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

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Significance and Relevance

This work is significant for advancing CO_2-modified Fischer-Tropsch synthesis (FTS) by demonstrating how tailored pre-treatment conditions affect catalyst phase composition and performance. By integrating Na-Fe_3O_4 with controlled carburization techniques, the study highlights the formation of specific iron carbides, notably ε'-$Fe_{2.2}C$, which enhance hydrocarbon yield and selectivity toward long-chain products. The use of Mössbauer spectroscopy, DHA, and chemometrics provides a comprehensive analysis of phase transformations and product distributions. These insights are critical for optimizing catalysts in CO_2-to-fuel conversion processes, paving the way for sustainable and efficient fuel production.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling / Sustainable and clean energy production and transport.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The rising demand for sustainable fuels has driven advancements in CO_2 conversion technologies, particularly in Fischer-Tropsch synthesis (FTS) for producing liquid hydrocarbons. This study examines the effects of various pre-treatment conditions on a Na-Fe_3O_4 catalyst in CO_2-modified FTS[1], focusing on how iron carbide formation influences hydrocarbon yield and distribution. By exploring how different pre-treatment strategies impact catalyst efficiency and selectivity, this research provides valuable insights into optimizing the CO_2-to-hydrocarbon conversion pathway.

Materials and Methods

The Na-Fe_3O_4 catalyst was synthesized via a precipitation method, followed by a series of pre-treatment conditions, including activation and carburization at varying temperatures and gas atmospheres, to promote specific iron carbide phases: H_2 activation at 450°C (pretreatment A); H_2 activation at 450°C followed by carburization (CO/H_2 1:1 P=2 bar) at 300°C (AC) and at 400°C (AC400).

The activity of the catalysts was tested between 320°C and 380°C, $H_2/CO_2/N_2$: 15/5/3, 7 NL/h/g_{cat}, 360 °C, 23 bar. Characterization techniques such as XRD, Mössbauer spectroscopy, and Detailed Hydrocarbon Analysis (DHA) were employed to evaluate the catalyst's bulk composition, surface properties, and resulting hydrocarbon distributions. Principal Component Analysis (PCA) was applied to DHA data to examine correlations between the hydrocarbon product distribution and the iron carbide phases of the catalyst, induced by the pretreatment and the specific reaction conditions (also replicating the composition of a feed deriving from the recirculation of primary unreacted or uncondensed species, i.e. mainly CO and CH_4).

Results and Discussion

The results reveal that pre-treatment conditions significantly influence the formation of active iron carbides **(Fig.1-right)**. Carburization at 400°C (AC400) proved optimal, promoting ε'-$Fe_{2.2}C$ formation while minimizing α-Fe content, an inactive site for the reaction. The high-temperature carburization (400°C) an improved yield of C_5^+ hydrocarbons **(Fig.1-left)**, ranging from 14% to 18%, comprising a balanced light-to-heavy oil ratio, while A and AC lead to a predominance of light oil (T_{cond}<150°C) **(Fig.2)**. Although the Hagg Carbide (χ-Fe_5C_2) is the main phase often associated with CO_2 conversion activity, other carbides could play a role[2]: in this case, the presence of ε'-$Fe_{2.2}C$ enhanced the catalyst's selectivity for long-chain hydrocarbons, resulting in a diverse hydrocarbon distribution dominated by iso-paraffins, while shorter-chain olefins were predominant in other pre-treatment samples with lower or no ε'-$Fe_{2.2}C$ content. The combined use of Mössbauer, DHA, and chemometric analysis proved instrumental in identifying active carbide phases and understanding their impact on reaction pathways. These insights contribute to the development of tailored catalytic processes for CO_2-to-fuel conversion, highlighting the potential of optimized Na-Fe_3O_4 catalysts for sustainable fuel production.

