Structure–Acidity–Activity Relationships in Multifunctional Fe–Ni Catalysts for Jet-Range Hydrocarbon Production from Model Compound n-Hexadecane

Nikita Šarkov[1*], Mohideen Aliyar Jafeer Shanavas[1], Irina L. Simakova[1], Oryna Shevchuk[1,2], Olha Yevdokimova[1], Päivi Mäki-Arvela[1], Dmitry Yu. Murzin[1]

1 Johan Gadolin Process Chemistry Centre, Faculty of Science and Technology, Abo Akademi University, Henriksgatan 2, Turku 20500 Finland;

2 Chemistry Department, Taras Shevchenko National University of Kyiv, 12 Hetman Pavlo-Skoropadsky Str., Kyiv 01033, Ukraine

**Corresponding author: nikita.sarkov@abo.fi*

Highlights

- FeNi/Beta-38 shows a strong increase in conversion with increasing temperature.
- Total liquid yield on FeNi/Beta-38 decreases from 80.9% at 250 °C to 1.6% at 300 °C.
- FeNi/γ-Al_2O_3 maintains high liquid yields (75–82%) at moderate conversion levels.
- Gas formation increases on the zeolite-supported catalyst at higher temperature.

1. Introduction

The rational design of multifunctional catalysts integrating metallic and acidic active sites is essential for the efficient production of Sustainable Aviation Fuel (SAF) from renewable feedstocks. Achieving selective conversion of long-chain hydrocarbons into jet-range products (C8–C15) requires precise control over the balance between hydrogenation/deoxygenation and cracking functionalities.

To establish clear structure–acidity–activity relationships before upgrading complex microbial oils, n-hexadecane was used as a model compound. Two bimetallic Fe–Ni catalysts supported on materials with different acidity and pore structure microporous zeolite Beta-38 and mesoporous γ-Al_2O_3 - were investigated to evaluate how support acidity influences conversion, liquid yield, and gas formation.

2. Methods

Bimetallic catalysts containing 5 wt.% Fe and 5 wt.% Ni were prepared by wet impregnation on Beta-38 and γ-Al_2O_3 supports. Textural properties were determined by N_2 physisorption, acidity by pyridine adsorption FTIR, and structural characteristics by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

Catalytic experiments were conducted in a stainless-steel tubular fixed-bed reactor operating in continuous co-current down-flow mode. The catalyst (0.3 g) was tested using n-hexadecane at 30 bar total pressure, 15 molar excess of hydrogen, and a liquid flow rate of 0.04 mL min^{-1}. The reaction was conducted under a stepwise temperature program at 250, 275, and 300 °C, followed by a return to 250 °C, with 60 min time-on-stream at each temperature. Liquid products were analyzed by gas chromatography (GC–FID), while gaseous products were monitored online using a micro gas chromatograph (microGC).

3. Results and Discussion

Textural characterization showed clear differences between the catalysts. FeNi/Beta-38 had a high BET surface area (484 m^2 g^{-1}) and significant microporosity (micropore volume 0.171 cm^3 g^{-1}), confirming that the zeolite Beta structure was preserved after metal loading. In contrast, FeNi/γ-Al_2O_3 exhibited a lower surface area (244 m^2 g^{-1}) but a much higher total pore volume (0.79 cm^3 g^{-1}) and larger mesopores (15 nm).

Pyridine-FTIR revealed a high amount of Lewis acid sites (421 µmol g^{-1} at 150 °C) and strong Brønsted acid sites remaining up to 450 °C (103 µmol g^{-1}), confirming the bifunctional nature of the zeolite-supported catalyst. In contrast, FeNi/γ-Al_2O_3 showed much lower acidity, with Lewis and Brønsted acid site concentrations in the range of ~7–21 and ~2–6 μmol g^{-1}, respectively. This difference in acidity contributes to the observed catalytic behavior. The combination of strong acidity and microporous structure promotes enhanced cracking within the zeolite pores.

TEM analysis showed well-dispersed FeNi nanoparticles with an average size of ~4.8 nm for the zeolite-supported catalyst. XRD confirmed preservation of the zeolite Beta framework, with minor hematite reflections and no detectable Ni–Fe alloy phase. For the alumina-supported catalyst, only broad γ-Al_2O_3 reflections were observed, indicating the presence of highly dispersed or amorphous metal species.

Catalytic performance strongly depended on support acidity. FeNi/Beta-38 showed a strong increase in conversion with temperature, approaching complete conversion at 300 °C. However, total liquid yield decreased from 80.9% at 250 °C to 1.6% at 300 °C due to extensive cracking and formation of C_1–C_4 gases. Although strong acidity promoted C–C bond cleavage and formation of lighter hydrocarbons within the jet-fuel range (C8–C15), excessive cracking led to a major loss of liquid products. This behavior is linked to the high acidity and microporous nature of the zeolite support.

In contrast, FeNi/γ-Al_2O_3 showed moderate conversion, reaching 30–33% at 300 °C, while maintaining high liquid yields (75–82%). At this temperature, jet-range hydrocarbons (C9–C15, including isomers) reached 9.7 area% in the liquid, corresponding to an estimated ~7–8% jet-range liquid yield based on the total liquid yield. The wider mesoporous structure and lower acidity of alumina reduce excessive cracking and help preserve the liquid hydrocarbon fraction. Gas formation was lower and consisted mainly of methane, while the liquid phase remained largely dominated by unreacted C16, indicating limited cracking activity under the tested conditions.

4. Conclusions

This study shows that the design of multifunctional Fe–Ni catalysts for SAF precursor production critically depends on support acidity. Strong zeolitic acidity leads to very high conversion but also causes over-cracking, whereas mesoporous alumina maintains high liquid yields at moderate conversion. A balanced combination of metallic and acidic sites is therefore essential for selective production of jet-range hydrocarbons from renewable feedstocks.

Keywords
Hydrocracking; Multifunctional catalysis; Jet-range hydrocarbons; Sustainable aviation fuel.