

CO₂ conversion to light hydrocarbons over K/Fe₂O₃-Al₂O₃ synthesized via the reverse microemulsion method

by

Zixuan Lin

A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

Master of Applied Science

in

Chemical Engineering

Waterloo, Ontario, Canada, 2025

© Zixuan Lin 2025

AUTHOR's DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

The increasing concentration of atmospheric carbon dioxide (CO₂), primarily driven by human activity, has intensified global concerns over climate change. One promising strategy to address this issue is the catalytic conversion of CO₂ into valuable hydrocarbons, offering a sustainable route for emission reduction and fuel production. Potassium-promoted iron-based catalysts were investigated for CO₂ hydrogenation via a modified Fischer–Tropsch (FT) process.

High specific surface area catalysts were synthesized using the reverse microemulsion method, enabling controlled particle size and dispersion. The effects of potassium (K) loading (0–11.3 wt%), active phase, support, H₂:CO₂ feed ratio (1–4), reaction temperature (300–500 °C), pressure (4–12 bar), and GHSV (750–4000 mL/(g_{cat}·h)) were examined. Catalytic performance was evaluated by CO₂ conversion, C₂⁺ hydrocarbon selectivity, and space time yield (STY). Fresh and spent catalysts were characterized using XRD, TPR, BET, TEM, TGA-FTIR, and ICP techniques.

The 7.8%K/Fe₂O₃-Al₂O₃ catalyst exhibited the highest activity, achieving 50% CO₂ conversion, 53% C₂⁺ selectivity, and a STY of 7.72 mmol/(g_{cat}·h) at 11 bar, 1000 mL/(g_{cat}·h), and 400 °C. In contrast, the catalyst without potassium showed significantly lower performance, with 24% conversion, 12% selectivity, and a STY of 0.87 mmol/(g_{cat}·h). The enhanced activity is attributed to the formation of active χ -Fe₅C₂ and Fe₃O₄ phases under reaction conditions, facilitated by the uniform nanoscale morphology of the catalysts synthesized via the reverse microemulsion method.

Acknowledgments

I would like to thank my supervisor, Professor David Simakov, for the continuous support and patient guidance during my program.

I would also like to thank my committee members, Professor Aiping Yu, Professor Hector Budman, for their precious comments and suggestions on my project.

This work would not have been possible without the help and advice from Professor Ali Izadbakhsh, Dr. Yasaman Ghaffarisaeidabad, Dr. Yue Yu, Anik Ashirwadam, Wenxuan Xia, and Maryory Ocana.

I would also like to acknowledge the support of the Waterloo Institute of Sustainable Energy (WISE), the Ontario Centers of Excellence (OCE), the Canada Foundation for Innovation (CFI), and the Natural Science and Engineering Research Council (NSERC).

Finally, but importantly, I would like to thank my dear parents and friends for their support and encouragement.

Table of Contents

AUTHOR's DECLARATION.....	ii
Abstract.....	iii
Acknowledgments.....	iv
List of Figures	vii
List of Tables	x
List of Abbreviations	xi
Chapter 1 Background	1
1.1 Global warming and CO ₂ emission	1
1.2 Project objective	2
1.3 Thesis outline	3
Chapter 2 Literature Review	4
2.1 Reaction pathways for CO ₂	4
2.2 Fischer-Tropsch synthesis	5
2.3 CO ₂ hydrogenation catalysts	7
2.4 Reverse micro-emulsion (RME) method for catalyst preparation.....	9
Chapter 3 Methodology	12
3.1 X-ray powder diffraction (XRD).....	12
3.2 Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES).....	13
3.3 Temperature-programmed reduction (TPR).....	14
3.4 Surface area analysis (SAA).....	15
3.5 Transmission electron microscopy (TEM)	16
3.6 Thermogravimetric analysis (TGA)	16
3.7 IR detector for catalytic performance evaluation	17
3.8 Gas chromatograph (Micro GC).....	18
Chapter 4 Experiment Setup	19
4.1 Catalysts synthesis.....	19
4.2 Catalysts characterization	21
4.3 Flow system setup	22

4.4 Reaction test	23
Chapter 5 CO ₂ Conversion to Light Hydrocarbons over K/Fe ₂ O ₃ -Al ₂ O ₃ Catalyst	25
5.1 Catalyst characterization	25
5.1.1 Chemical composition, morphology, and crystallinity.....	25
5.1.2 Temperature-programmed reduction.....	28
5.1.3 Nanomorphology and elemental distribution at the nanoscale.....	30
5.2 Catalytic performance evaluation.....	32
Chapter 6 Catalyst Composition Modification and Reaction Conditions Optimization for Improving CO ₂ Conversion and Selectivity of Hydrocarbons.....	37
6.1 Effect of catalyst composition	37
6.1.1 Effect of support.....	37
6.1.2 Effect of active phase	39
6.1.3 Effect of promoter	41
6.2 Effect of reaction conditions	44
6.2.1 Effect of feed ratio.....	44
6.2.2 Effect of GHSV	46
6.2.3 Effect of temperature.....	47
6.2.4 Effect of pressure.....	48
Chapter 7 Conclusion and Future Work	50
7.1 Conclusion.....	50
7.2 Future work	52
References.....	54

List of Figures

Figure 1. CO ₂ concentration increment in the atmosphere from 1979 to 2023 [2].	1
Figure 2. a) Structure of a reverse micelle. b) Mechanism of nanoparticle reaction [22].	10
Figure 3. Bragg's law schematic.	12
Figure 4. ICP-OES schematic diagram.	13
Figure 5. Diagram of GC	18
Figure 6. Schematic of RME K/Fe ₂ O ₃ -Al ₂ O ₃ synthesis	19
Figure 7. RME preparation procedure	20
Figure 8. Catalysts preparation procedure	21
Figure 9. A diagram of the flow system setup. Abbreviations: BPR – back pressure regulator, FM – flow meter, FTIR – Fourier transform infrared gas analyzer, GC – gas chromatograph, MFC – mass flow controller, PI – pressure indicator, PRV- pressure release valve, TC – thermocouple, TI – temperature indicator, RH – relative humidity sensor.	23
Figure 10. BET profile of fresh (a) and spent (b) catalysts with different K loadings.	26
Figure 11. XRD patterns of fresh and spent catalysts (a) and spent catalysts only (b). For spent samples, the following reaction conditions were used: T = 300-400 °C, H ₂ /CO ₂ = 4, GHSV = 3,000 mL/(g _{cat} ·h), P = 11 bar, time-on-stream = 50 h.	28
Figure 12. H ₂ -TPR profiles of as-prepared, calcined (a), and spent, after 50 h on stream (b) catalysts, comparing the catalysts with different K loadings.	29
Figure 13. TEM images of fresh RME 7.8%K/Fe ₂ O ₃ -Al ₂ O ₃ catalysts with particle size distribution.	30
Figure 14. TEM images of spent, after 96 h on stream, RME 7.8%K/Fe ₂ O ₃ -Al ₂ O ₃ catalysts with particle size distribution.	31

Figure 15. Catalytic performance evaluation of RME K/Fe ₂ O ₃ -Al ₂ O ₃ shows selectivity to C ₂ + for T = 300-400 °C (a) and C ₂ + space time yield for T = 300-400 °C (b), and selectivity to C ₂ + and C ₂ + space time yield for different K loadings at T = 400 °C (c). Operation conditions: H ₂ /CO ₂ = 4, GHSV = 3,000 mL/(g _{cat} ·h), P = 11 bar.....	33
Figure 16. Catalytic performance evaluation of RME 7.8%K/Fe ₂ O ₃ -Al ₂ O ₃ shows product distribution, CO ₂ conversion (X, squares), and carbon balance (CB, circles) (a) and C ₂ + selectivity and C ₂ + yield (b). Operation conditions: H ₂ /CO ₂ = 4, GHSV = 3,000 mL/(g _{cat} ·h), P = 11 bar.	34
Figure 17. Stability test of the RME 7.8%K/Fe ₂ O ₃ -Al ₂ O ₃ catalyst, showing product distribution, CO ₂ conversion (X, squares) (a), C ₂ + selectivity and STY (b), TGA-FTIR (c), and XRD pattern (d). Operating conditions: T = 400 °C, H ₂ /CO ₂ = 4, GHSV = 3,000 mL/(g _{cat} ·h), P = 11 bar.	36
Figure 18. Catalytic performance evaluation of RME 7.8%K/Fe ₂ O ₃ -32%Al ₂ O ₃ -32%CeO ₂ shows product distribution, CO ₂ conversion, and C ₂ + space time yield. Operation conditions: GHSV = 3,000 mL/(g _{cat} ·h), P = 11 bar.....	38
Figure 19. Catalytic performance evaluation of RME 7.8%K/Fe ₂ O ₃ -3%CuO-Al ₂ O ₃ shows product distribution, CO ₂ conversion, and C ₂ + space time yield. Operation conditions: GHSV = 3,000 mL/(g _{cat} ·h), P = 11 bar.....	39
Figure 20. Catalytic performance evaluation of RME 7.8%K/Fe ₂ O ₃ -11%CoO-Al ₂ O ₃ shows product distribution, CO ₂ conversion, and C ₂ + space time yield. Operation conditions: GHSV = 3,000 mL/(g _{cat} ·h), P = 11 bar.....	41
Figure 21. Catalytic performance evaluation of RME 7.8%Na/Fe ₂ O ₃ -Al ₂ O ₃ shows product distribution, CO ₂ conversion, and C ₂ + space time yield. Operation conditions: GHSV = 3,000 mL/(g _{cat} ·h), P = 11 bar.	42

Figure 22. Catalytic performance evaluation of RME 3%Cu/7.8%K/Fe ₂ O ₃ -Al ₂ O ₃ shows product distribution, CO ₂ conversion, and C ₂ + space time yield. Operation conditions: GHSV = 3,000 mL/(g _{cat} ·h), P = 11 bar.....	43
Figure 23. Catalytic performance evaluation of RME 1%Ru/7.8%K/Fe ₂ O ₃ -32%Al ₂ O ₃ -32%CeO ₂ shows product distribution, CO ₂ conversion, and C ₂ + space time yield. Operation conditions: GHSV = 3,000 mL/(g _{cat} ·h), P = 11 bar.....	44
Figure 24. Catalytic performance evaluation of RME 3.6%K/Fe ₂ O ₃ -Al ₂ O ₃ shows product distribution, CO ₂ conversion, and C ₂ + space time yield. Operation conditions: T = 400 °C, GHSV = 3,000 mL/(g _{cat} ·h), P = 11 bar.....	45
Figure 25. Catalytic performance evaluation of RME 7.8%K/Fe ₂ O ₃ -Al ₂ O ₃ shows product distribution, CO ₂ conversion, and C ₂ + space time yield. Operation conditions: T = 400 °C, H ₂ /CO ₂ = 4, P = 11 bar.	46
Figure 26. Catalytic performance evaluation of RME 7.8%K/Fe ₂ O ₃ -Al ₂ O ₃ shows product distribution, CO ₂ conversion, and C ₂ + space time yield. Operation conditions: GHSV = 1,000 mL/(g _{cat} ·h), H ₂ /CO ₂ = 4, P = 11 bar.....	48
Figure 27. Catalytic performance evaluation of RME 7.8%K/Fe ₂ O ₃ -Al ₂ O ₃ shows product distribution, CO ₂ conversion, and C ₂ + space time yield. Operation conditions: T = 400 °C, GHSV = 1,000 mL/(g _{cat} ·h), H ₂ /CO ₂ = 4.	49

List of Tables

Table 1. Summary of catalysts on direct CO ₂ hydrogenation to hydrocarbons	9
Table 2. Specific surface area (SSA), ICP-measured loading (L), and crystallite size were calculated from XRD patterns (D_{XRD}) for fresh (calcined) and spent (post-reaction) catalysts. For spent samples, the following reaction conditions were used: T = 300-400 °C, H ₂ /CO ₂ = 4, GHSV = 3,000 mL/(g _{cat} ·h), P = 11 bar; total time-on-stream was 50 h.	26

List of Abbreviations

BET	Brunauer–Emmett–Teller
CB	carbon balance, %
CCS	carbon capture and storage
CCU	carbon capture and utilization
D _{SSA}	SSA-based particle size, nm
D _{XRD}	XRD-based particle size, nm
f _i	CO ₂ conversion to species i
FT	Fischer-Tropsch
FTIR	Fourier transform infrared spectroscopy
GHG	greenhouse gas
GHSV	gas hourly space velocity at STP, mL/(g _{cat} ·h)
ICP-OES	inductively coupled plasma with optical emission spectrometry
IR	infrared
L _i	species i loading, wt%
NA	Avogadro constant
P	absolute pressure, bar
RME	reverse microemulsion
RWGS	reverse water gas shift
S _i	selectivity to species i
SSA	specific surface area
STY	space time yield (mol C/(g _{cat} ·h))
T	temperature, °C
TCD	thermal conductivity detector
TEM	transmission electron microscopy
TGA	thermo-gravimetric analysis
TPR	temperature programmed reduction
X _{CO2}	CO ₂ conversion
XRD	X-ray diffraction
Y	yield, %
y _i	mole fraction of species i
ΔH ₂₉₈ [°]	reaction enthalpy, kJ/mol

Greek letters

α	H ₂ :CO ₂ ratio in the feed
θ	diffraction angle, °
λ	X-ray wavelength, nm
ρ_p	particle density, g/cm ³

Chapter 1 Background

1.1 Global warming and CO₂ emission

Climate change poses a significant risk to environmental sustainability and global development, primarily because of the increasing concentrations of greenhouse gases (GHGs) in the air. Among these gases, CO₂ is the primary contributor, mostly emitted through the combustion of fossil fuels, industrial activities, and deforestation. Rising CO₂ levels from around 337 parts per million in 1979 to 419 parts per million in 2023, an increase of more than 20% in 45 years, as shown in **Figure 1**. It has caused a series of negative environmental effects, such as increasing global temperatures, severe weather patterns, and rising sea levels [1] .

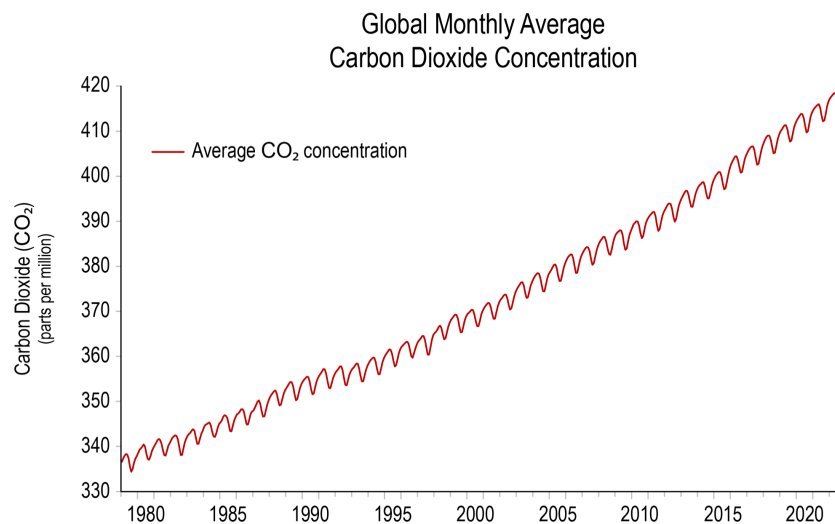


Figure 1. CO₂ concentration increment in the atmosphere from 1979 to 2023 [2].

Therefore, mitigating the impact of CO₂ emissions is critical to achieving climate goals. Carbon capture and storage (CCS) and carbon capture and utilization (CCU) are

key strategies for reducing CO₂ [3]. CCS focuses on capturing CO₂ from industrial or energy sources and storing it in a deep geological formation. CCU is a process to convert CO₂ into valuable products, providing both mitigation and resource recovery. One of the promising CCU routes is the conversion of CO₂ into light hydrocarbons, such as methane, ethylene, and short-chain alkanes. These hydrocarbons are essential feedstocks to produce plastics, chemicals, and fuels [4]. Their synthesis from CO₂ and renewable hydrogen promotes a circular carbon economy. Among the thermal reaction pathways, the Fischer-Tropsch (FT) synthesis stands out because of its ability to convert syngas (CO and H₂) into a wide range of hydrocarbons. When integrated with CO₂ hydrogenation and the reverse water-gas shift (RWGS) reaction, FT synthesis provides a potential approach to convert CO₂ into synthetic fuels and valuable chemicals.

1.2 Project objective

The main goal of this thesis is to investigate CO₂ conversion into light hydrocarbons via the FT synthesis using various catalysts prepared by the reverse micro-emulsion (RME) method. The catalysts need to have a high surface area to provide enough active sites for reaction, high activity, and high selectivity towards C₂+ hydrocarbons. The effect of promoter, active phase, and support on catalytic activity, selectivity, and stability in FT synthesis needs to be examined. The study focuses on the catalyst synthesis and characterization, optimizing reaction conditions, and evaluating performance parameters. This research aims to develop a method for achieving high CO₂ conversion, high selectivity, and yields to hydrocarbons.

