Promoted Fe catalyst for direct conversion of CO_2 into *e-crude*

Mattia Piacentini[1], Beda Rolandi[1], Alessandro Porta[1], Luca Lietti[1], Carlo Giorgio Visconti[1]*
[1]*Laboratory of Catalysis and Catalytic Processes, Department of Energy*
Politecnico di Milano, via La Masa 34, 20156, Milano ITALY
* carlo.visconti@polimi.it

Significance and Relevance

A promoted iron-based catalyst was tested under conditions favoring high selectivity to *e-crude*, primarily in the C_8-C_{16} range, with CH_4 and C_2-C_4 paraffins accounting for less than 15%. The catalyst showed a reversible deactivation, mainly driven by water partial pressure.

Preferred and 2nd choice for the topic: CO_2 Utilization and Recycling
Preferred presentation: Oral and short oral preferred

Introduction and Motivations

Developing a direct process to convert CO_2 into long-chain hydrocarbons via modified Fischer-Tropsch (MFT) is highly promising for producing sustainable e-fuels for high energy density applications (e.g. aviation fuels). MFT produces a wide range of products, distributed across gas and condensed phases. The condensate phase, referred to as *e-crude*, contains a mixture of high energy density hydrocarbons, making it ideal for applications like aviation where energy density is essential. However, MFT catalysts are susceptible to deactivation due to oxidation of iron carbides, the active phase for the chain growth of the Fischer-Tropsch [1]. In this work, a promoted iron-based catalyst was tested in conditions to achieve a high selectivity to *e-crude*, with minimal production of CH_4 and lower paraffins. Despite a long exposure to a high partial pressure of water caused evolving performances during time on stream, the catalyst showed reversible deactivation.

Materials and Methods

Following the procedure reported in [2], a co-precipitated Fe-Zn oxide was promoted by incipient wetness impregnation with potassium carbonate and copper nitrate. The final catalyst composition was 100Fe:10Zn:1Cu:4K on a molar basis.

High pressure catalytic tests have been carried out in a fixed bed stainless steel (AISI 316 L) reactor with an internal diameter of 1.1 cm, located inside an electrical tubular oven. The effluent gases exiting the reactor were sent firstly to a hot trap kept at 120 °C to remove heavier hydrocarbons (up to C_{35}) and then to a cold trap kept at 2 °C, to remove the lighter fraction and water. Incondensable gases leaving the vessels were periodically analyzed by an on-line GC. Prior to the reaction the catalyst was activated in-situ with syngas (H_2/CO= 2 mol/mol) at 270 °C for 1h at atmospheric pressure.

Results and Discussion

The catalyst was tested for more than 900 hours on stream, investigating different operating conditions. The catalyst reaches pseudo steady state after about one day on stream, showing high selectivity to C_{5+} and low selectivity to light hydrogenated compounds (CH_4 and lower paraffins) in most of the investigated conditions. Interestingly, CO_2 conversion is higher than the thermodynamic equilibrium of the sole RWGS reaction. The ratio between the RWGS reaction quotient and the equilibrium constant (Kp_{RWGS}/Keq_{RWGS}) is always between 0.7 and 1, suggesting that the RWGS is close to its equilibrium. Thus, the consecutive FT converts CO into hydrocarbons, removing the product of the RWGS from the reaction environment increasing the overall conversion. Stability check points (colored areas in Fig 1) show that catalyst performances evolve over time. For example, comparing areas “B” and “D”, CO_2 conversion decreases significantly from 33% to 23%, together with an increase in CO selectivity from 14% to 35%. Consequently, selectivity to C_{5+} drops from 51% to 29%. This deactivation is attributed to H_2O partial pressure. Indeed, at 30 barg and 350°C the partial pressure of H_2O reaches 8 barg (area “C” in Fig 1), leading to iron carbide oxidation to iron oxide and reduced FT activity. The sample was regenerated at

350°C and 5 barg (area “E” in Fig 1) where low partial pressure of H_2O and high partial pressure of CO restored most of the carbide phase and FT catalytic activity. The yellow area “F” in Fig 1 shows that, after the regeneration, the catalyst's performance is restored to levels comparable to area "B"**.** Figure 2 shows the complete product distribution obtained at 300 °C, 30 barg and 6 L(STP)/h/gcat (area “A” Fig 1). The product distribution closely follows a bimodal Anderson-Schultz-Flory (ASF) model, with a change in slope at C_{15}. The product pool consists primarily of linear olefins, but also includes branched hydrocarbons, linear paraffins and a non-negligible amount of alcohols. Notably, about 60% of the produced *e-crude* is within the C_8-C_{16} range, making it particularly suited for aviation fuels applications.

