Zeolite effect on Fe-based Fischer-Tropsch for e-fuel production

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Introduction. This work is significant in advancing CO_2-modified Fischer-Tropsch synthesis (FTS) by exploring the role of zeolite acidity in influencing Na-Fe_3O_4 catalyst selectivity and product distribution. Combining extensive characterization techniques, including DHA and Mössbauer, with chemometric tools provide a broad understanding of how iron phase composition and zeolite choice impact HCs profiles.

Materials and methods. The Na-Fe_3O_4 catalyst was synthesized and combined with commercial zeolites, then subjected to optimized pre-treatment conditions based on prior work[1]. Catalytic tests were carried out varying the temperature from 340°C to 380°C flowing 7 NL/h/g_{cat} ($H_2/CO_2/N_2$ equal to 15/5/3) at 23 bar. Catalyst and product characterizations were performed using XRD, Mössbauer spectroscopy, and Detailed Hydrocarbon Analysis (DHA) to examine bulk composition, surface properties, and hydrocarbon distributions. Principal Component Analysis (PCA) was applied to the DHA data to reveal correlations between molecular compositions and test conditions, highlighting how different zeolites influence hydrocarbon profiles.

Results and discussion. Two pretreatment methods were evaluated: H_2 activation (pretreatment A) and H_2 activation followed by carburization (CO/H_2) at 400°C (pretreatment AC400). The H_2 activation facilitated the formation of Hägg carbide (χ-Fe_5C_2), producing hydrocarbons mainly in the gasoline range. In contrast, the AC400 pretreatment promoted the formation of ε'-$Fe_{2.2}C$, a more active phase selective for longer-chain hydrocarbons[1]. Both pretreatments were combined with three MFI zeolites with increasing acidity (SiO_2/Al_2O_3 ratios of 23, 80, and 117). The addition of zeolites shifted the oil product distribution from olefin/naphthene-rich to iso-paraffin/aromatic-dominant compositions. DHA identified and quantified over 150 hydrocarbons, clarifying how zeolite acidity influences reaction mechanisms. Chemometric analysis, particularly PCA, identified recurring patterns in hydrocarbon formation associated with different SiO_2/Al_2O_3 ratios. Mössbauer spectroscopy further clarified the influence of zeolites, showing changes in both product distribution and phase transformations during FTS. This study demonstrates the importance of integrating multiple characterization techniques, including detailed analysis of both liquid products and catalyst structures, to provide a comprehensive understanding of CO_2-modified FTS. The synergistic use of DHA, PCA, and Mössbauer spectroscopy offers a novel and thorough approach for optimizing catalysts and reaction pathways in sustainable fuel production.

Keywords: CO_2 Conversion; Fischer-Tropsch; e-fuels; SAF; zeolite

References: [1] A. Tauro, F. Salomone, F. Celoria *et al. Chem. Eng. J.* **2025**, 515, 163154.