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Good Thesis Awards

Physical Science Section

Dr. Napaphut Dolsiririttigul

Doctoral Degree Program

Major in Chemical Engineering

KU KASETSART UNIVERSITY

KUChE

Tuning Iron-Based Catalysts for Light Olefin Synthesis via Support Selection and Metal Promoter Interactions

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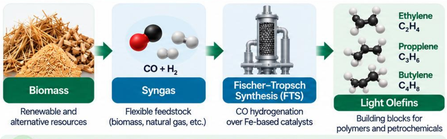
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Abstract

Light olefins are important petrochemical building blocks, and their direct production from syngas provides a promising route for converting carbon-containing feedstocks into value-added chemicals. This work investigated Fe-based catalysts through support selection, Co addition, and H_2/CO ratio optimization, focusing on activity, light-olefin productivity, active-phase formation, and stability. Among SiO_2, TiO_2, and Al_2O_3 supports, FeCo/KAl showed the highest C_2-C_4 olefin space-time yield of 17.2 mmol g_{cat}^{-1} h^{-1} at 360 °C and 20 bar, compared with 11.2 and 0.7 mmol g_{cat}^{-1} h^{-1} for FeCo/KTi and FeCo/KSi. Al_2O_3 promoted Fe dispersion and Fe_5C_2 formation. During 96 h testing, FeCo/KAl remained stable at 360 °C, while severe deactivation occurred at 300 °C due to wax accumulation. Co addition improved Fe reducibility and catalyst stability. An H_2/CO ratio of 3:1 gave the highest light-olefin productivity, reaching 18.1 and 17.3 mmol g_{cat}^{-1} h^{-1} for FeKAl and FeCoKAl, respectively. The results demonstrate that balancing metal support interaction, hydrogen availability, active Fe-carbide formation, and carbon deposition is essential for designing productive and stable Fe-based catalysts for syngas-to-light-olefin synthesis.

MOTIVATION

Why light olefins from syngas?



Light olefins are essential building blocks for polymers and petrochemicals.

Syngas offers a flexible route to hydrocarbons and can be produced from alternative carbon resources.

The key challenge is directing Fischer–Tropsch synthesis toward C_2–C_4 olefins rather than undesired products (e.g., methane, paraffins, oxygenates).

Catalyst design determines where the carbon goes.

RESEARCH OBJECTIVE & STRATEGY

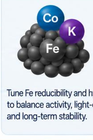
How can Fe-based catalysts be tuned to improve light-olefin productivity while maintaining catalytic stability?

1 SUPPORT SELECTION



Selected support: Al_2O_3

2 CATALYST & REACTION OPTIMIZATION



H_2/CO ratio

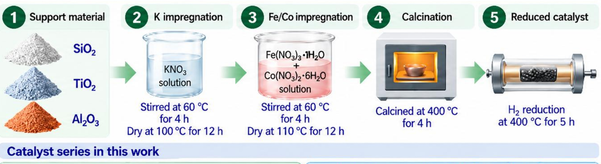
Tune Fe reducibility and hydrogen availability to balance activity, light-olefin formation, and long-term stability.

From support selection to optimized Fe-based catalysts for productive and stable light-olefin synthesis.

EXPERIMENTAL OVERVIEW

Catalyst Preparation & Reaction Testing

Catalyst preparation (two-step impregnation method)

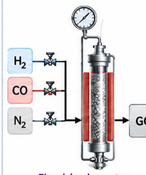


Catalyst series in this work

Part 1: Support selection
FeCo/KSi | FeCo/KTi | FeCo/KAl

Part 2: Co promotion & H_2/CO optimization
FeKAl | FeCoKAl
(H_2/CO = 1:1, 3:1, 5:1, 7:1)

Catalytic testing (fixed-bed reactor)



Fixed-bed reactor (in tubular furnace)

Reaction conditions

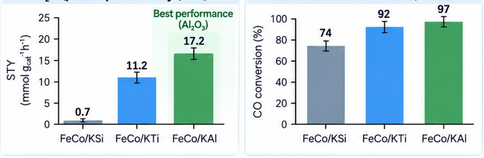
Catalyst	0.5 g (packed in 3/8 in. tube)
Pressure	20 bar
Temperature	300–380 °C
Total flowrate	60 mL min^{-1} (H_2:CO:N_2 = 1:1:X)
H_2-CO ratio	1 – 7
Stability test	up to 96 h

PART 1 — SUPPORT SELECTION

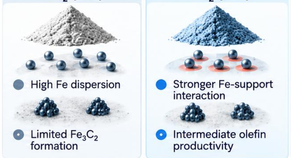
How does the support affect light-olefin production?

