

Effect of pre-treatment conditions on Fe-based catalyst for e-fuel production via modified Fischer-Tropsch synthesis

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Highlights

- Optimization of operative conditions for e-fuel development system on pilot plant scale
- Effect of pre-treatment conditions on catalyst stability and product distribution
- Detailed characterization of produced liquid phase
- Broad analysis of the catalyst behaviour after each pre-treatment step.

1. Introduction

Synthetic fuels produced through the Fischer-Tropsch process represent a remarkable innovation in the world of energy production. In an era where sustainable and environmentally friendly energy sources are gaining prominence, synthetic fuels offer a bridge between traditional fossil fuels and a cleaner energy future. In this work, the so-called “modified” Fischer-Tropsch process [1-2] is investigated by studying the suitable catalyst configuration, pre-treatment, and operative conditions. Iron-based catalysts are generally doped with alkali or earth-alkali metals which favors the selectivity towards longer chain hydrocarbon. Doped catalyst can be also coupled with zeolites that allow oligomerization, isomerization, and aromatization which are fundamental to obtaining a liquid product as close as possible to the specific requirement of commercial fuels. In this work, the effect of different reduction and calcination atmospheres and temperatures on the iron active phase are evaluated to maximize the yield in longer olefins with a detailed analysis of the produced liquid phase, and catalyst characterization. The dynamic behaviour of the active phase which undergoes structural changes has been also analyzed with in-situ spectroscopy techniques which allow the analysis of the iron phases present on fresh, activated and spent catalysts [3-4].

2. Methods

Fe₃O₄ was synthesized from FeCl₂ e FeCl₃ and doped with Na via wet impregnation in two batches at 1% and 5% wt. Na/Fe₃O₄ [3]. Pre-treatments and catalytic tests are performed in a fixed-bed reactor (ID: 10 mm) with a space velocity between 6 and 20 NL/h/g_{cat}. Pre-treatments consist of a calcination step and one (or multiple) reduction step with H₂, CO or a mixture of both following literature works [4-5]. Different gas mixtures, temperature and pressure have been evaluated. The catalyst was then tested with a mixture of H₂/CO₂/N₂ in the range 280-400 °C. The oil phase has been carefully analyzed to obtain a precise qualitative and quantitative analysis of all hydrocarbons that have been collected during the catalytic tests. Detailed characterization of fresh, pre-treated and spent catalysts has been conducted to analyze how the active phase transformation influenced product distribution.

3. Results and discussion

As reported in the literature [2-3] a higher amount of promoter increases both CO₂ conversion and hydrocarbon product selectivity, but different pre-treatment atmospheres play a significant role in the product distribution. A significant role in product distribution is played by the formation of new active sites on the catalyst surface which are known as Hägg carbide (Fe₅C₂). The presence of iron carbide

moves the product distribution towards longer hydrocarbon chains increasing the yield of the produced heavy oil (C_{15+}) and slightly reducing the olefin/paraffin ratio in the C_2 - C_5 range. If the formation of iron carbide is too predominant the catalyst shows much higher selectivity towards liquid products but undergoes faster deactivation phenomena. The best pre-treatment is the one that maximizes the light oil fraction (C_6 - C_{14}), the olefin/paraffin ratio in the C_2 - C_5 range and guarantees the highest stability of the catalyst over time (**Fig.1**) and it is strictly linked to the catalyst modifications as noted in the post-treatment/post-test characterizations of the samples (X-ray diffractograms, spectroscopy and microscopy analyses). In Figure 1 a typical catalytic test is shown where the sample, after the pre-treatment, is tested at different temperatures for 150 hours (where $T_2 > T_1 > T_4 > T_3$). The test highlights that the catalyst not only is stable at the end of the test but improves its performance over time. The composition of the light oil in terms of olefins, paraffins, aromatics and naphthenes concentration has been evaluated with Detailed Hydrocarbon Analysis (DHA) while the boiling point of both light and heavy oil produced has been evaluated with a standard distillation method (ASTM D86).

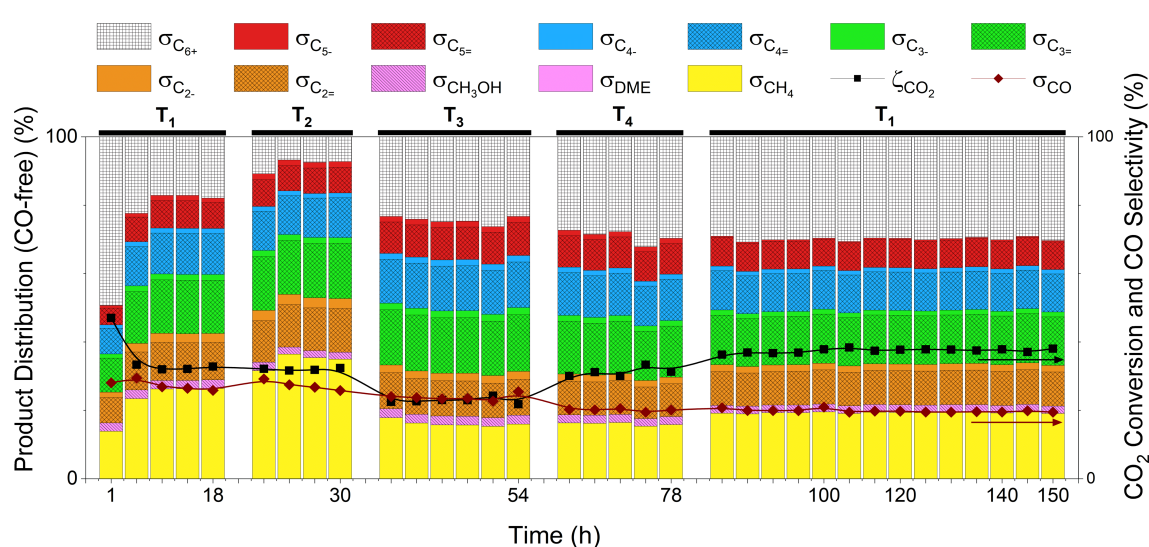


Figure 1. Catalytic test after pre-treatment. GHSV 7 NL/h/g_{cat}, 300-400 °C, 23 bara, H₂/CO₂ = 3.

4. Conclusions

The optimization of the catalyst pre-treatment is essential for the preparation of the catalyst in the perspective of a future scale-up of the system with Fe-based active phase coupled with zeolite. The presence of the zeolite allows the hydrogenation and isomerization of the light olefins increasing the C_6 - C_{14} yield making the process economically feasible for producing e-fuels on a large scale.

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Keywords

CO₂ Conversion; e-fuels; Fischer-Tropsch synthesis; Fe-based catalysts