1.3 Thesis outline

Chapter 2 provides a review including reaction pathways for CO₂ conversion, Fischer-Tropsch process, catalysts for CO₂ hydrogenation reaction, and preparation of RME catalysts.

Chapters 3 and 4 introduce the methodology of catalyst characterization, which includes X-ray powder diffraction (XRD), inductively coupled plasma optical emission spectroscopy (ICP-OES), temperature-programmed reduction (TPR), surface area analysis (SAA), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), IR detector, gas chromatograph (Micro GC) and the flow system setup for catalytic performance tests.

Chapters 5 and 6 give the results and discuss catalyst characterization, reaction test performance evaluation, catalyst composition modification, and reaction conditions optimization. It explains the structure, composition, and strength of fresh and spent catalysts.

Chapter 7 concludes the presented results and provides potential improvements of the catalysts and possible research directions.

Chapter 2 Literature Review

2.1 Reaction pathways for CO₂

CO₂ is not only the primary greenhouse gas driving climate change but also a plentiful, low-cost C1 feedstock with great potential for conversion into value-added chemicals and fuels. Over the past decades, a variety of strategies have arisen for CO₂ conversion:

1. Thermochemical routes: depend on high temperatures (usually between 300–1000 °C) and sometimes elevated pressures to drive the conversion of CO₂ into CO, CH₄, or hydrocarbons. The most common thermochemical reactions include the reverse water-gas shift (RWGS) reaction, methanation, and dry reforming of methane (DRM). While industrially mature, these processes are energy-intensive and require a significant supply of H₂ [5].

2. Photochemical and photocatalytic systems use semiconductor catalysts (e.g., TiO₂, perovskites, carbon nitrides) to reduce CO₂ under mild conditions, producing CO, formate, or methanol. However, these systems are now facing problems such as low conversion rates, poor product selectivity, and catalyst stability [6].

3. Electrochemical reduction: uses renewable electricity in ambient conditions. Silver and gold electrodes favor CO, while copper produces multi-carbon compounds (e.g., ethylene and ethanol). Major challenges include high overpotentials, low selectivity, and insufficient catalyst durability [7].

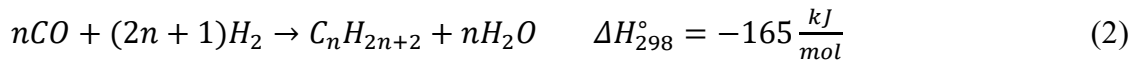
4. Biological and hybrid bio-inspired techniques: use enzymes (e.g., CO dehydrogenase) or whole cells to convert CO₂ in ambient conditions with high selectivity. However, enzyme stability and cofactor regeneration are still required for research [8].

Among the various CO₂ conversion strategies, thermocatalytic pathways stand out because of their ability to scale up and to produce a wide range of sustainable fuels and chemicals. These pathways are based on well-established industrial processes such as RWGS and FT reaction, which offer high reaction rates. Different hydrocarbons can be produced by adjusting the catalyst composition and operating conditions. Additionally, the process can achieve net-zero or even carbon-negative emissions by using renewable hydrogen. Thermocatalytic systems have advantages in being less sensitive to feedstock impurities, durable catalysts, and potential for heat integration, which enhances the overall efficiency.

2.2 Fischer-Tropsch synthesis

The reaction sequence begins with the conversion of CO₂ to CO through the RWGS reaction eq. (1). The resulting CO then adsorbs onto the catalyst surface, where it undergoes the FT reaction eq. (2), converting syngas (CO and H₂) into hydrocarbons. This process plays a key role in producing synthetic fuels and other valuable chemicals. A major challenge is to design catalysts that produce long-chain hydrocarbons while minimizing methane production. During FT synthesis, adsorbed CO dissociates on the catalyst surface into C and O fragments. The C atoms couple to form growing CH₂-rich

chains, which are subsequently hydrogenated and desorbed as hydrocarbons [9]. By tailoring catalyst composition [10], support materials, particle size, and reaction parameters (temperature, pressure, H₂/CO₂ ratio, GHSV), the reaction can be optimized to yield fuels, light olefins, waxes, and more. The CO₂ hydrocarbons pathway, powered by renewable H₂ and captured CO₂, offers a promising solution for sustainable fuel and chemical production.



The CO₂ hydrogenation is always accompanied by other side reactions [11]. The Sabatier reaction eq. (3), the methanation of CO eq. (4), and methanol production eq. (5). The selectivity of each reaction is highly dependent on the catalyst type and the support materials. CO₂ will be adsorbed on the catalyst's surface differently, leading to various intermediates and reaction pathways. Eqs. (6) and (7) explain why carbon deposition forms during catalyst degradation, which will block the pores on the surface and decrease the surface area, which is related to the activity of the catalysts. However,

the fouling catalysts caused by carbon can be regenerated by combustion and oxidation under suitable conditions.

2.3 CO₂ hydrogenation catalysts

The thermocatalytic conversion of CO₂ to light hydrocarbons (C₂-C₄) typically proceeds through a two-step route involving the RWGS reaction followed by FT synthesis. Efficient catalyst design is critical to steer product distribution toward light hydrocarbons while minimizing undesired CH₄ formation.

Among the most extensively studied are iron-based catalysts, which are known for their dual activity in RWGS and FT reactions, cost-effectiveness, and tolerance to water produced during the reaction. In CO₂ hydrogenation over Fe-based catalysts, the Fe₃O₄ phase catalyzes the RWGS reaction, and the Hägg iron carbide (χ -Fe₅C₂) phase provides active sites for CO hydrogenation and chain-growth [12]. Al₂O₃ is a commonly used support because of its high surface area, mechanical strength, and ability to influence iron dispersion and reducibility, and subsequently affect hydrocarbon selectivity during CO₂ hydrogenation [13].

Iron catalysts are often promoted with potassium, copper, or manganese to enhance CO₂ activation and hydrocarbon chain growth. Alkali metals like potassium can increase the basicity of the catalyst surface, enhance CO₂ adsorption, and suppress methane selectivity, promoting olefin formation [14]. The addition of sodium enhances the adsorption of CO₂, facilitates the formation and stability of active species Fe₅C₂, increasing CO₂ conversion and alkenes selectivity [15].

The integration of bifunctional catalysts that combine metal sites with acidic supports further improves product distribution. The addition of potassium to the Fe-Cu catalyst was also effective in improving the selectivity for C₂⁺ hydrocarbons. XPS results showed that the addition of potassium to the Fe and Fe-Cu catalysts modified the electronic structure of each surface component, thereby increasing the carbon coverage of the catalyst surface, which served as a carbon source for chain growth [16]. In Fe-Co/K-Al₂O₃ systems, potassium not only promotes iron carburization but also alters surface basicity, suppressing over-hydrogenation of olefins and enhancing selectivity toward light C₂-C₄ olefins [17]. The proximity of RWGS active metal sites and FT selective phases is essential to ensure sequential conversion and control over hydrocarbon chain growth. **Table 1** provides a summary of catalysts on direct CO₂ hydrogenation to hydrocarbons under various reaction conditions such as temperature, pressure, feed ratio, and GHSV, underlining their capability to convert CO₂ and their affinity towards hydrocarbons formation.

Control over catalyst morphology is critically important in catalytic performance. Among the key morphological parameters, particle size plays a significant role in influencing the reaction rate. Effective catalysts should exhibit high activity, stability, and good selectivity toward C₂⁺ hydrocarbons. The performance of thermocatalysts is strongly dependent on particle size, dispersibility, and surface area. A high surface area provides a greater number of active sites, thereby enhancing the overall reaction rate. Since smaller particles typically offer a higher surface area per unit mass, reducing particle size remains a primary objective in designing efficient catalysts.

Table 1. Summary of catalysts on direct CO₂ hydrogenation to hydrocarbons

Catalyst	GHSV, ml/(g h)	H ₂ /CO ₂	P, bar	T, °C	X(CO ₂), %	S(CO), %	S(C ₂ +), %	Hydrocarbon distribution, %			Ref
								C1	C2-C4	C5+	
15%Co- 6%K/Al ₂ O ₃	1200	3	5	300	42.3	8.2	24.2	73.6	24.3	2.1	[18]
15%Co- 8%K/Al ₂ O ₃	1200	3	5	300	12.2	33.5	50.6	23.9	76.1	0.0	
8.7%K-57.7%Fe- 7.5%Cu/Al ₂ O ₃	5000	3	25	300	37.0	9.5	80.0	13.6	33.9	52.5	[16]
8.7%K-2.6%Co- 12.4%Fe/Al ₂ O ₃	3600	3	11	300	31.0	18.0	69.0	15.9	84.1	-	[19]
2.6%K-2.8%Cu- 12.2%Fe/Al ₂ O ₃	3600	3	11	300	31.4	16.0	69.0	17.9	82.1	-	[20]
2.21%K- 7.46%Fe/4.18%La -Al ₂ O ₃	2000	3	10	300	24.5	37.5	55.1	11.8	30.3	57.9	[21]
2.21%K- 7.73%Fe/4.35%Ce -Al ₂ O ₃	2000	3	10	300	21.0	34.2	58.6	11.0	28.4	60.6	
2.22%K- 7.77%Fe/5.84%Y- Al ₂ O ₃	2000	3	10	300	22.7	40.6	53.2	10.4	29.8	59.8	
7.8%K/27.9%Fe- Al ₂ O ₃	1000	4	11	400	50.0	22.5	53.1	47.0	43.0	10.0	this work

2.4 Reverse micro-emulsion (RME) method for catalyst preparation

The RME method [22] is an advanced and widely used technique for synthesizing nanostructured catalysts, especially metallic and metal oxide nanoparticles. This

method is based on the formation of reverse (water-in-oil) micro-emulsions (**Figure 2**), which are thermodynamically stable. The system contains isotropic mixtures composed of water, oil, and surfactant. Nanoscale water droplets are scattered across a continuous nonpolar oil phase and stabilized by surfactant molecules that form a protective monolayer at the water–oil interface. These droplets, also known as reverse micelles, function as nanoreactors that allow chemical reactions to be contained inside a small spatial area, providing precise control over particle nucleation and growth.

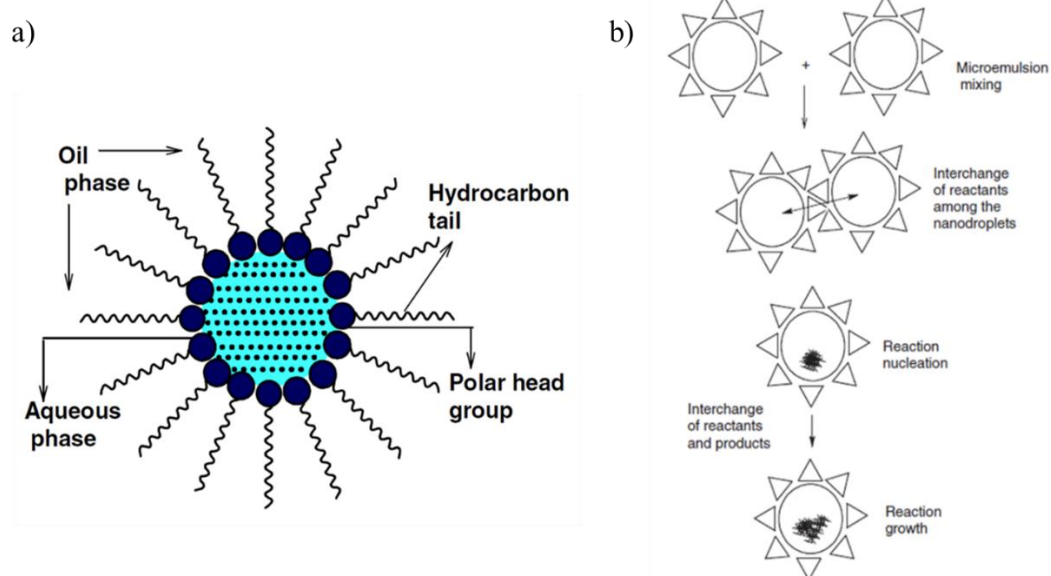


Figure 2. a) Structure of a reverse micelle. b) Mechanism of nanoparticle reaction [22].

The catalyst synthesis via the RME method involves the preparation of three separate reverse micro-emulsions. One contains the aqueous solution of the metal precursor (e.g., metal salts), the other contains the support material (e.g., aluminum oxide), and the third consists of a reducing or precipitating agent (e.g., sodium hydroxide or ammonium hydroxide). When these emulsions are mixed, dynamic interactions between the micelles lead to transient fusion and exchange of contents. As

a result, the reagents from each micelle come into contact within the confined aqueous cores, causing the reaction. This spatial restriction avoids excessive particle growth and agglomeration, resulting in uniform nanoparticle size formation and morphology.

After nanoparticle formation, the product is separated from the micro-emulsion system. This is achieved by destabilizing the emulsion with a polar solvent such as ethanol or water. The resulting precipitate is then collected via centrifugation, thoroughly washed to remove surfactants and residual organic compounds, before being dried. The final product is a dry nanoparticulate catalyst with a high surface area and narrow particle size distribution.

The RME method has several advantages for catalyst preparation. These include the ability to finely tune particle size and shape, achieve good dispersion of active phases, and high surface areas with uniform active sites. However, the method also has limitations [23], especially require a large amount of organic solvents and surfactants, which can cause environmental and economic issues. Additionally, removing surfactants from the final product requires extensive washing and thermal treatment. Despite these drawbacks, the RME method is a powerful technique in the field of nano catalyst synthesis, particularly when uniformity and size control are critical parameters.

Chapter 3 Methodology

3.1 X-ray powder diffraction (XRD)

X-ray powder diffraction (XRD) is a versatile non-destructive analytical technique used to analyze physical properties such as phase composition, crystal structure of solid materials. XRD works by irradiating a material with incident X-rays and then measuring the intensities and scattering angles of the X-rays that leave the material, as shown in **Figure 3**.

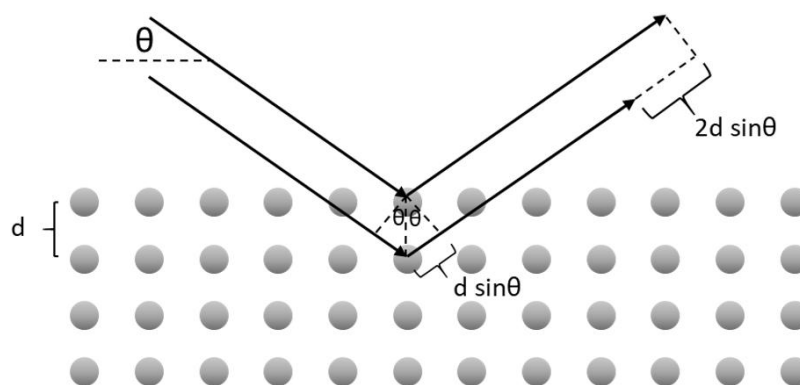


Figure 3. Bragg's law schematic.

In Bragg's law [24], $2d\sin\theta = n\lambda$ is a fundamental concept in understanding XRD. In this equation, λ is the wavelength of the X-ray, n is any positive integer, d is the plane spacing, and θ is the angle of the X-ray beam with respect to these planes. Rigaku MiniFlex II was used to obtain XRD patterns, which were then analyzed with Bruker EVA software. This diffraction pattern is a chemical fingerprint, and it can be used to identify chemicals by comparing it to a database of previously known patterns. The size

of the crystal grains was determined by utilizing the Scherrer equation in the Bruker EVA software, eq (8).

$$D_{XRD} = \frac{K\lambda}{\beta \cos \theta} \quad (8)$$

3.2 Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES)

ICP-OES is an analytical technique used to quantify the concentration of specific elements within a sample. It works on the principle that atoms and ions can absorb energy to move electrons from the ground state to an excited state. When an electron returns to its original or a lower energy level, it emits light of a specific wavelength. The wavelength of the emitted light depends on the type of atom or ion, and the energy levels the electron is moving between. The amount of light released at each wavelength is proportional to the number of atoms or ions making the transition [25].

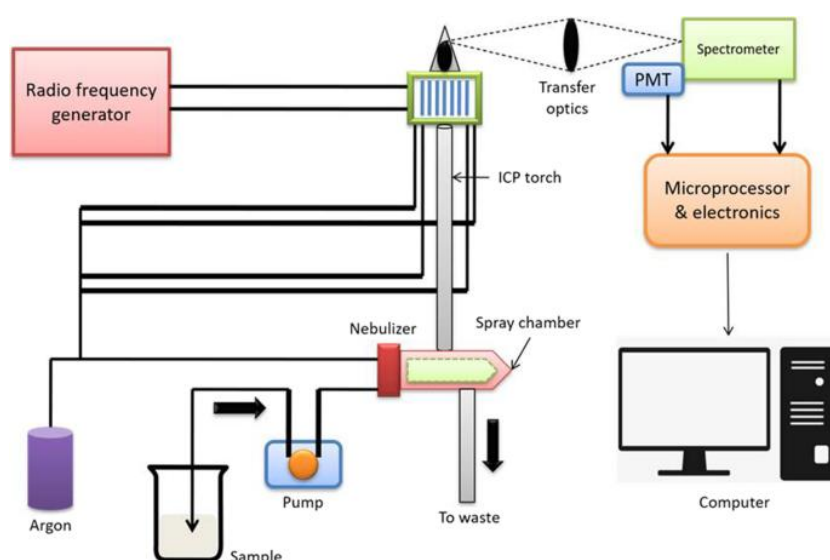


Figure 4. ICP-OES schematic diagram.