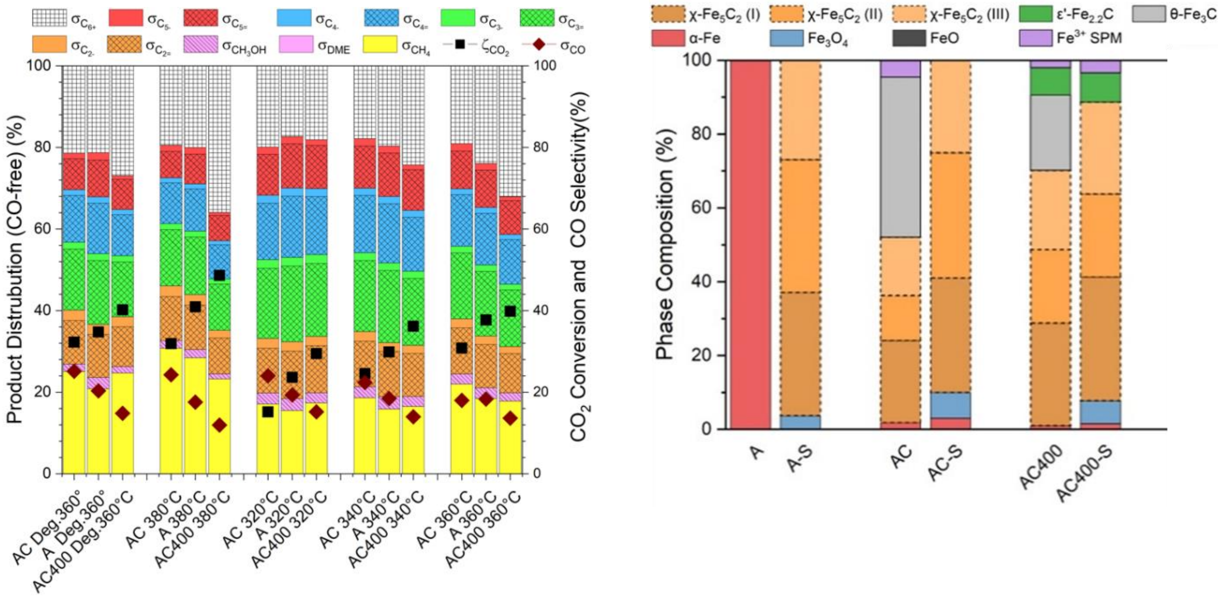

Figure 1 CO_2 conversion and product selectivity at different reaction temperatures (left); phases distribution in fresh and spent (S) samples tested at 360°C (right).

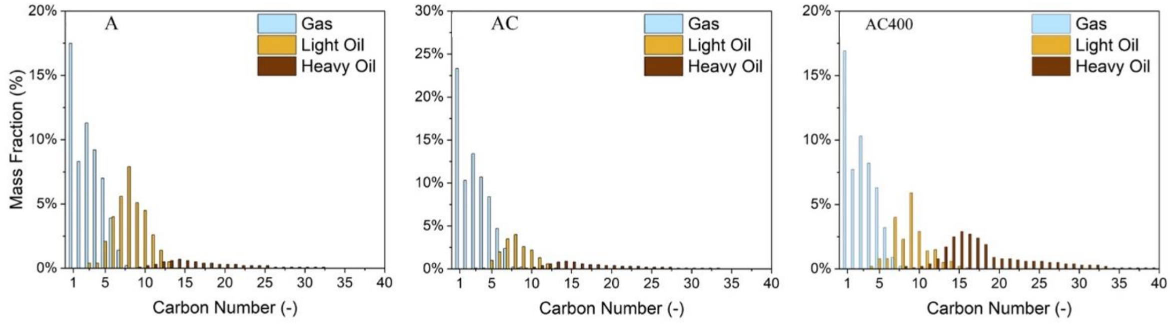

Figure 2 Product distribution subdivided by gaseous, light oil (T_b<150°C) and heavy oil (T_b>150°C).

References

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