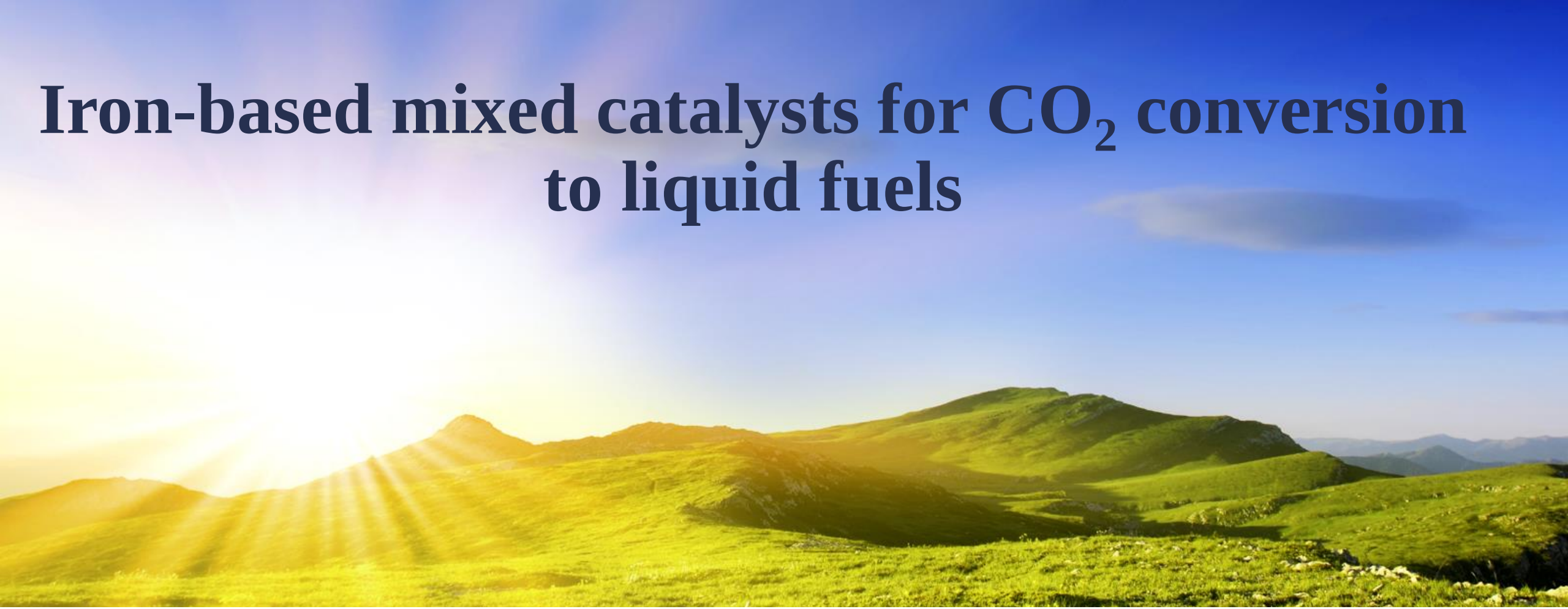
Iron-based mixed catalysts for CO_2 conversion to liquid fuels



Hungarian Catalysis Society

Presented by: Ali Shan Malik (Ph.D.)
(Postdoctoral Fellow - Prof. Andras Sapi's Research Group)
Department of Applied & Environmental Chemistry, Szeged University, Szeged

Agenda

- Profile Summary
- Current Research Overview
- Research Introduction
- Experimental Design
- Catalyst Performance Evaluation
- Catalyst Characterization

Ali Shan Malik Ph.D.

Postdoctoral Fellow

Profile Summary

Solution-oriented chemical engineer/research scientist backed by experience of over 06 years in collaborative (Industry & Academic) research in

- Applied heterogeneous catalysis
- Kinetics studies
- Materials characterization via advanced tools with strong expertise in spectroscopies (e.g., in situ DRIFTS and XPS) and TEM/STEM
- Structure-activity relationships, and reaction mechanisms leading to successful investigation of novel materials for direct CO_2 conversion into methanol, dimethyl ether and C_{5+} hydrocarbons
- And over 10 years in project & resource management, process optimization and knowledge of industry

Current Affiliation & Research Team: At present, working in Prof. Andras research group at Szeged University on CO_2 Conversion to C_{5+} hydrocarbons and process scale up; involved in catalyst synthesis, characterization and catalyst performance evaluation

Previous Affiliations: Worked with Prof. Maguy Research Group at Khalifa University, UAE and with Prof. M. A, Daous at King Abdulaziz University, KSA.