3.3 Temperature-programmed reduction (TPR)

Temperature-programmed reduction (TPR) is a material characterization process commonly used in catalysis studies. It examines the surface chemistry of metals and metal oxides under varying thermal conditions. TPR can acquire quantitative and qualitative data relating to the reducing gas mixtures that are made to flow over metallic samples. This process provides accurate insights into catalyst reducibility and reaction rates in the presence of metal surfaces.

In a TPR experiment, a fixed amount of metal catalyst is placed in a fixed-bed reactor. A reducing gas (10% H₂ in Argon) is passed through the catalyst at a controlled flow rate while the reactor is heated at a defined ramping rate. As the temperature increases, the metal oxides on the catalyst begin to reduce at specific temperatures. Since the flow rate of the reducing gas remains constant, any change in hydrogen concentration after passing through the catalyst bed is directly proportional to the extent of reduction [26].

This change in hydrogen concentration is continuously monitored by a thermal conductivity detector (TCD), and the resulting signal is recorded to produce a TPR curve. Each peak in the curve generally corresponds to a distinct reducible species or oxidation state within the catalyst, and the integrated area under each peak is proportional to the amount of hydrogen consumed.

3.4 Surface area analysis (SAA)

The Brunauer–Emmett–Teller (BET) theory [27] describes the physical adsorption of gas molecules on a solid surface and is widely used to determine the specific surface area of materials. In this study, the sample is cooled using a coolant (liquid nitrogen) while an adsorbate gas (10% N₂ in Helium) is introduced. As the gas adsorbs onto the sample surface, the concentration of the adsorbate in the gas mixture decreases, which is detected as a peak in the TCD signal.

When adsorption reaches equilibrium, the concentration of adsorbate in the gas stream stabilizes, and the TCD signal returns to its baseline. Cooling is then stopped by lowering the Dewar flask. The adsorbate begins to desorb from the sample surface. This causes a temporary increase in the concentration of the adsorbate in the gas mixture, leading to another peak in the TCD signal. After desorption is complete, the TCD signal returns to baseline. Since the desorption peak is typically sharper and more distinct, it is generally preferred for accurate integration and calculation of surface area.

The BET model is represented by eq. (9), where p is the equilibrium pressure of the adsorbate gas, p_0 is the saturated vapor pressure of the adsorbed gas at the measurement temperature, V is the volume of gas absorbed at pressure p , V_m is the volume of gas required to form a monolayer on the surface, C is a constant.

By measuring a series of p and V , $p/V(p_0-p)$ is plotted against p/p_0 plot, and a straight line can be obtained. The slope of the line is $(C-1)/V_m C$, and the intercept is $1/V_m C$, so that V_m and constant C can be calculated. Using the surface area equation,

eq. (10), the specific surface area can be obtained. Where NA is the Avogadro constant, s is the adsorption cross-sectional area of the adsorbed species, V_m^{STP} is the molar volume of gas at standard temperature and pressure (typically 22,414 mL/mol), and a is the quality of the adsorbent material.

$$\frac{P}{V(p_0-p)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \times \frac{p}{p_0} \quad (9)$$

$$S_{BET} = \frac{(V_m N_A s)}{V_m^{STP} a} \quad (10)$$

3.5 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a powerful imaging and analytical technique used to visualize the internal structure of materials at atomic resolution. It enables detailed analysis of composition, morphology, and structure at the nanoscale. TEM operates by transmitting a high-energy electron beam through a thin sample (less than 50 nm thick) to produce high-resolution images. Due to their extremely short wavelengths, electrons can resolve fine structural features that are beyond the capabilities of light-based microscopy. The interaction of transmitted and scattered electrons with the sample generates detailed images that reveal both structural and compositional information at the atomic level [28].

3.6 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) measures changes in a material's weight, either loss or gain, and the rate of that change as a function of temperature and time. It provides valuable insights into various material properties, including thermal and

oxidative stability, the composition of multi-component systems, estimated product lifetimes, decomposition kinetics, moisture and volatile content, and residual matter after analysis. Weight loss observed during TGA can result from decomposition (chemical bond breaking), evaporation (loss of volatiles at high temperatures), reduction (reaction with reducing atmospheres such as hydrogen or ammonia), or desorption (release of surface-bound species). Conversely, weight gain may occur due to oxidation (reaction with oxidizing atmospheres) or absorption (uptake of gases or vapors). All these transformations are kinetic processes, meaning they occur at rates influenced by the specific conditions of the analysis [29].

In this study, air is used as the reaction gas in TGA. The system was heated up slowly from 25 °C to 800 °C, and the weight change alongside temperature was recorded. The outline of TGA is connected to FTIR, which measures the off gases. The weight decrease in this study mainly represents desorption of the water or CO₂ on the surface and the oxidation of the deposited carbon during the reaction. The coking degree of our catalysts after reaction can be analyzed.

3.7 IR detector for catalytic performance evaluation

An IR analyzer is used to measure the outlet stream of the reactor continuously. The detector consists of a source of infrared light, an optical filter to select the proper wavelength, and an optical infrared receiver. As the gas flows into the space between the source and receiver, the target gas absorbs some of the infrared energy. The receiver detects this drop in received energy as a measure of the gas concentration. The

adsorption of CO_2 , CH_4 , and CO in the stream was measured at the same time and processed into a digital signal for display [30].

3.8 Gas chromatograph (Micro GC)

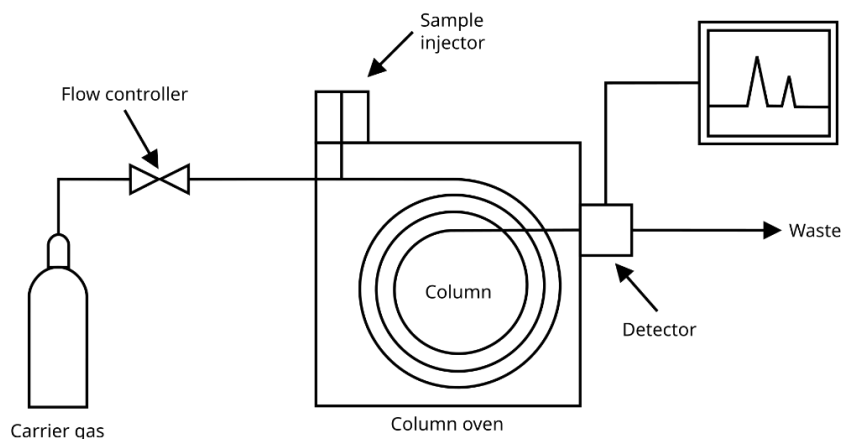


Figure 5. Diagram of GC

A gas chromatograph (GC) is a powerful analytical technique used to separate and analyze compounds that can be vaporized without decomposition. GC operates on the principle of partitioning compounds between a stationary phase and a mobile gas phase. The sample is vaporized and carried by Helium, an inert gas (the mobile phase), through a column containing the stationary phase. Components exit the column at different rates, resulting in a Gaussian-shaped distribution peak [31].

Chapter 4 Experiment Setup

4.1 Catalysts synthesis

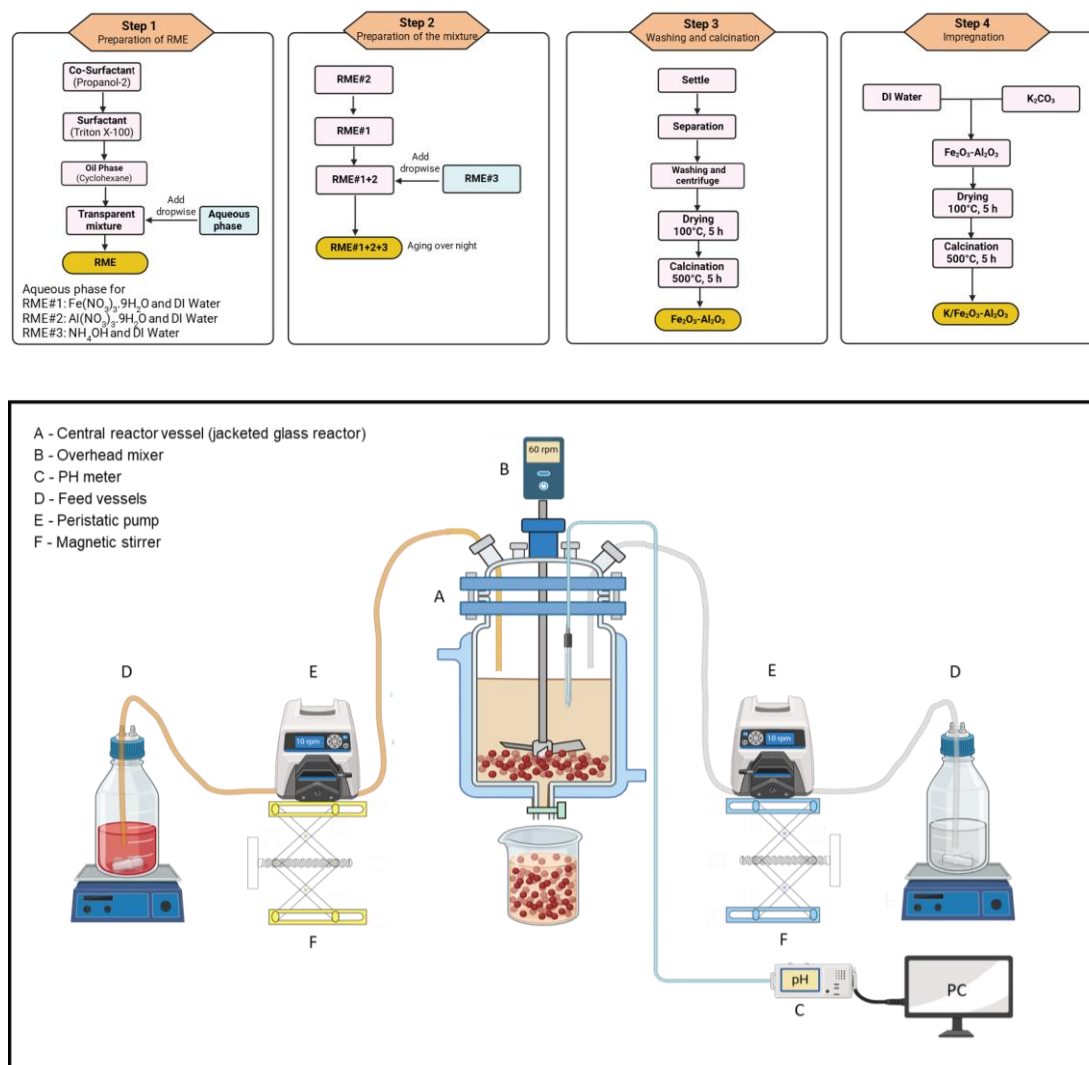


Figure 6. Schematic of RME $\text{K/Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ synthesis

Three RMEs containing ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sigma-Aldrich) and aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Fisher Scientific), and ammonium hydroxide solution (NH_4OH , LabChem Inc.) were prepared to synthesize $\gamma\text{-Al}_2\text{O}_3$ -supported Fe catalyst. Target loading was 30 wt% Fe in $\gamma\text{-Al}_2\text{O}_3$. RMEs were made by mixing aqueous phase (DI water), surfactant (Triton X-100, Acros Organics), co-surfactant

(propanol-2, Sigma-Aldrich), and oil phase (cyclohexane, Sigma-Aldrich) in the volumetric ratio of 1.5:1:4.5:3.5. The prepared RMEs were mixed in the sequence illustrated in **Figure 6**. Briefly, RME #1 ferric nitrate RME was added into RME #2 aluminum nitrate RME dropwise using a peristaltic pump and mixed for 30 minutes. RME #3 NH_4OH RME (acting as a precipitation agent) was added dropwise immediately to prevent the precipitation of large particles caused by phase separation with pH monitoring. The resulting mixture was mixed using a stirrer in a 2L reactor overnight, and then the precipitate was settled for easy separation, as shown in **Figure 7**.

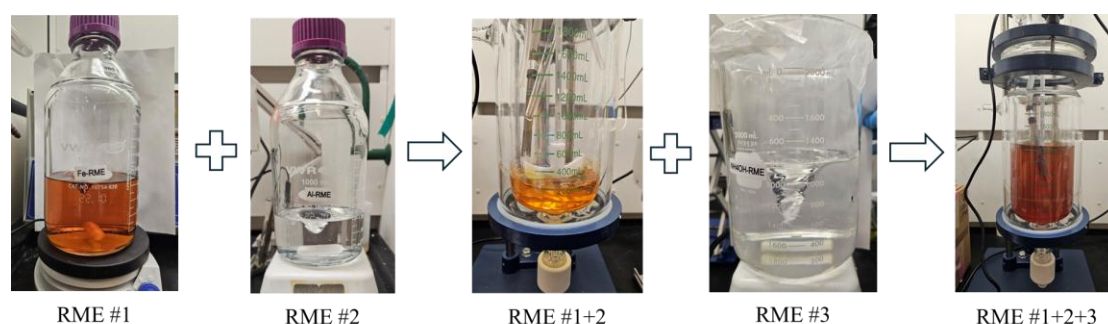


Figure 7. RME preparation procedure

The upper phase was taken out using a peristaltic pump. The resulting gel-like precipitate was washed in the 2L reactor and separated by centrifugation with subsequent washing by a mixture of ethanol and deionized water (2:1). This centrifugation/washing procedure was repeated 4 times until no oil phase was observed. The washed precipitate was collected and dried overnight at 100 °C. After that, the precipitate was first calcined at 500 °C for 5 h under air flow. The 5 grams of catalyst were split into 5 portions, and K with different concentrations (0-11.3 wt%) was

subsequently added by wet impregnation using a diluted K_2CO_3 solution (0.13 mol/L) as an impregnation medium. After that, the precipitate was second dried and calcined at 500 °C for 5 h under air flow, as shown in **Figure 8**. To prepare for the reaction, the powder catalysts were pelletized and sieved into 250-425 μm pellets. The synthesized catalyst was denoted as RME K/ Fe_2O_3 - Al_2O_3 .

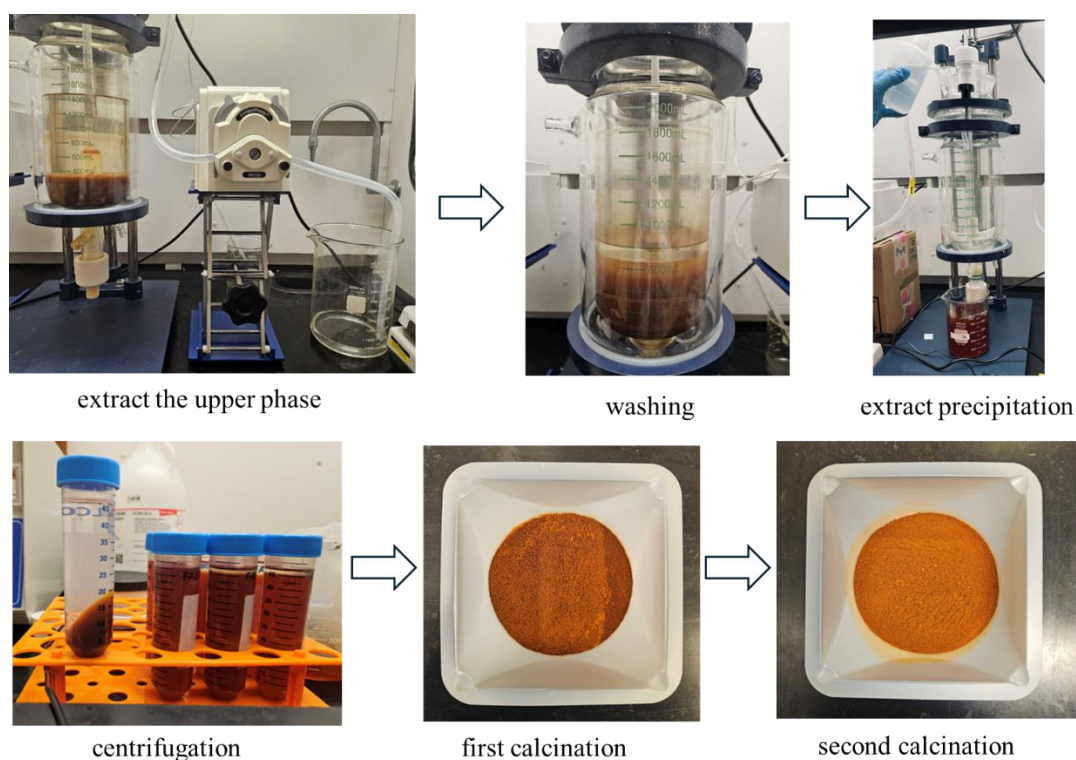


Figure 8. Catalysts preparation procedure

4.2 Catalysts characterization

X-ray diffraction (XRD) was performed using a Rigaku Miniflex II, and the resulting patterns were analyzed using Bruker EVA. The metal loadings were measured using inductively coupled plasma optical emission spectrometry (ICP-OES) (Prodigy SPEC, Leeman Labs Inc). Transmission electron microscopy (TEM) images were

obtained from a JEOL F200 STEM high-resolution transmission electron microscope. Specific surface area (SSA) measurements (single point BET measurement by the flow adsorption technique) and H₂ temperature-programmed reduction (TPR) were carried out using a catalyst characterization equipment (AMI-300Lite, Altamira Instruments) outfitted with a thermal conductivity detector. Thermal gravimetric analysis (TGA) was carried out using TGA 55 (TA Instruments), and ca. 15 mg of catalysts was heated in 60 mL/min air from 25-800 °C with ramping rate of 10 °C/min, with the output line linked to an FTIR analyzer (MultiGasTM 2030, MKS Instruments) for off-gas analysis.