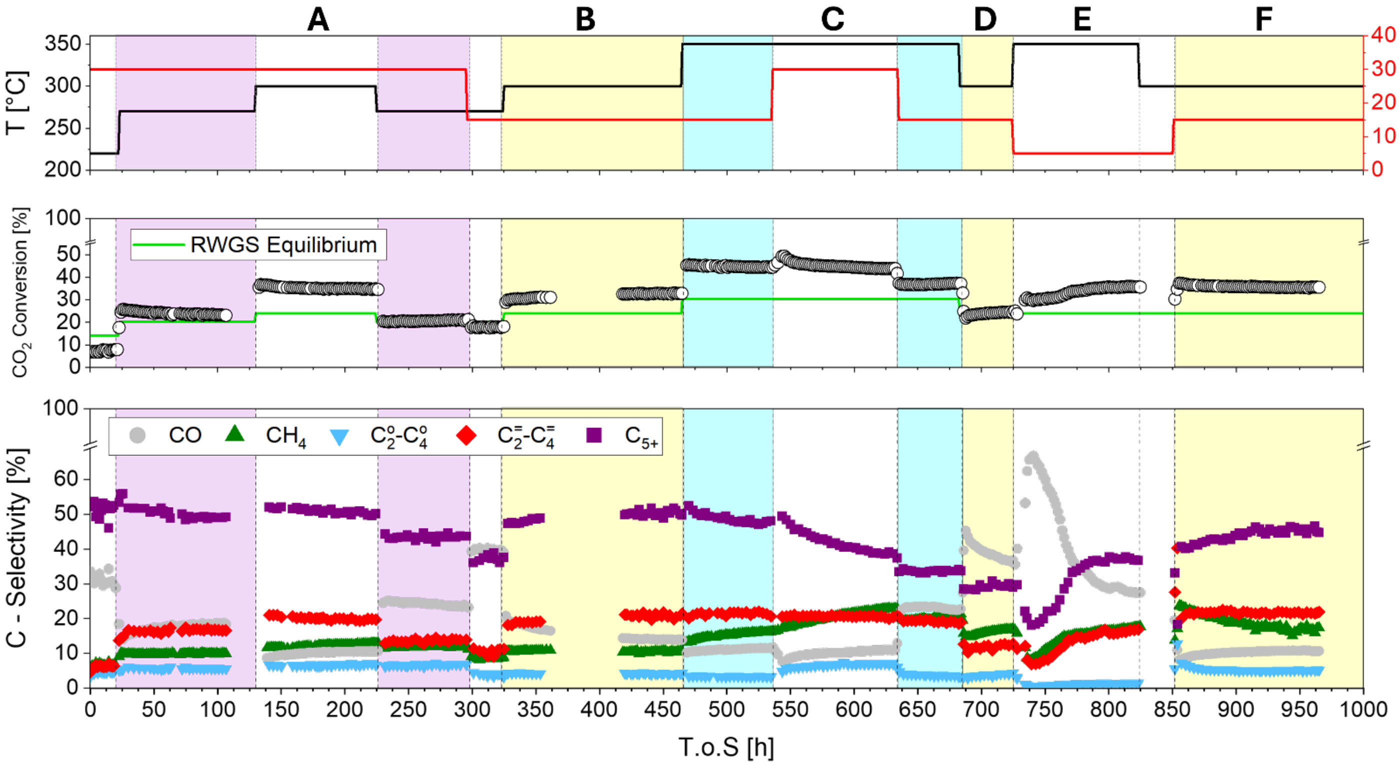

Figure 1. From top: Operative conditions, CO_2 Conversion and product selectivity as function of ToS. All data are obtained at 6 L(STP)/h/gcat.

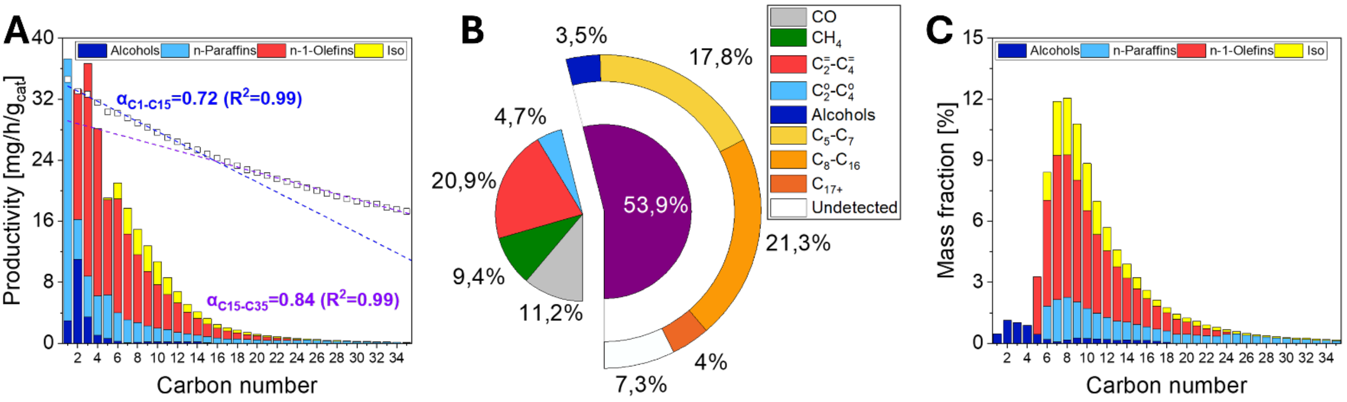

Figure 2. A) Complete product distribution and ASF plot B) Complete carbon-based selectivity C) *e-crude* characterization. Operating conditions: 300 °C, 30 barg and 6 L(STP)/h/gcat.

References

1. Ramos et al., Appl. Catal. B 2024, 347, 123794
2. M. Martinelli et al., Catalysis Today 2014, 228, 77