is currently gaining interest as it allows the production of sustainable fossil-free liquid fuels. The proposed process discussed here is an upgrading of the well-known Fischer-Tropsch synthesis. The concept deals with two cascade reactions in one pot, with first the conversion of CO<sub>2</sub> into CO via the reverse water gas shift (RWGS) reaction, which is then followed by the Fischer-Tropsch Synthesis (FTS). Instead of using a Fe-based catalyst, which can carry out both reactions, we have chosen the strategy to decouple the two functions (RWGS and FT) on two different catalysts within the same reactor. The FTS shall shift the equilibrium of the RWGS reaction (which alone would be limited to 15-20% of conversion at 250°C) by converting the CO into hydrocarbons. This strategy shall enable optimization of the catalyst pair and thus lower the temperature of the reaction thanks to the equilibrium shift to gain selectivity in the liquid fraction. The challenge lies in maximizing the activity of the RWGS catalyst but also in the ability of the FT catalyst to be highly selective. Methane production is the main concern as the energetic barrier of CH<sub>4</sub> formation is generally lower than that of the RWGS reaction, so the goal will be to minimize methane selectivity. Here we report the study of different combinations of copper-based RWGS catalysts with different cobalt-based FTS catalysts. We investigated their behaviors under mild process conditions by the use of high-throughput experimentation. Our results show that at 250°C and 20 bars, Cobalt catalysts mainly act as methanation catalysts. Indeed, CH<sub>4</sub> selectivity never drops under 80% despite the addition of various promoters (Nb, K, Pt, Cu) on the catalyst and its coupling with active RWGS catalysts. However, we show that the activity of the RWGS catalyst has an impact and can lead to longer hydrocarbons chains selectivities (C<sub>2</sub><sup>+</sup>) of about 10%. We studied the influence of the reduction temperature on the activity and selectivity of the tandem catalyst system. Similar selectivity and conversion were obtained at reduction temperatures between 250-400°C. This leads to the question of the active phase of the cobalt catalysts, which is currently investigated by magnetic measurements and DRIFTS. Thus, in coupling it with a more selective FT catalyst, better results are expected. This was achieved using a cobalt/iron FTS catalyst. The CH<sub>4</sub> selectivity dropped to 62% at 265°C, 20 bars, and a GHSV of 2500ml/h/gcat. We propose that the conditions used for the cobalt catalysts could have generated this methanation because these catalysts are known to have their best performance around 210°C in classical FTS, whereas the iron catalysts are more flexible but are also known to have an RWGS activity.

**Keywords :** cobalt-copper catalytic systems, CO<sub>2</sub>-hydrogenation, Fischer-Tropsch synthesis, hydrocarbons, low-temperature process

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