4.3 Flow system setup

The flow system for reaction tests is shown in **Figure 9**. The system includes mass flow controllers of CO₂, H₂, and N₂, a temperature-programmable furnace, a cooling coil, a mist trap, back-pressure regulators, silica gel columns, an IR gas analyzer (IR-208, infrared industries Inc.), a gas chromatograph (Micro GC, Inficon Inc.), and an FTIR gas analyzer (MultiGasTM 2030, MKS Instruments). The Micro GC instrument was used for quantitative analysis of carbonaceous species, while the IR and FTIR gas analyzer were used for dynamic monitoring and steady state verification. A 1/4"-1/2" fixed-bed stainless steel reactor containing 1 gram of pelletized catalyst was used to evaluate the catalytic performance.

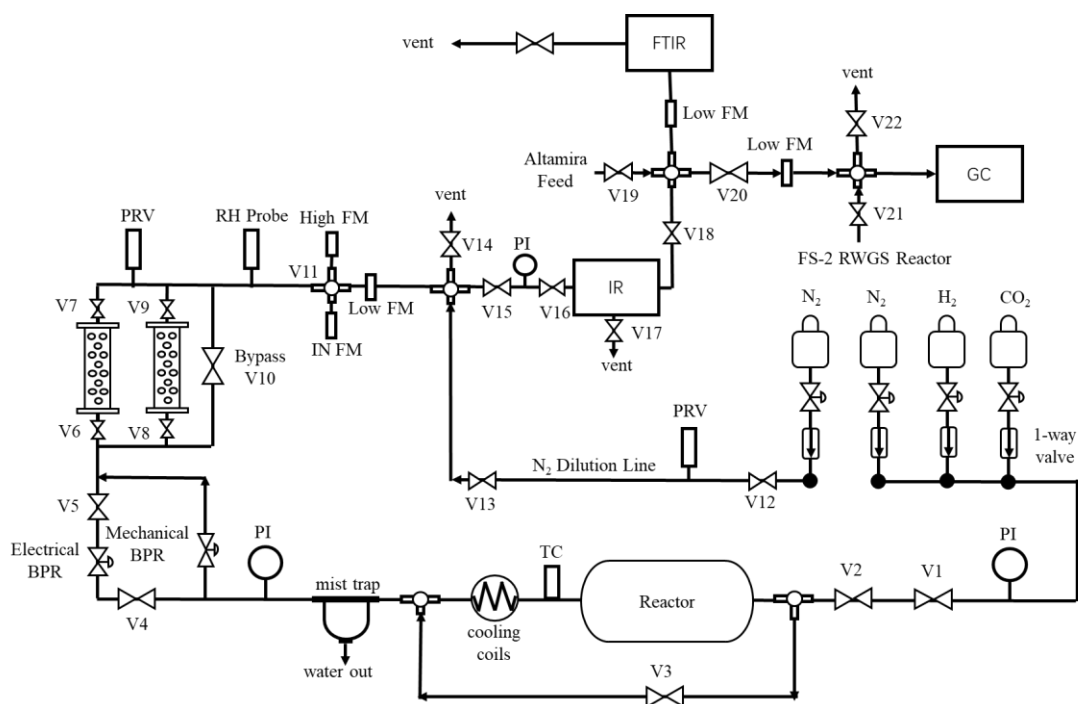


Figure 9. A diagram of the flow system setup. Abbreviations: BPR – back pressure regulator, FM – flow meter, FTIR – Fourier transform infrared gas analyzer, GC – gas chromatograph, MFC – mass flow controller, PI – pressure indicator, PRV- pressure release valve, TC – thermocouple, TI – temperature indicator, RH – relative humidity sensor.

4.4 Reaction test

Before reaction tests, all catalysts were reduced under pure H₂ flow (200 mL/min) at 400 °C overnight at atmospheric pressure. After reduction, the feed stream was switched to H₂ and CO₂ at a ratio of 4:1. The pressure was increased and maintained at 11 bar for catalytic performance evaluation at a constant space velocity of 3,000 mL h⁻¹ g_{cat}⁻¹. The feed stream was introduced into the reactor after a baseline was obtained by bypassing the reactor. When the reaction conditions were changed stepwise, the step duration was at least 3 h for each step to allow for complete stabilization (as confirmed

by continuous monitoring of the FTIR signals of CO₂ and reaction products). The concentration of products was taken from the GC. GHSV and V_m represent gas hour space velocity and molar volume of gas at room temperature and atmospheric pressure (24.0 L), respectively. CO₂ conversion, selectivity to C₂+, and space time yield (STY) were calculated according to the following equations (y_{CO} , y_{CO_2} , y_{CH_4} are mole fractions on dry basis, i.e., after removal of the condensate from the outlet stream):

$$X_{CO_2} = \frac{y_{CH_4} + y_{CO} + \sum x \cdot y_{C_xH_y}}{y_{CO_2} + y_{CH_4} + y_{CO} + \sum x \cdot y_{C_xH_y}} \quad (11)$$

$$S_{C_xH_y} = \frac{\sum x \cdot y_{C_xH_y}}{y_{CH_4} + y_{CO} + \sum x \cdot y_{C_xH_y}} \quad (12)$$

$$STY = \frac{X_{CO_2} \cdot S_{C_2+} \cdot GHSV}{V_m \times (\alpha + 1)} \quad (13)$$

Carbon balance (CB) was calculated by the following equation (α and f are H₂: CO₂ feed ratio and conversion to corresponding products, respectively).

$$CB = (y_{CO_2} + y_{CO} + y_{CH_4} + \sum x \cdot y_{C_xH_y}) \cdot \left(1 + \alpha - f_{CO} - 4f_{CH_4} - \sum \frac{4x+y}{2x} \cdot f_{C_xH_y}\right) \quad (14)$$

Carbon balance was continuously monitored in all experiments.

Chapter 5 CO₂ Conversion to Light Hydrocarbons over K/Fe₂O₃-Al₂O₃ Catalyst

5.1 Catalyst characterization

5.1.1 Chemical composition, morphology, and crystallinity

Fresh (calcined) and spent (post-reaction) catalysts were characterized via ICP-OES and XRD to investigate elemental composition and crystallinity. Elemental composition analysis showed Fe loadings in the 27-29.8 wt% range (**Table 1**), with an average value of 28.3 ± 1.3 wt%, i.e., 4.59% standard deviation. The target loading was 30 wt% Fe/Al₂O₃. K loadings were 0-11.3 wt%. The target values were 0-12.3 wt%.

SSA values of as-prepared catalysts (after calcination) are listed in **Table 1** (a typical standard deviation between repeated measurements was less than 8 m²/g). Fe₂O₃-Al₂O₃ has the highest SSA value (301.4 m²/g), which emphasizes the RME method's advantage in synthesizing high surface area materials. The SSA values of Fe₂O₃-Al₂O₃ decreased with the increase in K amount. The addition of K changes the distribution of iron oxide on the catalyst surface. It specifically impacts iron dispersion, which is critical for maintaining a large surface area. A reduced effective surface area for catalytic activity may arise from a more clustered arrangement of iron species [32, 33]. For spent catalysts after 50 h on stream, there was a significant reduction of SSA as shown in **Figure 10**, probably attributed to sintering.

Table 2. Specific surface area (SSA), ICP-measured loading (L), and crystallite size were calculated from XRD patterns (D_{XRD}) for fresh (calcined) and spent (post-reaction) catalysts. For spent samples, the following reaction conditions were used: $T = 300$ - 400 °C, $\text{H}_2/\text{CO}_2 = 4$, $\text{GHSV} = 3,000 \text{ mL}/(\text{g}_{\text{cat}}\cdot\text{h})$, $P = 11 \text{ bar}$; total time-on-stream was 50 h.

Target, wt%		L, wt%		SSA, m^2/g		D_{XRD} , nm (spent)		
K	Fe_2O_3	K	Fe_2O_3	fresh	spent	Al_2O_3	Fe_3O_4	Fe_5C_2
0	30.0	0	29.8	301.4	223.4	6.1	16.4	*
3.4	29.0	3.6	28.8	299.7	242.5	7.0	20.5	31.0
6.5	28.1	6.2	28.0	274.8	188.6	---	---	---
9.5	27.2	7.8	27.9	156.8	167.8	5.3	13.0	29.7
12.3	26.3	11.3	27.0	161.2	88.1	---	---	---

*no carbide formation

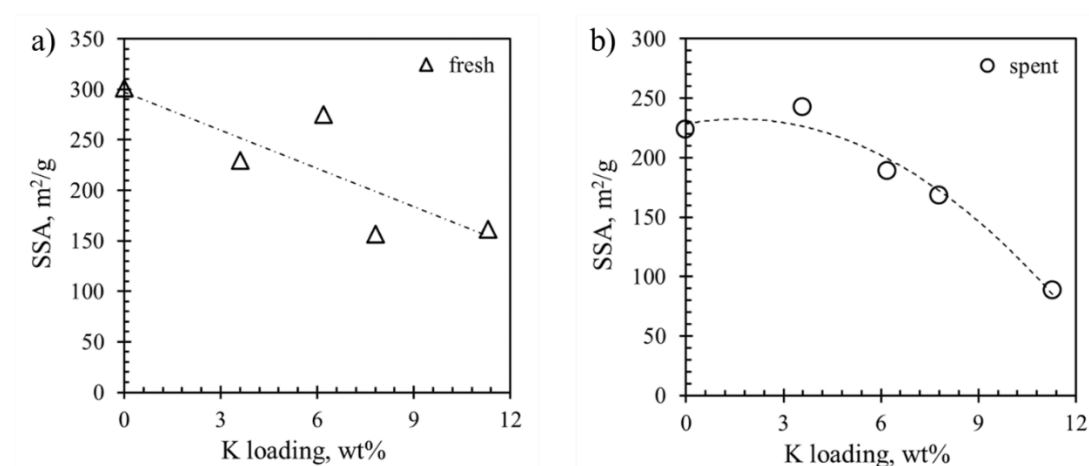


Figure 10. BET profile of fresh (a) and spent (b) catalysts with different K loadings.

Fresh and spent catalysts were characterized using XRD to investigate the crystallite size. Scherrer equation (eq. 8) was used for crystallite size calculation, which is reported in **Table 2**. In the fresh sample, as shown in **Figure 11a**, diffraction peaks observed at 33.3° and 35.5° characterize the $\alpha\text{-Fe}_2\text{O}_3$ phase (PDF: 33-0664). The two peaks detected at 45.8° and 66.8° are characteristic of $\gamma\text{-Al}_2\text{O}_3$ (PDF: 29-1486). In spent catalysts, as shown in **Figure 11b**, 0%, 3.6%, and 7.8% K loading were examined. Fe_2O_3 was transformed to Fe_3O_4 since the catalysts were under a highly reducing environment, with the characteristic peaks located at 30.1° , 35.4° , 43.1° , 53.4° , 56.9° , and 62.5° (PDF: 19-0629) observed. The $\gamma\text{-Al}_2\text{O}_3$ phase was also clearly identified at 45.8° and 66.8° . $\chi\text{-Fe}_5\text{C}_2$ located at 39.4° , 40.9° , 43.5° , 44.2° , 47.3° , and 50.2° (PDF: 36-1248) was detected. As K loading increased, the characteristic peaks became sharper. Fe_2O_3 and Fe_3O_4 are precursors of $\chi\text{-Fe}_5\text{C}_2$, which is widely reported as an active phase in the iron-based FT synthesis. The structure evolution of the Fe catalyst starts from Fe_2O_3 oxidation to Fe_3O_4 by CO_2 and is further generated to $\chi\text{-Fe}_5\text{C}_2$ [34]. This observation indicates that the increase in K promoter loading facilitated the transformation of magnetite to carbide.

The crystallite size of spent samples was calculated from selected clear peaks obtained in XRD from **Figure 11b**. The $\gamma\text{-Al}_2\text{O}_3$ crystallite size was calculated using peaks located at 66.8° since the peak located at 45.8° overlapped with the other two species. The Fe_3O_4 crystallite size was calculated using peaks located at 30.1° , 35.4° , and 62.5° . For the $\chi\text{-Fe}_5\text{C}_2$ phase, the crystallite size was calculated using peaks located at 39.4° , 40.9° , and 50.2° , as other peaks were either overlapping or not clear. The χ -

Fe_5C_2 crystallite size is relatively large, although the related peaks were not clear, which can cause significant errors in crystallite size evaluation. Still, qualitatively speaking, the $\chi\text{-Fe}_5\text{C}_2$ peaks are rather sharp, which indicates a relatively large crystallite size.

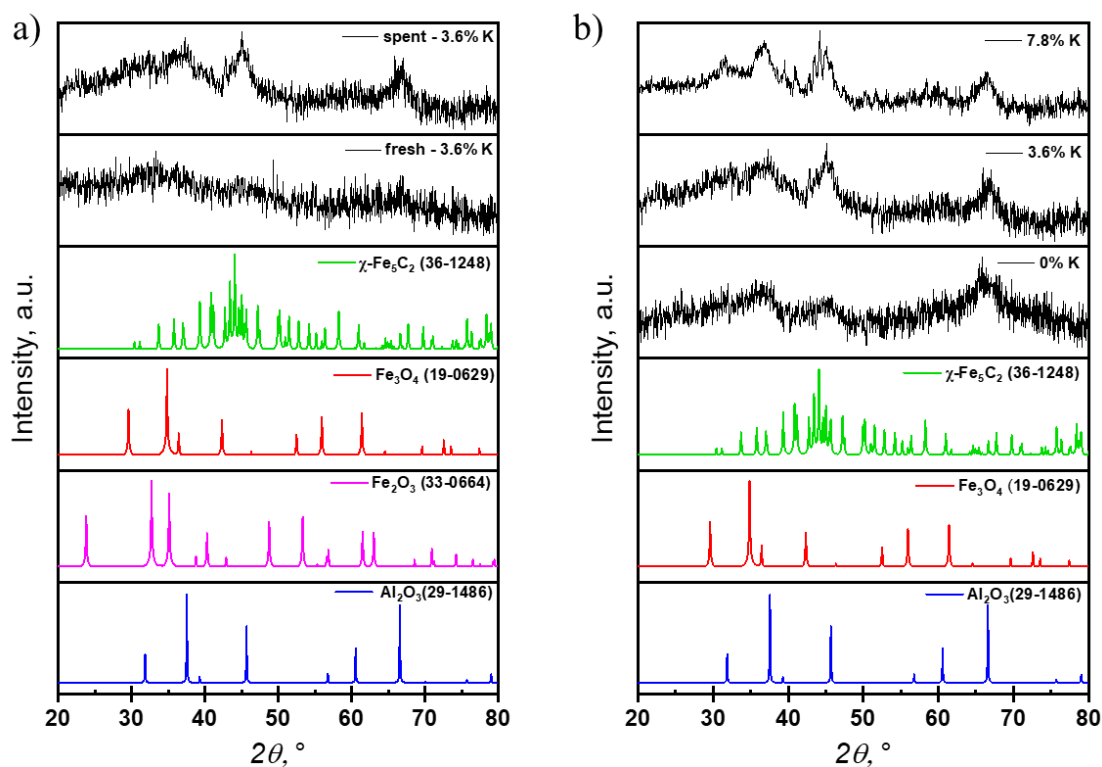


Figure 11. XRD patterns of fresh and spent catalysts (a) and spent catalysts only (b).

For spent samples, the following reaction conditions were used: $T = 300\text{--}400\text{ }^{\circ}\text{C}$, $\text{H}_2/\text{CO}_2 = 4$, $\text{GHSV} = 3,000\text{ mL}/(\text{g}_{\text{cat}}\cdot\text{h})$, $P = 11\text{ bar}$, time-on-stream = 50 h.