Catalytic performance

Reaction conditions: 360 °C, 20 bar



Why does Al_2O_3 perform better?

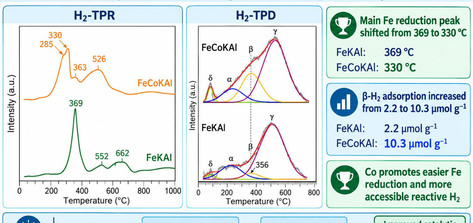


Al_2O_3 showed the highest overall activity and light-olefin productivity.

Support is not merely a carrier — it governs Fe phase evolution and light-olefin productivity.

PART 2 — ROLE OF Co

Co improves Fe reducibility and reactive H_2 availability



Main Fe reduction peak shifted from 369 to 330 °C
FeKAl: 369 °C
FeCoKAl: 330 °C

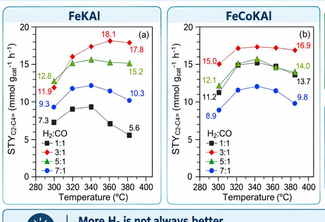
β-H_2 adsorption increased from 2.2 to 10.3 μmol g^{-1}
FeKAl: 2.2 μmol g^{-1}
FeCoKAl: **10.3** μmol g^{-1}

Co promotes easier Fe reduction and more accessible reactive H_2

Co addition → Easier Fe reduction + More reactive H_2 → Improved catalytic environment

PART 2 — EFFECT OF H_2/CO RATIO ON LIGHT-OLEFIN PRODUCTIVITY

Finding the right H_2/CO balance



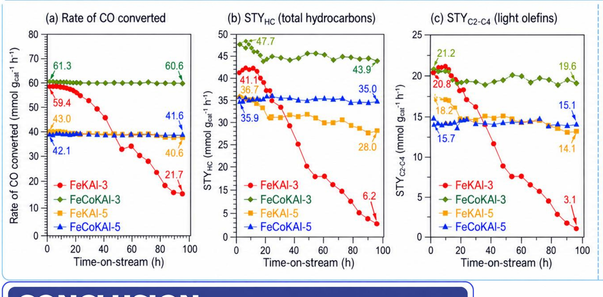
Optimal H_2/CO = 3:1
FeKAl: **18.1** mmol g_{cat}^{-1} h^{-1}
FeCoKAl: **17.3** mmol g_{cat}^{-1} h^{-1}

Co maintained high light-olefin productivity under H_2-lean conditions
FeCoKAl: **15.3** mmol g_{cat}^{-1} h^{-1}
at H_2/CO = **1:1** and **340 °C**

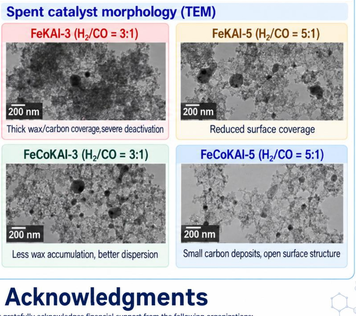
More H_2 is not always better.
A moderate H_2/CO ratio (3:1) provided the best balance for light-olefin production.

Long-Term Stability and Catalyst Deactivation (96 h)

Co addition suppresses wax/carbon deposition and improves stability.



Spent catalyst morphology (TEM)



CONCLUSION

Al_2O_3 was the most favorable support for light-olefin production, giving a C_2–C_4 olefin STY of **17.2 mmol g_{cat}^{-1} h^{-1}** at **360 °C and 20 bar.**

Co promotion improved Fe reducibility and reactive hydrogen availability, lowering the main Fe reduction peak from **369** to **330 °C** and increasing β-H_2 adsorption capacity from **2.2** to **10.3 μmol g^{-1}.**

An **H_2/CO ratio of 3:1** gave the highest light-olefin productivity, reaching **18.1 mmol g_{cat}^{-1} h^{-1}** for FeKAl and **17.3 mmol g_{cat}^{-1} h^{-1}** for FeCoKAl.

Co also improved long-term stability; at H_2/CO = 3:1, the CO-conversion-rate loss decreased from **63.5%** for FeKAl-3 to only **1.1%** for FeCoKAl-3 over 96 h.

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PUBLICATIONS

Chemical Engineering Journal
Dolsiririttigul et al. (2024) 480, 148196

Fuel
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Molecular Catalysis
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Thesis Book File