5.1.2 Temperature-programmed reduction

H_2 -TPR results of fresh (calcined) and spent (post-reaction) catalysts are summarized in **Figure 12**. For TPR profiles of the fresh catalyst, the low-temperature peak centered at ca. $380\text{ }^{\circ}\text{C}$ corresponds to Fe_2O_3 being reduced to Fe_3O_4 . The high-temperature peak centered at ca. $640\text{ }^{\circ}\text{C}$ observed for all catalysts indicates the direct reduction of Fe_3O_4 to Fe^0 [35]. Therefore, the TPR profiles indicated the two-step

reduction ($\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}^0$). With an increase in K concentration, the first peak shifted gradually towards a higher temperature, while the starting point of the second peak moved to a lower temperature, indicating that potassium addition retarded the initial reduction while facilitating the reduction of Fe_3O_4 to Fe^0 [36].

Qualitatively similar TPR profiles were obtained for all spent catalysts, with the two reduction peaks (located at somewhat different temperatures) observed. The first peak, that located in the 280-350 °C range, is related to post-reaction residuals on the catalyst surface. The second peak starts to appear at ca. 660 °C, a similar temperature range as the $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}^0$ reduction peak in fresh catalysts from **Figure 12a**.

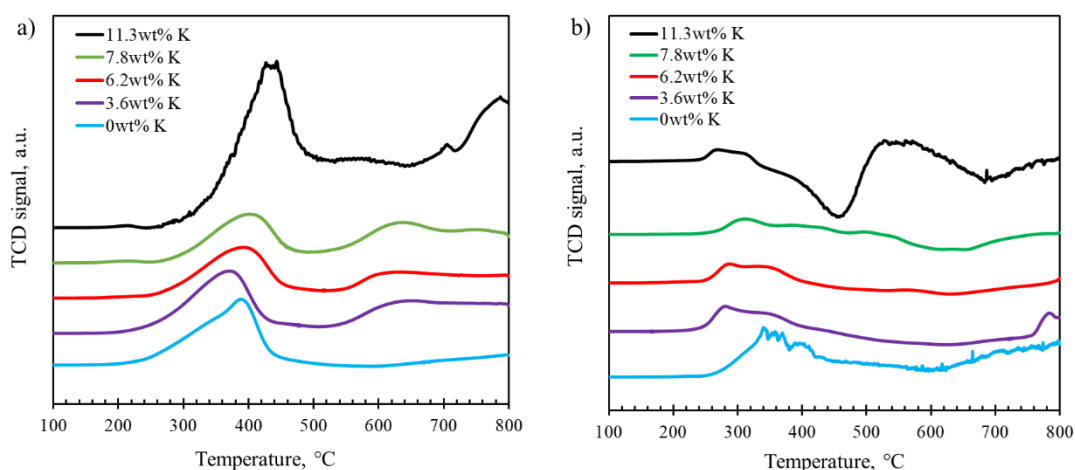


Figure 12. H₂-TPR profiles of as-prepared, calcined (a), and spent, after 50 h on stream (b) catalysts, comparing the catalysts with different K loadings.

5.1.3 Nanomorphology and elemental distribution at the nanoscale

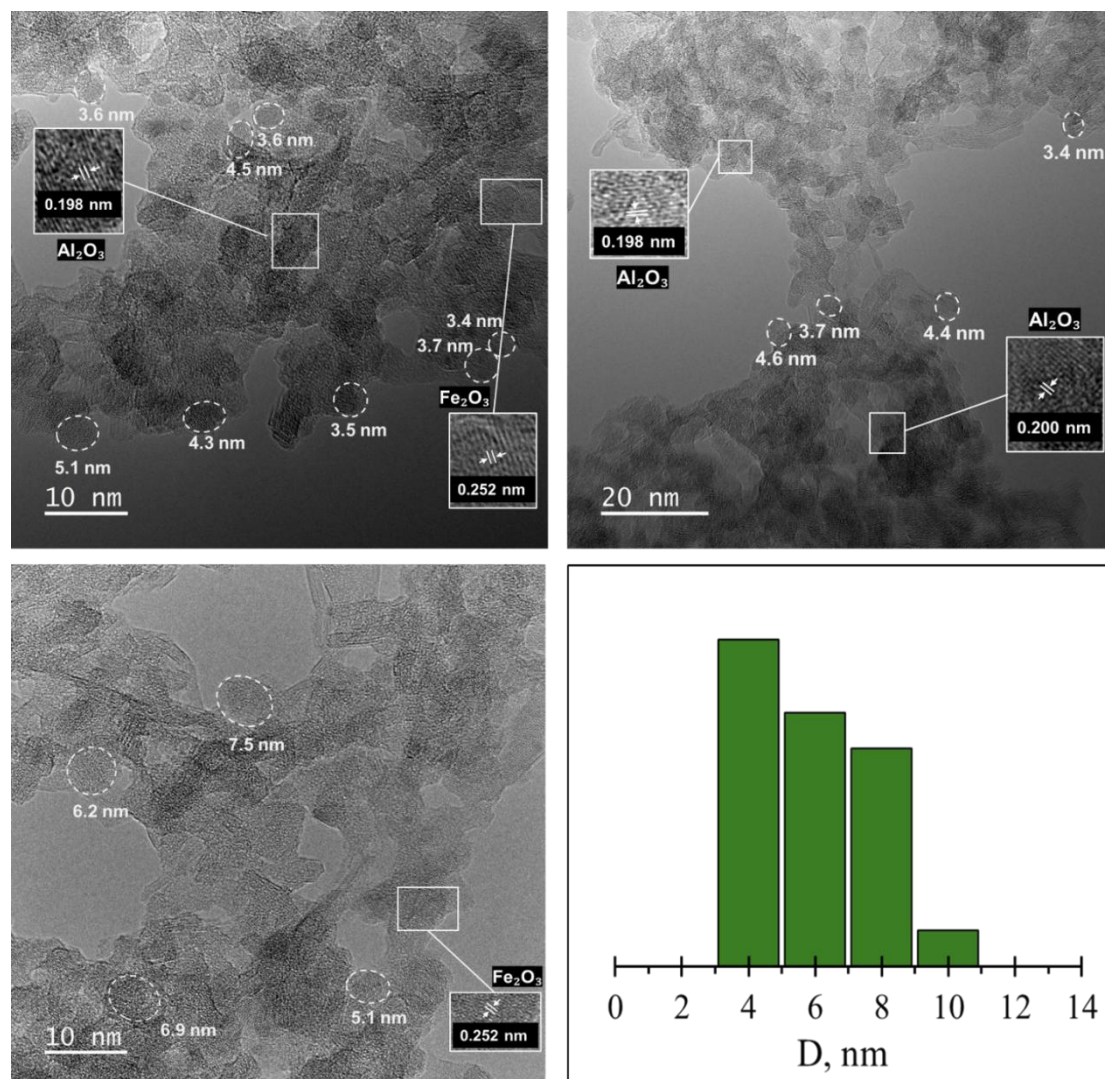


Figure 13. TEM images of fresh RME 7.8%K/Fe₂O₃-Al₂O₃ catalysts with particle size distribution.

Transmission electron microscopy (TEM) analysis of the fresh RME 7.8%K/Fe₂O₃-Al₂O₃ catalyst revealed a mixture of amorphous regions and areas containing relatively uniform, well-dispersed crystalline nanoparticles (**Figure 13**), with an average particle size of 5.0 ± 2.0 nm. d-Spacing measurements identified these nanoparticles as a combination of Fe₂O₃ and Al₂O₃ phases. Specifically, Fe₂O₃ exhibited a lattice spacing of 0.252 nm, corresponding to the (110) crystallographic

plane, while Al_2O_3 was characterized by a d-spacing of 0.198 nm, assigned to the (400) plane.

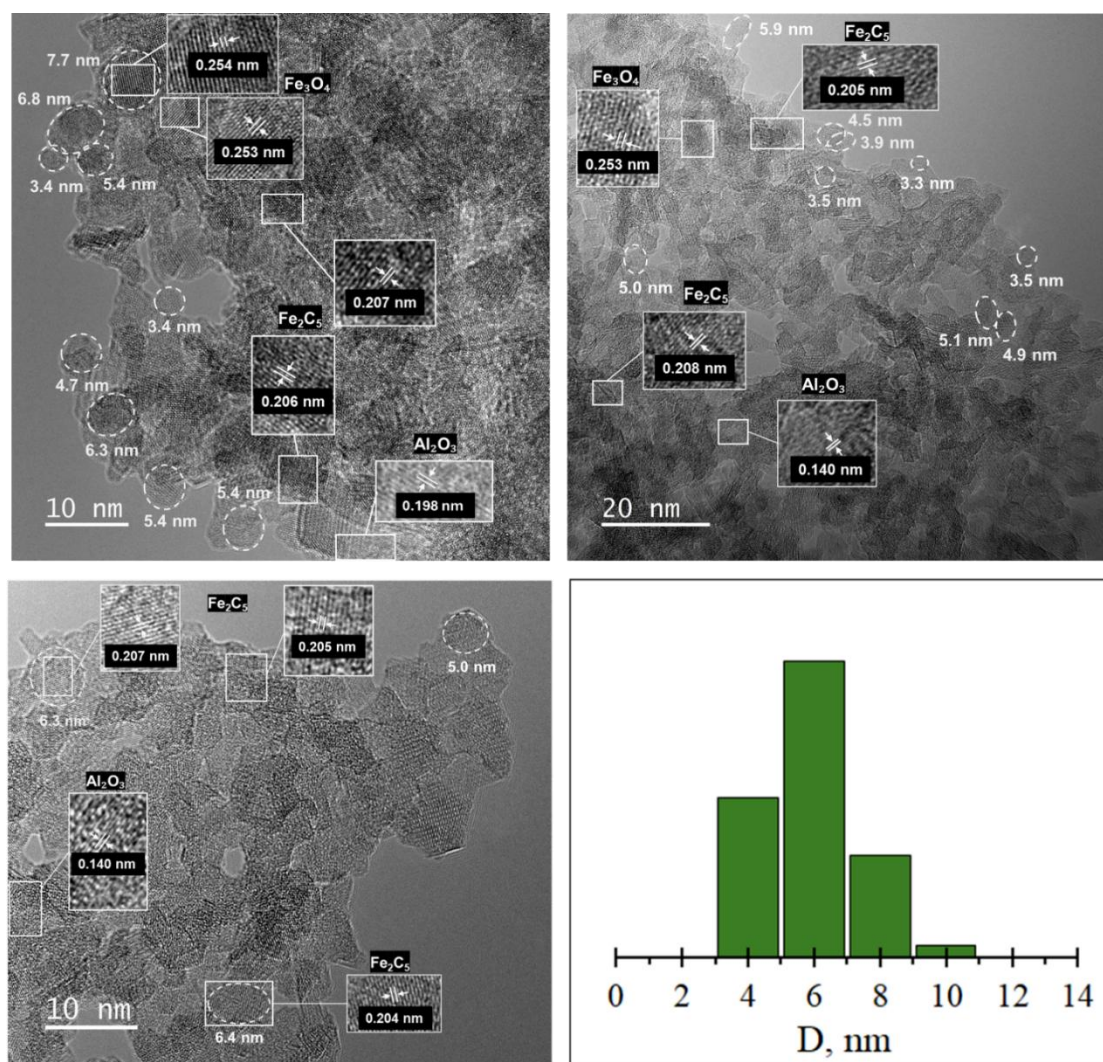


Figure 14. TEM images of spent, after 96 h on stream, RME 7.8%K/ Fe_2O_3 - Al_2O_3 catalysts with particle size distribution.

After 96 hours of time-on-stream operation, TEM analysis of the spent catalyst (**Figure 14**) indicated that nanoparticles smaller than 10 nm remained predominant, with a slightly increased average particle size of 6.0 ± 3.0 nm. However, X-ray diffraction (XRD) analysis (**Table 2**) revealed the formation of larger crystalline domains, with average crystallite sizes of 13.0 nm for Fe_3O_4 and 29.7 nm for χ - Fe_5C_2 .

d-Spacing analysis confirmed the presence of multiple crystalline phases, including γ - Al_2O_3 , Fe_3O_4 , and χ - Fe_5C_2 . The χ - Fe_5C_2 phase, also known as Hägg carbide, was identified by characteristic d-spacings of 0.205 nm and 0.208 nm, corresponding to the (510) and (021) planes, respectively [37]. Fe_3O_4 was identified by a d-spacing of 0.253 nm, attributed to the (311) plane, while γ - Al_2O_3 was confirmed by d-spacings of 0.198 nm and 0.140 nm, corresponding to the (400) and (440) planes, respectively.

The detection of χ - Fe_5C_2 , a known active phase in Fischer-Tropsch synthesis, by both d-spacing and XRD analysis (**Figure 11**), underscores the structural evolution of the catalyst under reaction conditions.

5.2 Catalytic performance evaluation

Conventionally, direct hydrogenation of CO_2 is composed of two stages: CO hydrogenation to generate hydrocarbons and CO_2 reduction by reverse water gas shift (RWGS). Since the RWGS reaction is endothermic, it will be advantageous at higher temperatures from a thermodynamic perspective, thus offering high CO_2 conversions. On the other hand, the exothermic process of hydrocarbon chain synthesis benefits from low temperatures. Therefore, it is essential to find the optimal temperature that benefits direct CO_2 hydrogenation.

Reaction tests were performed to investigate the effect of temperature and K-promoter, as shown in **Figure 15**. Selectivity to C_2^+ increased along with the increase in temperature and K concentration. Comparing the result of K-promoted and unpromoted catalysts, the highest selectivity (0.46) and the space time yield (STY) 6.46

mmol/(g_{cat}·h) was achieved at 400 °C for 7.8%K/Fe₂O₃-Al₂O₃, while STY at 400 °C was only 0.35 mmol/(g_{cat}·h) for RME K/Fe₂O₃-Al₂O₃ without K promoter, as shown in **Figure 15a-b**. Further increase of K concentration to 11.3 wt% did not help in improving the results. **Figure 15c** shows that the selectivity and space time yield (STY) dropped to 0.42 and 5.40 mmol/(g_{cat}·h) at 400 °C for 11.3%K/Fe₂O₃-Al₂O₃, respectively. In contrast, while K is beneficial in moderation, excessive doping can hinder catalyst performance by destabilizing active sites and altering reaction pathways, leading to lower overall efficiency in FT synthesis [38].

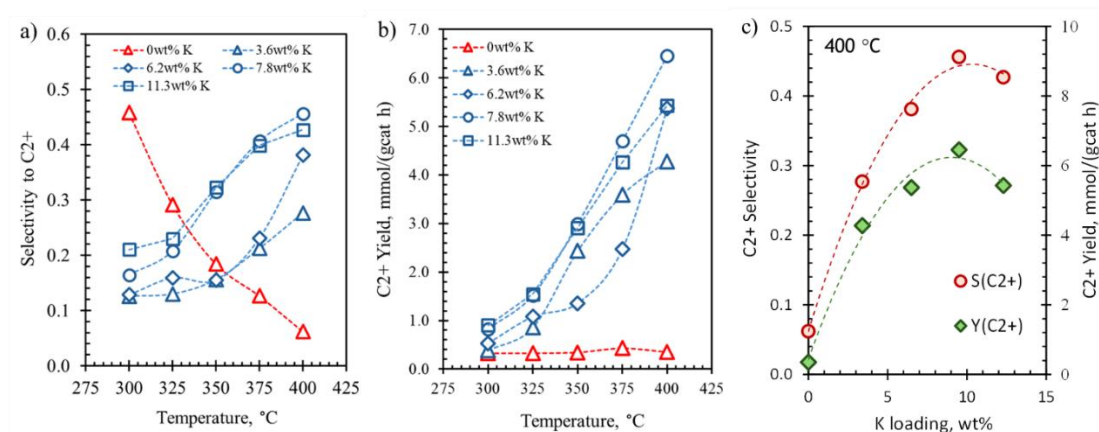


Figure 15. Catalytic performance evaluation of RME K/Fe₂O₃-Al₂O₃ shows selectivity to C₂⁺ for T = 300-400 °C (a) and C₂⁺ space time yield for T = 300-400 °C (b), and selectivity to C₂⁺ and C₂⁺ space time yield for different K loadings at T = 400 °C (c). Operation conditions: H₂/CO₂ = 4, GHSV = 3,000 mL/(g_{cat}·h), P = 11 bar.

The best performance catalyst, 7.8%K/Fe₂O₃-Al₂O₃ was tested at temperatures ranging from 300 °C to 500 °C to investigate the optimum temperature in **Figure 16a-b**. CO₂ conversion increased significantly from 16% to 50% as temperature increased from 300 °C to 500 °C. Selectivity to C₂⁺ and STY increased to 0.46 and 6.4

mmol/(g_{cat}·h) at the optimum temperature of 400°C. Then they decreased in the 400-500°C range since CO became the dominant part of the product due to the RWGS reaction being favored at high temperatures.

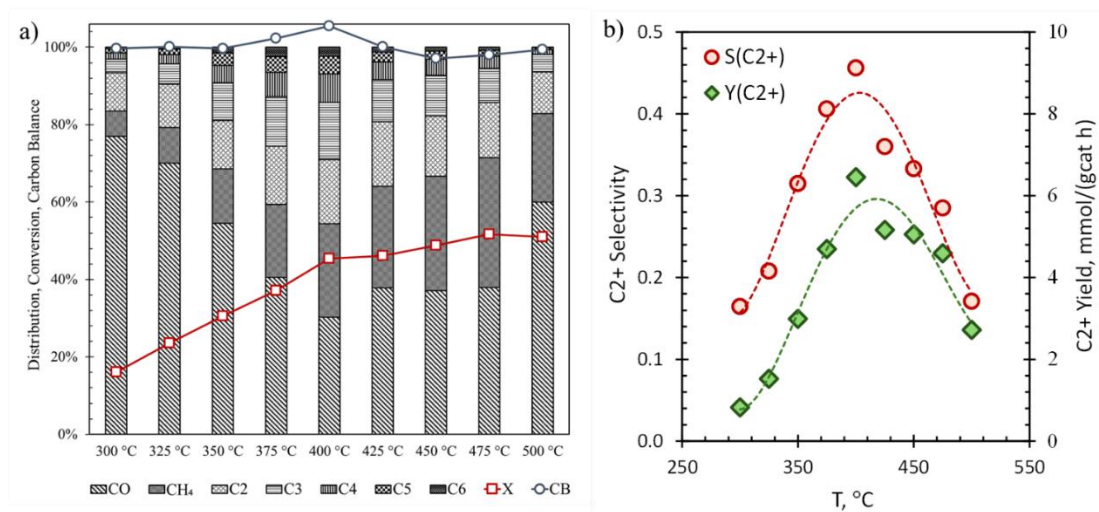


Figure 16. Catalytic performance evaluation of RME 7.8%K/Fe₂O₃-Al₂O₃ shows product distribution, CO₂ conversion (X, squares), and carbon balance (CB, circles) (a) and C₂+ selectivity and C₂+ yield (b). Operation conditions: H₂/CO₂ = 4, GHSV = 3,000 mL/(g_{cat}·h), P = 11 bar.

Since stability is a crucial descriptor of the performance of a catalytic material, RME 7.8%K/Fe₂O₃-Al₂O₃ was tested on stream for 96 h at the optimum condition, as shown in **Figure 17a-b**. The conversion experienced a 4% decline during the experiments. The production efficiency of C₂+ hydrocarbons decreased gradually, which can be revealed from the dropping selectivity. CO started becoming the dominant product from 40 h, but the CH₄ fraction remained constant, indicating that CO might be the biggest competitor of light hydrocarbons. The catalyst phase with χ -Fe₅C₂ is obtained from XRD, as shown in **Figure 17d**, after a long time on stream, which is

necessary to obtain high FT activity [39]. TGA-FTIR for spent catalysts after the stability test is shown in **Figure 17c**. Three distinct CO₂ peaks represent the presence of three carbonaceous species. The first peak at 200°C, associated with a clear CO peak, is related to carbon deposition via a combination of CO dissociation. The second and third peaks at 280 °C and 340°C, which overlap with a shoulder in the CO signal, can be associated with amorphous carbon deposited on the catalyst surface [40]. Overall, the three CO₂ peaks correspond to ca. 5% weight loss, followed by an additional 3% and 3% weight loss. It indicates the coke formation on the catalyst, which caused the deactivation of the catalyst, leading to lower selectivity.

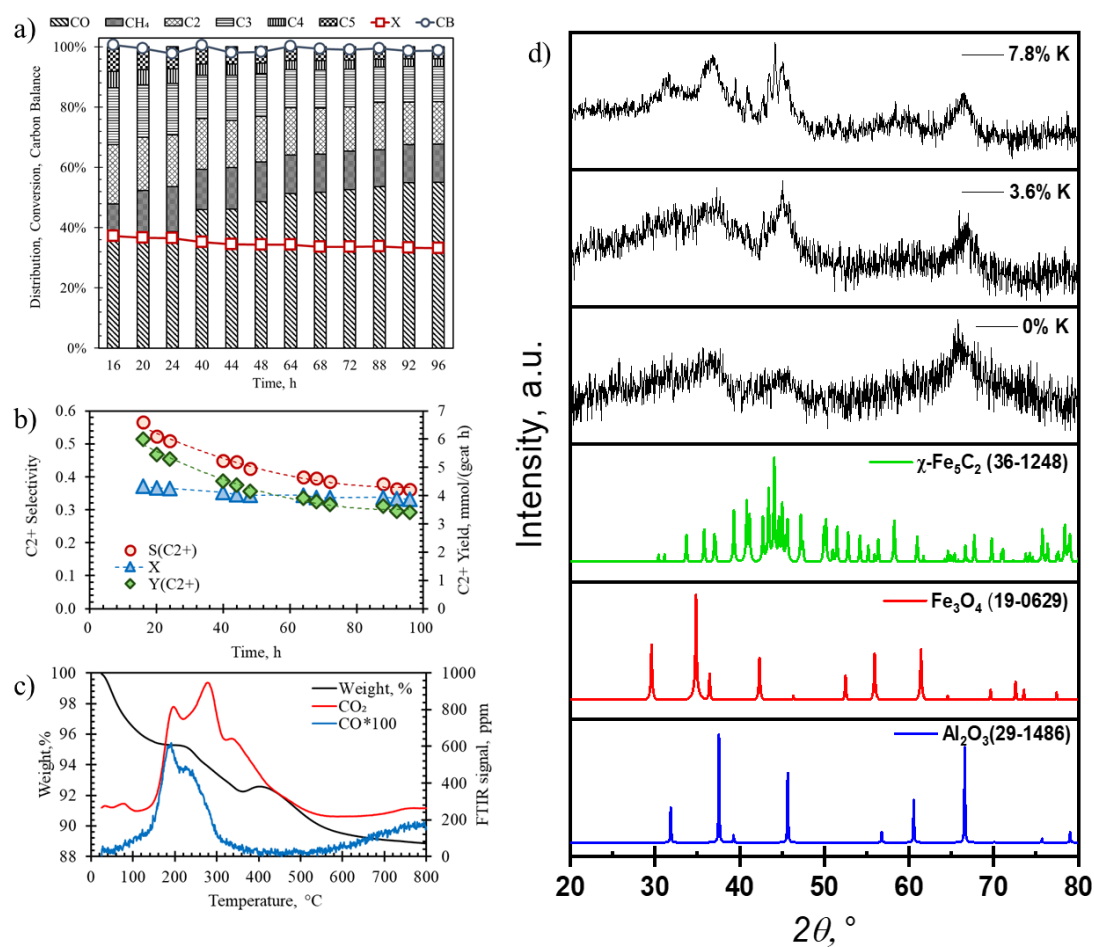


Figure 17. Stability test of the RME 7.8%K/Fe₂O₃-Al₂O₃ catalyst, showing product distribution, CO₂ conversion (X, squares) (a), C₂+ selectivity and STY (b), TGA-FTIR (c), and XRD pattern (d). Operating conditions: T = 400 °C, H₂/CO₂ = 4, GHSV = 3,000 mL/(g_{cat}·h), P = 11 bar.

Chapter 6 Catalyst Composition Modification and Reaction Conditions Optimization for Improving CO₂ Conversion and Selectivity of Hydrocarbons

6.1 Effect of catalyst composition

In FT synthesis, hydrocarbons are produced from the syngas over an iron-based or cobalt-based catalyst. Iron-based catalyst has been successfully applied in industry since its low cost and high RWGS reaction activity, and high C₂+ selectivity. An alkali promoter, such as potassium or sodium [41] that added to the catalyst can improve the carburization and reduce CH₄ formation, and the other metals, like copper or ruthenium [42] can improve the RWGS activity. Support material like Al₂O₃ can improve the structural stability and provide high chemisorption capacity to absorb CO₂ [43]. CeO₂ has high oxygen vacancies on the catalyst surface that can be active sites for CO₂ absorption and thereby enhance the catalytic activity for the RWGS reaction. Modifications were executed over the best-performing baseline catalyst, 7.8%K/Fe₂O₃-Al₂O₃, to investigate the impact of promoter, active phase, and support on FT synthesis.

6.1.1 Effect of support

The effect of support was investigated by replacing half of the original Al₂O₃ support with CeO₂ support. The idea is to have a high surface area and stability from Al₂O₃ and high RWGS activity from CeO₂. The reaction was executed under GHSV = 3,000 mL/(g_{cat}·h), P = 11 bar, and temperature ranging from 300°C to 500 °C, as shown in **Figure 18**. The conversion rose from 11% to 45% as temperature increased from

300°C to 500°C, but C2+ STY stopped increasing when reaching 3.9 mmol/(g_{cat}·h) at the optimum temperature 450°C, then dropped to 2.8 mmol/(g_{cat}·h) at a higher temperature of 500°C. The C2+ STY was significantly lower than that of 7.8%K/Fe₂O₃-Al₂O₃. The reason could be that the CeO₂ is favorable for the RWGS reaction, which can facilitate the CO₂ conversion, but it is towards the selectivity to the CO product [44]. Compared with the results obtained from **Figure 16**, where the CO contributed 30% in the product at 400°C, here the CO product is nearly 60%. It could explain why the C2+ STY was reduced by half when replacing half of the original Al₂O₃ support with CeO₂ support. The effect of CeO₂ support on FT synthesis could be further investigated by modifying the concentrations of CeO₂.

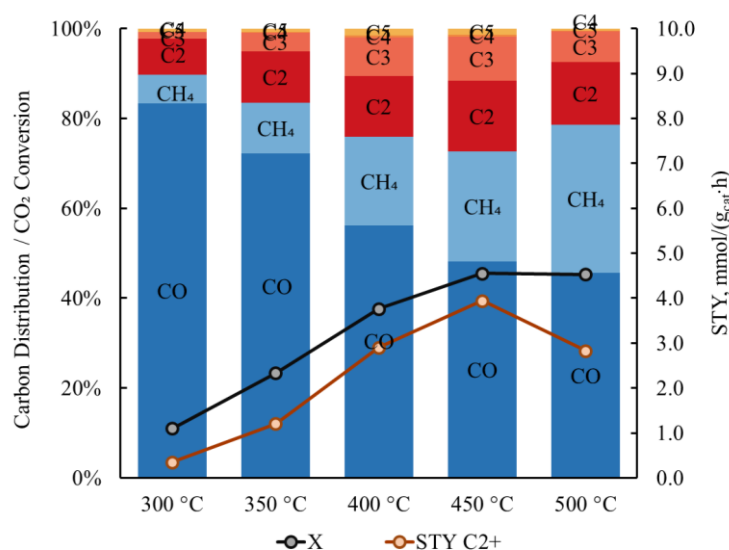


Figure 18. Catalytic performance evaluation of RME 7.8%K/Fe₂O₃-32%Al₂O₃-32%CeO₂ shows product distribution, CO₂ conversion, and C2+ space time yield. Operation conditions: GHSV = 3,000 mL/(g_{cat}·h), P = 11 bar.

6.1.2 Effect of active phase

The bimetallic system was investigated by adding the active phase Fe-Cu into the catalyst. **Figure 19** shows the results of the catalytic performance of 7.8%K/Fe₂O₃-3%CuO-Al₂O₃ under the operation condition at GHSV = 3,000 mL/(g_{cat}·h), P = 11 bar. CO₂ conversion increased from 13% to 45% as temperature increased from 300 °C to 500 °C, while C2+ STY achieved 4.5 mmol/(g_{cat}·h) at the optimum temperature of 400 °C, then dropped to 3.1 mmol/(g_{cat}·h) at higher temperatures. As indicated that the C2+ STY was relatively low, suggesting that the addition of Cu promotes the RWGS reaction to produce more CO than converting it to C2+ hydrocarbons.

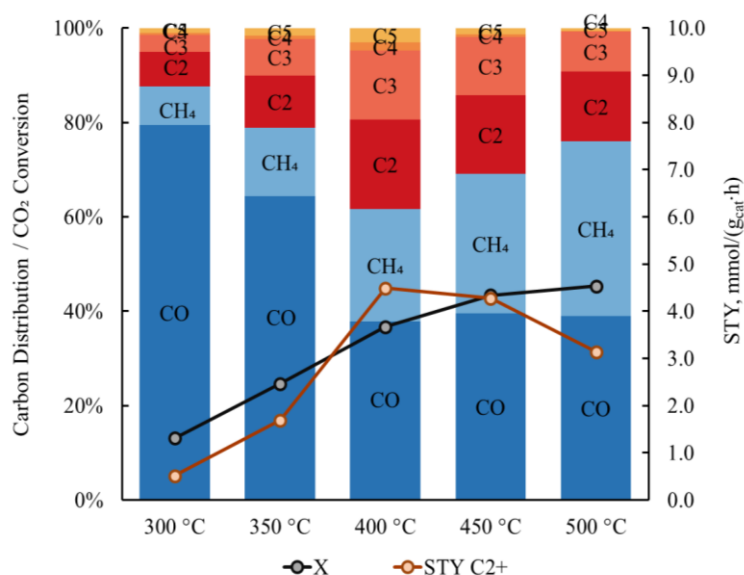


Figure 19. Catalytic performance evaluation of RME 7.8%K/Fe₂O₃-3%CuO-Al₂O₃ shows product distribution, CO₂ conversion, and C2+ space time yield. Operation conditions: GHSV = 3,000 mL/(g_{cat}·h), P = 11 bar.

Another bimetallic system, Fe-Co, was investigated. The reaction test of 7.8%K/Fe₂O₃-11%CoO-Al₂O₃ was operated at the same conditions, GHSV = 3,000

mL/(g_{cat}·h), P =11 bar, as shown in **Figure 20**. The CO₂ conversion had a significant increase from 17% to 57% as the temperature rose from 300 °C to 500 °C. C2+ STY increased from 0.6 mmol/(g_{cat}·h) to 5.1 mmol/(g_{cat}·h) at the optimum temperature of 400°C, then decreased to 2.63 mmol/(g_{cat}·h) at higher temperatures. The lack of promotional effect from Co addition to the K/Fe-Al₂O₃ catalyst may be attributed to several plausible factors. Co addition may have occupied or blocked active Fe surface sites, thereby reducing the number of available catalytic centers. Moreover, since Fe and Co tend to operate under somewhat different optimal conditions, their combination might have resulted in unfavorable synergistic interactions. Co-based catalysts typically exhibit optimal activity in the low-temperature FT range of 200-300 °C. However, the reaction conditions used in this study were more aligned with those typical for iron catalysts, which are significantly higher than cobalt's preferred temperature range. At elevated temperatures, cobalt is known to promote excessive methane formation and may become less selective toward long-chain hydrocarbons [18].

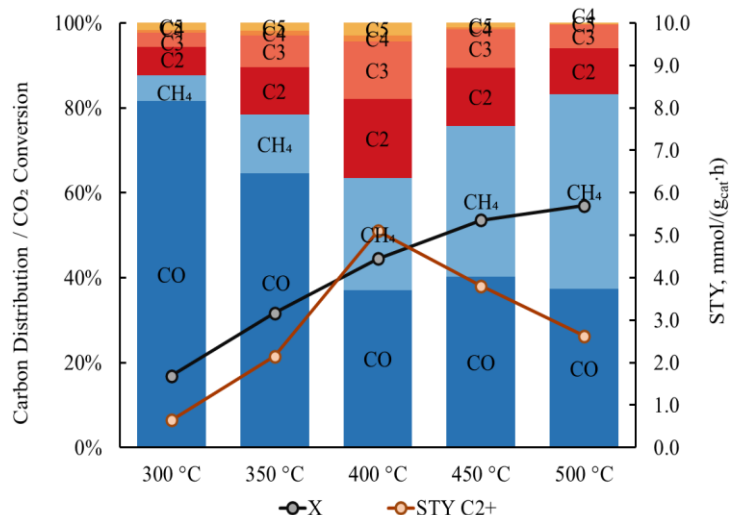


Figure 20. Catalytic performance evaluation of RME 7.8%K/Fe₂O₃-11%CoO-Al₂O₃ shows product distribution, CO₂ conversion, and C₂⁺ space time yield. Operation conditions: GHSV = 3,000 mL/(g_{cat}·h), P = 11 bar.

6.1.3 Effect of promoter

To investigate the effect of the promoter, the same concentration of sodium as the optimum concentration of potassium was added on top of the Fe₂O₃-Al₂O₃ catalyst. The reaction was operated at the same conditions, GHSV = 3,000 mL/(g_{cat}·h) and P = 11 bar, as the results shown in **Figure 21**. The C₁ compound dominated 80% of the product across all temperature range. Though conversion increased from 7.8% to 54.6% from 300 °C to 500 °C, it achieved similar results as the K-promoted catalyst, as shown in **Figure 16**, the optimum C₂⁺ STY was only 3.3 mmol/(g_{cat}·h) at 450 °C, much lower than 6.4 mmol/(g_{cat}·h) achieved from 7.8%K/Fe₂O₃-Al₂O₃. A presumable reason is that Na content is proportional to Fe₂C₅ content, which plays an important role in converting CO₂ and H₂ into CH_n species [41]. The addition of Na also affects the catalyst surface

basicity that correlates with the hydrocarbon selectivity in the CO₂ hydrogenation process [45]. The addition of Na can improve the surface basicity of the catalyst, therefore facilitating the adsorption of acidic CO₂ [46]. Since Na is less basic than K, it could be the reason that its selectivity is less than that of the K-promoted catalyst. A series of Na with different concentrations should be performed on this catalyst to find out the optimum Na concentration.

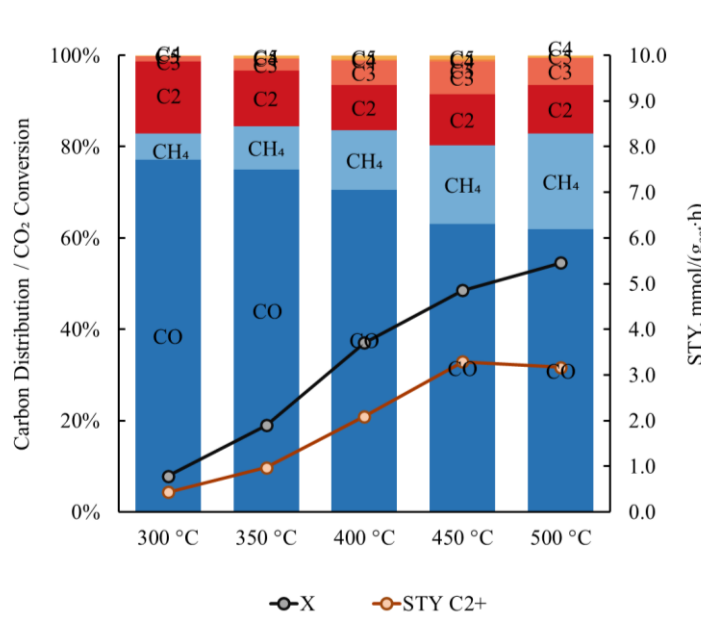


Figure 21. Catalytic performance evaluation of RME 7.8%Na/Fe₂O₃-Al₂O₃ shows product distribution, CO₂ conversion, and C₂+ space time yield. Operation conditions: GHSV = 3,000 mL/(g_{cat}·h), P = 11 bar.

The effect of Cu promoter is investigated by adding 3 wt% of Cu on top of the baseline catalyst 7.8%K/Fe₂O₃-Al₂O₃. The reaction was performed at temperatures ranging from 300 °C to 500 °C with GHSV = 3,000 mL/(g_{cat}·h) and P = 11 bar, as the results shown in **Figure 22**. CO₂ conversion increased from 13% to 47% as temperature

rose from 300 °C to 500 °C, and the C2+ STY increased to 4.9 mmol/(g_{cat}·h) at the optimum temperature of 450 °C, then dropped to 3.4 mmol/(g_{cat}·h) at a higher temperature of 500 °C. The reason could be that the excessive impregnation of the promoter blocks the active phase, therefore decreasing the catalytic activity [47]. A smaller amount of total promoter should be doped in the Fe₂O₃-Al₂O₃ catalyst.

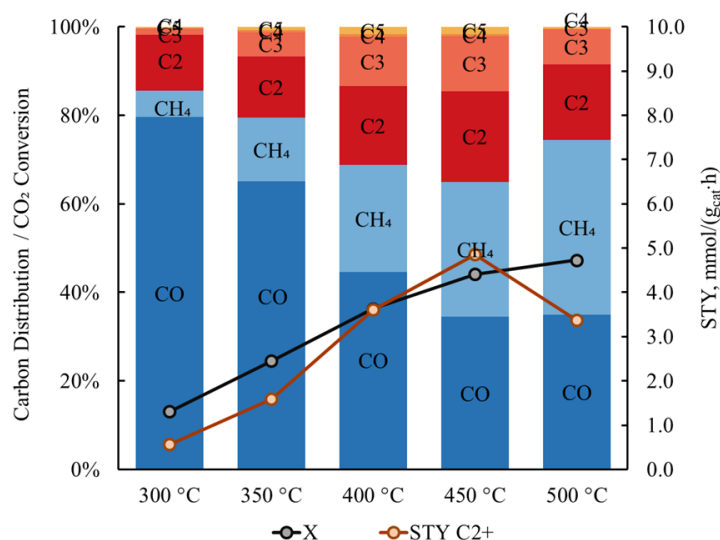


Figure 22. Catalytic performance evaluation of RME 3%Cu/7.8%K/Fe₂O₃-Al₂O₃ shows product distribution, CO₂ conversion, and C2+ space time yield. Operation conditions: GHSV = 3,000 mL/(g_{cat}·h), P = 11 bar.

The effect of the dual promoter was investigated by adding 1% of ruthenium (Ru) on top of the 7.8%K/Fe₂O₃-32%Al₂O₃-32%CeO₂. The catalyst undergoes a reaction test that operates at GHSV = 3,000 mL/(g_{cat}·h), P = 11 bar, as the results shown in **Figure 23**. The CO₂ conversion increased from 8.7% to 46.5% as temperature increased from 300°C to 500°C. C2+ STY reached a maximum 3.6 mmol/(g_{cat}·h) at the optimum temperature of 450°C. It is observed that the catalyst generated over 80% of the C1

product. High amount of CO at low temperatures and CH₄ at high temperatures. The reason could be that the Ru is favorable for the Sabatier reaction, which exhibits high CO₂ conversion and selectivity towards CH₄ formation [48].

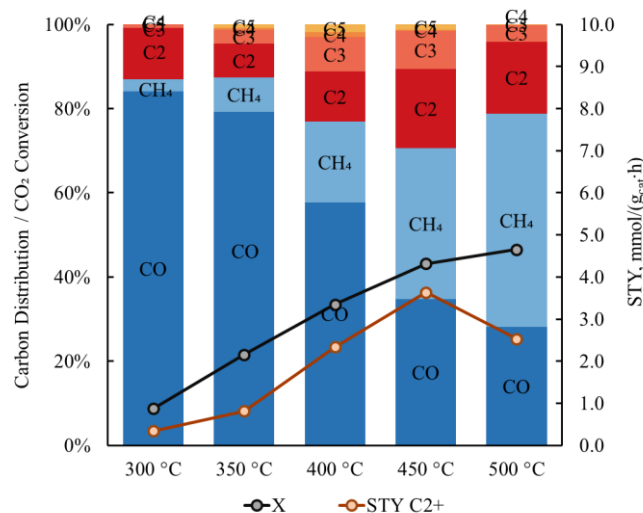


Figure 23. Catalytic performance evaluation of RME 1%Ru/7.8%K/Fe₂O₃-32%Al₂O₃-32%CeO₂ shows product distribution, CO₂ conversion, and C₂+ space time yield. Operation conditions: GHSV = 3,000 mL/(g_{cat}·h), P = 11 bar.

6.2 Effect of reaction conditions

To understand the impact of various reaction parameters on the direct CO₂ to hydrocarbons via FT synthesis, the effects of H₂/CO₂ ratio, gas hourly space velocity (GHSV), temperature, and pressure were investigated over the best-performing catalyst 7.8%K/Fe₂O₃-Al₂O₃ for improving CO₂ conversion and C₂+ selectivity.

6.2.1 Effect of feed ratio

The effect of the feed ratio H₂/CO₂ range from 1 to 4 was investigated over the

RME 3.6%K/Fe₂O₃-Al₂O₃, keeping constant the other operating conditions at T = 400°C, GHSV = 3,000 mL/(g_{cat}·h), and P = 11 bar, as shown in **Figure 24**. At H₂/CO₂ feed ratio 1:1, the CO₂ conversion was 22% and the C₂+ space time yield (STY) 2.3 mmol/(g_{cat}·h), with over 80% of C₁ product. At a low H₂/CO₂ feed ratio, the CO₂ absorption rate is higher than the H₂ absorption rate, which causes low activity for FT synthesis. As the feed ratio increases, a steady increase in conversion was observed, reaching 52% at an H₂/CO₂ feed ratio of 4:1. More C₂+ product was formed, with C₁ product shift from CO to CH₄. However, the C₂+ STY started to have a slightly decreasing trend when the feed ratio was increased from 3 to 4, since CH₄ became the dominant compound.

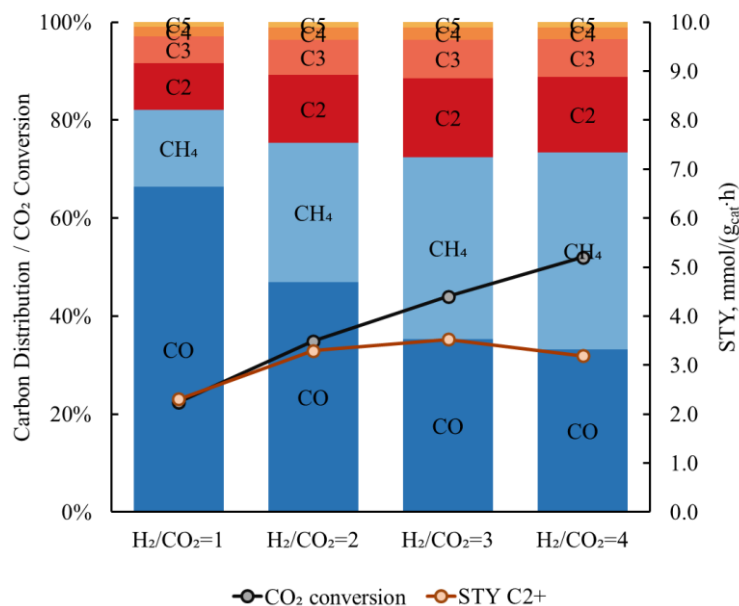


Figure 24. Catalytic performance evaluation of RME 3.6%K/Fe₂O₃-Al₂O₃ shows product distribution, CO₂ conversion, and C₂+ space time yield. Operation conditions: T = 400 °C, GHSV = 3,000 mL/(g_{cat}·h), P = 11 bar.

6.2.2 Effect of GHSV

Figure 25 depicts the effect of gas hourly space velocity (GHSV) on the catalytic performance at $T = 400\text{ }^{\circ}\text{C}$, $\text{H}_2/\text{CO}_2 = 4$, and $P = 11\text{ bar}$. As the GHSV increased from 750 to 4000 $\text{mL}/(\text{g}_{\text{cat}}\cdot\text{h})$, CO_2 conversion had a slight decrease from 45% to 40% due to the decrease in residence time of reactant and product. C_2+ STY rose to 7.5 $\text{mmol}/(\text{g}_{\text{cat}}\cdot\text{h})$ at an optimal GHSV = 1000 $\text{mL}/(\text{g}_{\text{cat}}\cdot\text{h})$, then decreased dramatically to 3.9 $\text{mmol}/(\text{g}_{\text{cat}}\cdot\text{h})$. It is noticeable that C_5+ has 25% at GHSV = 1000 $\text{mL}/(\text{g}_{\text{cat}}\cdot\text{h})$, while decrease to 10% at GHSV = 4000 $\text{mL}/(\text{g}_{\text{cat}}\cdot\text{h})$. It is because lower GHSV gives slow gas flow over the catalyst, thereby providing a longer residence time for the feed gas to react with the catalyst. It gives surface intermediates more time to undergo multiple C-C coupling steps, growing to longer-chain hydrocarbons before they desorb as CH_4 [49].

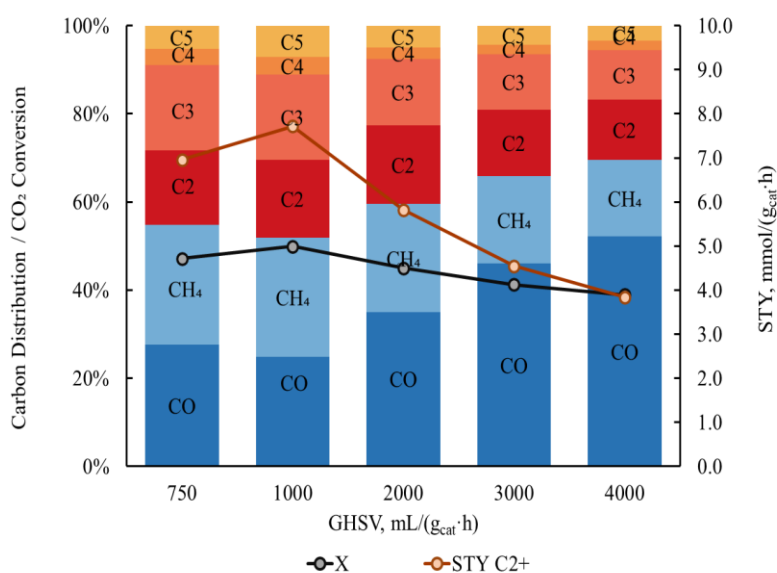


Figure 25. Catalytic performance evaluation of RME 7.8%K/Fe₂O₃-Al₂O₃ shows product distribution, CO₂ conversion, and C₂+ space time yield. Operation conditions: $T = 400\text{ }^{\circ}\text{C}$, $\text{H}_2/\text{CO}_2 = 4$, $P = 11\text{ bar}$.

6.2.3 Effect of temperature

The 7.8%K/Fe₂O₃-Al₂O₃ was analyzed over a range of temperatures from 350 °C to 450 °C, with 25 °C intervals at GHSV = 1,000 mL/(g_{cat}·h), H₂/CO₂ = 4, and P = 11 bar. A fine-tuning of the temperature reaction test was conducted, and it is expected that a reduction of the temperature rate increase can help with forming long-chain hydrocarbons. **Figure 26** shows that as temperature increased from 350 °C to 450 °C, conversion increased gradually from 30% to 50%, and C₂+ STY increased from 1.0 to 4.5 mmol/(g_{cat}·h). It is not surprising that the formation of CH₄ increases since high temperature causes the chain growth probability to decrease. According to Le Chatelier's principle [50], increasing temperature shifts the equilibrium toward smaller, less exothermic products. The overall FT synthesis is exothermic. CH₄ formation is more thermodynamically favored at elevated temperatures than higher hydrocarbons, which require more enthalpy [51].

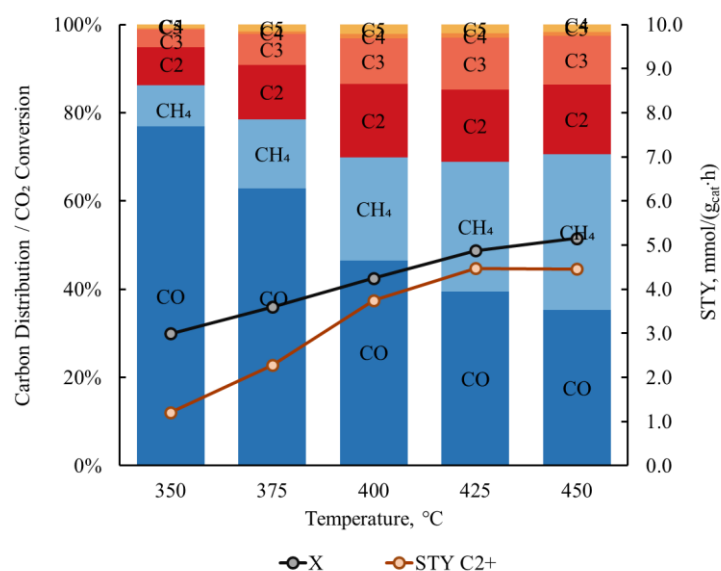


Figure 26. Catalytic performance evaluation of RME 7.8%K/Fe₂O₃-Al₂O₃ shows product distribution, CO₂ conversion, and C2+ space time yield. Operation conditions: GHSV = 1,000 mL/(g_{cat}·h), H₂/CO₂ = 4, P = 11 bar.

6.2.4 Effect of pressure

The effect of pressure on the 7.8%K/Fe₂O₃-Al₂O₃ was examined at different pressure levels (4, 6, 8, 10, 12 bar), keeping other reaction conditions constant at T = 400 °C, GHSV = 1,000 mL/(g_{cat}·h), H₂/CO₂ = 4. As shown in **Figure 27**, the conversion is not affected by changes in pressure, remaining constant at 41%. While the C2+ STY is increasing from 1.5 to 3.5 mmol/(g_{cat}·h), the CO concentration decreased from 80% to 45% as pressure increased from 4 to 12 bar. Le Chatelier's principle can explain the phenomena, increasing pressure favors products with fewer gas-phase molecules over gaseous ones like CO. High pressure drives the equilibrium toward forming liquid long-chain hydrocarbons. Also, high pressure increases the partial pressures of CO and H₂, which enhances the absorption rates of reactants onto the catalyst surface. It promotes

the formation of CH_n and C-C intermediates, which are key to chain propagation [52].

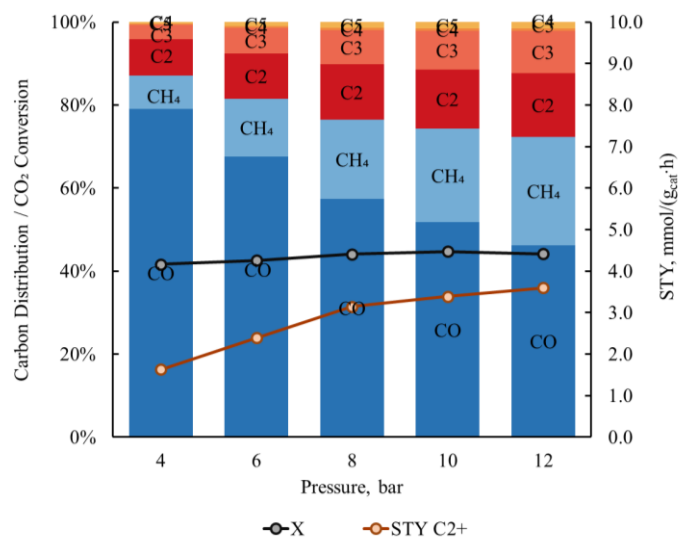


Figure 27. Catalytic performance evaluation of RME 7.8%K/Fe₂O₃-Al₂O₃ shows product distribution, CO₂ conversion, and C₂⁺ space time yield. Operation conditions:

T = 400 °C, GHSV = 1,000 mL/(g_{cat}·h), H₂/CO₂ = 4.

Chapter 7 Conclusion and Future Work

7.1 Conclusion

This study investigated the direct CO₂ hydrogenation to light hydrocarbons over various K/Fe₂O₃-Al₂O₃ catalysts synthesized by the reverse microemulsion (RME) method. Characterization tests like surface area analysis, ICP, XRD, TPR, TEM, and TGA-FTIR were carried out to investigate the composition and structural properties of both fresh and spent samples. A stability test for 100 h was performed to analyze the strength of the material. The impact of K concentration (0-11.3 wt%) on catalyst performance was identified in a range of temperatures. 7.8%K/Fe₂O₃-Al₂O₃ showed excellent performance in terms of CO₂ conversion and space-time yield of light hydrocarbons, attaining 45% conversion and 6.46 mmol/(g_{cat}·h) yield at 11 bar and 400 °C. Under these reaction conditions, selectivity towards C₂+ hydrocarbons was 46%, which was the highest selectivity achieved among the five tested catalysts.

The effect of different support (Al₂O₃, Al₂O₃-CeO₂) promoter (K, Na, Cu, Ru), and active phase (Fe-Cu, Fe-Co) were investigated for improving CO₂ conversion and C₂+ STY. Though all the catalysts showed high selectivity toward the C₁ product, either CO or CH₄, CO₂ conversion was still maintained at high levels. Also, it provided various ways for future investigations on improving C₂+ selectivity.

The effects of H₂/CO₂ ratio, GHSV, temperature, and pressure were examined on direct CO₂ hydrogenation to light hydrocarbons over the baseline catalyst, 7.8%K/Fe₂O₃-Al₂O₃ catalysts. The effect of the H₂/CO₂ ratio was initially investigated

using 3.6%K/Fe₂O₃-Al₂O₃ catalysts. A decrease in the ratio led to reduced CO₂ conversion, while optimal C₂⁺ selectivity was observed in the range of ratios 3-4, with a ratio of 4 achieving the highest CO₂ conversion.

The influence of GHSV on catalyst performance was evaluated. An increase in GHSV resulted in a slight decrease in CO₂ conversion and a significant drop in C₂⁺ selectivity. At 1000 mL/(g_{cat}·h), the catalyst demonstrated excellent performance, achieving 50% CO₂ conversion, 53% selectivity toward C₂⁺ hydrocarbons, and a space-time yield of 7.72 mmol/(g_{cat}·h) at 11 bar and 400 °C.

Subsequently, the effect of temperature was investigated. Lowering the temperature led to a decrease in both CO₂ conversion and C₂⁺ selectivity. Optimal performance was observed at 425°C, with 49% conversion, 34% C₂⁺ selectivity, and a space-time yield of 4.47 mmol/(g_{cat}·h) at 11 bar.

Finally, the impact of pressure was assessed. The catalyst maintained stable CO₂ conversion across the 4-12 bar range; however, both C₂⁺ selectivity and space-time yield declined with decreasing pressure, with the best selectivity achieved at 11 bar.

Overall, these findings highlight the strong potential of RME-synthesized 7.8%K/Fe₂O₃-Al₂O₃ catalysts for CO₂ hydrogenation, with reaction conditions playing a critical role in optimizing product distribution and yield. H₂/CO₂ ratio, fine-tuning GHSV, temperature, and pressure can effectively steer the reaction toward higher selectivity and productivity of light hydrocarbons, paving the way for more efficient

catalytic processes in CO₂ utilization, making it a promising candidate for further optimization to enhance conversion and selectivity.

7.2 Future work

There are several factors that affect FT synthesis, such as reactor design, operation conditions, and catalyst type. Among the catalyst factors, the material of the promoter, active phase, and support can influence the product selectivity. Future work can investigate more promoters with different concentrations, like manganese (Mn) or magnesium (Mg), and different types of support, such as silicon dioxide (SiO₂) or Titanium dioxide (TiO₂).

Achieving high chain growth and high conversion rates can be conflicting goals due to the poisoning of the catalyst by growing hydrocarbon chains. A dual reaction center model can be developed, which suggests that having two types of active sites on the catalyst can improve the efficiency of the reaction. This model could help maintain high conversion rates while also producing longer hydrocarbons, addressing the issue of catalyst poisoning.

Future research might investigate reaction mechanisms and pathways of the FT synthesis by density functional theory (DFT) analysis. Surface morphology and promoter elements (e.g., K, Na, Ru) should be studied to determine their effects on CO activation and C-C coupling pathways. Furthermore, combining DFT data with machine learning algorithms might greatly speed up the prediction of catalyst behavior

across compositional regions. Finally, experimental confirmation of DFT-predicted trends is strongly urged to improve the theoretical work's real-world relevance.

References

1. Hashimoto, K. and K. Hashimoto, *Global temperature and atmospheric carbon dioxide concentration*. Global carbon dioxide recycling: for global sustainable development by renewable energy, 2019: p. 5-17.
2. <https://www.globalchange.gov/indicators/atmospheric-carbon-dioxide>.
3. Moreaux, M., et al., *Carbon capture: Storage vs. utilization*. Journal of Environmental Economics and Management, 2024. **125**: p. 102976.
4. Mango, F.D., *The light hydrocarbons in petroleum: a critical review*. Organic Geochemistry, 1997. **26**(7-8): p. 417-440.
5. Karakaya, C. and J. Parks II, *Thermochemical processes for CO₂ hydrogenation to fuels and chemicals: Challenges and opportunities*. Applications in Energy and Combustion Science, 2023. **15**: p. 100171.
6. Zhang, J., et al., *Photocatalytic CO₂ reduction reaction: Influencing factors, reaction pathways and dominant catalysts*. Separation and Purification Technology, 2024. **328**: p. 125056.
7. Fan, Q., et al., *Electrochemical CO₂ reduction to C₂+ species: heterogeneous electrocatalysts, reaction pathways, and optimization strategies*. Materials today energy, 2018. **10**: p. 280-301.
8. Shi, J., et al., *Enzymatic conversion of carbon dioxide*. Chemical Society Reviews, 2015. **44**(17): p. 5981-6000.
9. Markvoort, A.J., et al., *Kinetics of the Fischer–Tropsch reaction*. Angewandte Chemie-International Edition, 2012. **51**(36): p. 9015.
10. Jia, J.-Y., et al., *Review of iron-based catalysts for carbon dioxide fischer–tropsch synthesis*. Transactions of Tianjin University, 2024. **30**(2): p. 178-197.
11. De, S., et al., *Advances in the design of heterogeneous catalysts and thermocatalytic processes for CO₂ utilization*. Acs Catalysis, 2020. **10**(23): p. 14147-14185.
12. Tavares, M., et al., *Modified fischer-tropsch synthesis: A review of highly selective catalysts for yielding olefins and higher hydrocarbons*. Frontiers in Nanotechnology, 2022. **4**: p. 978358.
13. Ding, F., et al., *CO₂ Hydrogenation to Hydrocarbons over Iron-based Catalyst: Effects of Physicochemical Properties of Al₂O₃ Supports*. Industrial & Engineering Chemistry Research, 2014. **53**(45): p. 17563-17569.
14. Farias, F., et al., *Effect of K promoter on the structure and catalytic behavior of supported iron-based catalysts in Fischer-Tropsch synthesis*. Brazilian Journal of Chemical Engineering, 2011. **28**: p. 495-504.
15. Liang, B., et al., *Effect of Na promoter on Fe-based catalyst for CO₂ hydrogenation to alkenes*. ACS Sustainable Chemistry & Engineering, 2018. **7**(1): p. 925-932.
16. Hwang, S.-M., et al., *Mechanistic insights into Cu and K promoted Fe-catalyzed production of liquid hydrocarbons via CO₂ hydrogenation*. Journal of CO₂ Utilization, 2019. **34**: p. 522-532.

17. Kim, K.Y., et al., *Cobalt ferrite nanoparticles to form a catalytic Co–Fe alloy carbide phase for selective CO₂ hydrogenation to light olefins*. *Acs Catalysis*, 2020. **10**(15): p. 8660-8671.
18. Khangale, P.R., R. Meijboom, and K. Jalama, *CO₂ hydrogenation to liquid hydrocarbons via modified Fischer–Tropsch over alumina-supported cobalt catalysts: Effect of operating temperature, pressure and potassium loading*. *Journal of CO₂ Utilization*, 2020. **41**: p. 101268.
19. Sathawong, R., et al., *Bimetallic Fe–Co catalysts for CO₂ hydrogenation to higher hydrocarbons*. *Journal of CO₂ Utilization*, 2013. **3**: p. 102-106.
20. Wang, W., et al., *Fe–Cu bimetallic catalysts for selective CO₂ hydrogenation to olefin-rich C₂+ hydrocarbons*. *Industrial & Engineering Chemistry Research*, 2018. **57**(13): p. 4535-4542.
21. Zhang, L., et al., *The rare earth elements modified FeK/Al₂O₃ catalysts for direct CO₂ hydrogenation to liquid hydrocarbons*. *Catalysis Today*, 2020. **356**: p. 613-621.
22. Malik, M.A., M.Y. Wani, and M.A. Hashim, *Microemulsion method: A novel route to synthesize organic and inorganic nanomaterials: 1st Nano Update*. *Arabian journal of Chemistry*, 2012. **5**(4): p. 397-417.
23. Eriksson, S., et al., *Preparation of catalysts from microemulsions and their applications in heterogeneous catalysis*. *Applied Catalysis A: General*, 2004. **265**(2): p. 207-219.
24. Monshi, A., M.R. Foroughi, and M.R. Monshi, *Modified Scherrer equation to estimate more accurately nano-crystallite size using XRD*. *World journal of nano science and engineering*, 2012. **2**(3): p. 154-160.
25. Khan, S.R., et al., *Inductively coupled plasma optical emission spectrometry (ICP-OES): a powerful analytical technique for elemental analysis*. *Food Analytical Methods*, 2022: p. 1-23.
26. *Chapter 11 Temperature programmed reduction and sulphiding*, in *Studies in Surface Science and Catalysis*, J.A. Moulijn, P.W.N.M. van Leeuwen, and R.A. van Santen, Editors. 1993, Elsevier. p. 401-417.
27. Anderson, R.B., *Modifications of the Brunauer, Emmett and Teller equation I*. *Journal of the American Chemical Society*, 1946. **68**(4): p. 686-691.
28. Kannan, M., *Transmission electron microscope—Principle, components and applications*. A textbook on fundamentals and applications of nanotechnology, 2018: p. 93-102.
29. Saadatkhah, N., et al., *Experimental methods in chemical engineering: Thermogravimetric analysis—TGA*. *The Canadian Journal of Chemical Engineering*, 2020. **98**(1): p. 34-43.
30. Crowder, J., et al., *Infrared methods for gas detection*. *Mid-Infrared Semiconductor Optoelectronics*, 2006: p. 595-613.
31. Regmi, B.P. and M. Agah, *Micro Gas Chromatography: An Overview of Critical Components and Their Integration*. *Analytical Chemistry*, 2018. **90**(22): p. 13133-13150.

32. Hoque, M.A., et al., *Chemical State of Potassium on the Surface of Iron Oxides: Effects of Potassium Precursor Concentration and Calcination Temperature*. Materials, 2022. **15**(20): p. 7378.
33. Kharlanov, A., G. Pankina, and V. Lunin, *Physicochemical Properties of Potassium-Promoted Fe-Containing Catalysts for the Hydrogenation of CO over Magnesium Aluminum Spinels: IR Spectroscopy*. Russian Journal of Physical Chemistry A, 2019. **93**: p. 2356-2364.
34. Han, X., et al., *Interface-Induced Phase Evolution and Spatial Distribution of Fe-Based Catalysts for Fischer–Tropsch Synthesis*. ACS Catalysis, 2023. **13**(10): p. 6525-6535.
35. Zieliński, J., et al., *Reduction of Fe₂O₃ with hydrogen*. Applied Catalysis A: General, 2010. **381**(1): p. 191-196.
36. Sai Prasad, P., et al., *Fischer–Tropsch synthesis by carbon dioxide hydrogenation on Fe-based catalysts*. Catalysis surveys from Asia, 2008. **12**: p. 170-183.
37. Fan, S., et al., *Confined Complexation Induced Size Control of Fe/Fe₂O₃/Fe₅C₂ Multicomponent Nanoparticles Embedded in Fe, N-Doped Mesoporous Carbon toward Efficient Oxygen Electrocatalysis*. ACS Sustainable Chemistry & Engineering, 2025.
38. Chang, H., et al., *Effects of Potassium Loading over Iron–Silica Interaction, Phase Evolution and Catalytic Behavior of Precipitated Iron-Based Catalysts for Fischer-Tropsch Synthesis*. Catalysts, 2022. **12**(8): p. 916.
39. Yang, C., et al., *Fe₅C₂ nanoparticles: a facile bromide-induced synthesis and as an active phase for Fischer–Tropsch synthesis*. Journal of the American Chemical Society, 2012. **134**(38): p. 15814-15821.
40. Warringham, R., et al., *Examining the temporal behavior of the hydrocarbonaceous overlayer on an iron based Fischer–Tropsch catalyst*. RSC advances, 2019. **9**(5): p. 2608-2617.
41. Liang, B., et al., *Effect of Na Promoter on Fe-Based Catalyst for CO₂ Hydrogenation to Alkenes*. ACS Sustainable Chemistry & Engineering, 2019. **7**(1): p. 925-932.
42. Aitbekova, A., et al., *Low-Temperature Restructuring of CeO₂-Supported Ru Nanoparticles Determines Selectivity in CO₂ Catalytic Reduction*. Journal of the American Chemical Society, 2018. **140**(42): p. 13736-13745.
43. Riedel, T., et al., *Comparative study of Fischer–Tropsch synthesis with H₂/CO and H₂/CO₂ syngas using Fe- and Co-based catalysts*. Applied Catalysis A: General, 1999. **186**(1): p. 201-213.
44. Ebrahimi, P., A. Kumar, and M. Khraisheh, *A Review of CeO₂ Supported Catalysts for CO₂ Reduction to CO through the Reverse Water Gas Shift Reaction*. Catalysts, 2022. **12**(10): p. 1101.
45. Dry, M.E. and G.J. Oosthuizen, *The correlation between catalyst surface basicity and hydrocarbon selectivity in the Fischer-Tropsch synthesis*. Journal of Catalysis, 1968. **11**(1): p. 18-24.

46. Wei, J., et al., *New insights into the effect of sodium on Fe₃O₄-based nanocatalysts for CO₂ hydrogenation to light olefins*. Catalysis Science & Technology, 2016. **6**(13): p. 4786-4793.
47. Heikkinen, N., et al., *Production of C₂– C₄ Olefins with Fischer-Tropsch-Synthesis: The Effect of Cu Promoter Loading on an Fe– Cu– K/SiO₂ Catalyst*. ChemCatChem, 2024. **16**(19): p. e202400560.
48. Moiola, E., N. Gallandat, and A. Züttel, *Parametric sensitivity in the Sabatier reaction over Ru/Al₂O₃—theoretical determination of the minimal requirements for reactor activation*. Reaction Chemistry & Engineering, 2019. **4**(1): p. 100-111.
49. Sarkari, M., F. Fazlollahi, and H. Atashi, *Fischer Tropsch Synthesis: The Promoter Effects, Operating Conditions, and Reactor Synthesis*. 2012. **10**(1).
50. Quílez-Pardo, J. and J.J. Solaz-Portolés, *Students' and teachers' misapplication of Le Chatelier's principle: Implications for the teaching of chemical equilibrium*. Journal of Research in Science teaching, 1995. **32**(9): p. 939-957.
51. Dry, M.E., *Practical and theoretical aspects of the catalytic Fischer-Tropsch process*. Applied Catalysis A: General, 1996. **138**(2): p. 319-344.
52. Khan, M.K., et al., *Selective conversion of carbon dioxide into liquid hydrocarbons and long-chain α -olefins over Fe-Amorphous AlO_x bifunctional catalysts*. Acs Catalysis, 2020. **10**(18): p. 10325-10338.