Prof. Andras Sapi
Assistant Professor
Department of Applied and Environmental Chemistry, Szeged University, Hungary

Dr Sara Najari
Postdoctoral Fellow
Szeged University

Henrik Bali
PhD Student
Szeged University

CO_2 Conversion to Liquid Hydrocarbons

Motivation

- ✓CO_2 – an important C_1 building block – possesses great potential to be used as a feedstock for a variety of fuels and chemicals
- ✓Turning CO_2 into liquid hydrocarbons is highly interesting due to higher energy densities and greater economic benefits
- ✓Reduction in greenhouse gas emission addressing global warming concerns
- ✓An alternative to depleting fossil fuel sources

CO_2 Conversion to Liquid Hydrocarbons

Challenges

- ✓ CO_2 is a highly oxidized, less reactive and thermodynamically stable molecule ($\Delta G° \sim -394$ kJ/mol)
- ✓ Turning CO_2 into high-value hydrocarbons (HCs) – mostly C_{5+} HCs is relatively more challenging due to the high barrier associated with the C–C coupling, low selectivity due to C_1 products and poor stability

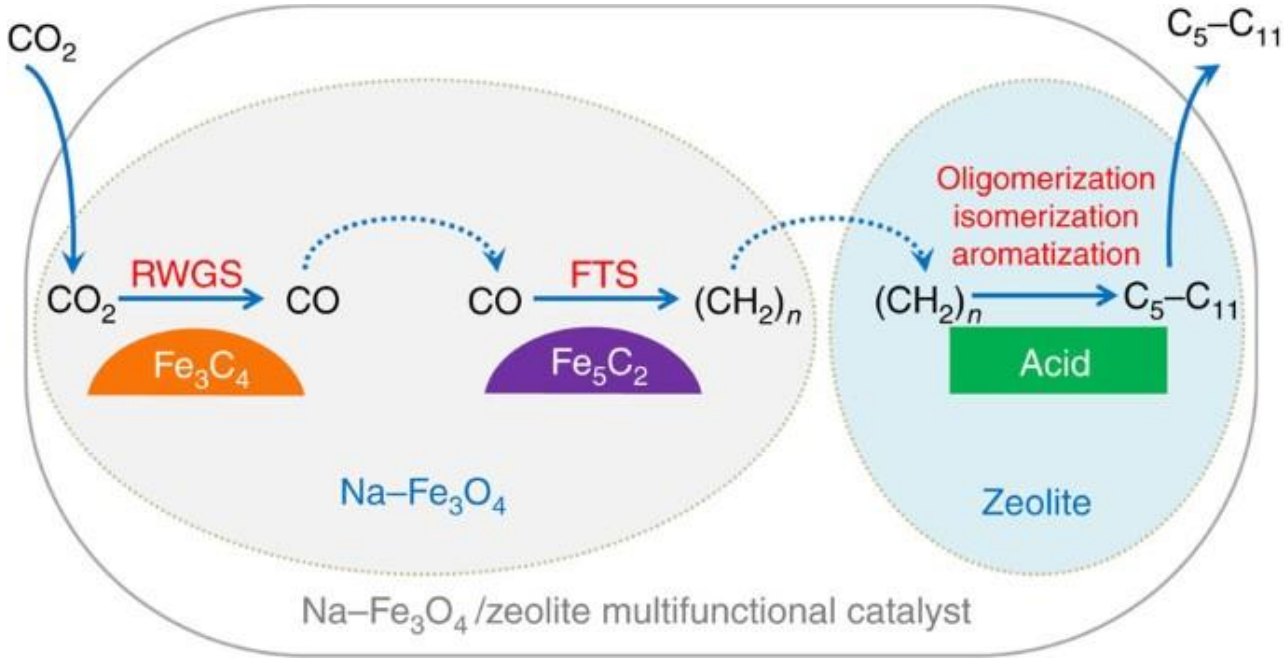
Key Actions

- ✓ Efficient materials design strategies; tandem catalysis approach
- ✓ Deeper insight of the structure sensitivity, role of active sites and promoters
- ✓ Proximity effects of multi-active sites; Efficient catalyst design brings opportunities to improve catalytic activity and selectivity for CO_2 conversion by tuning the key adjustable factors such as active metals, supports, promoters, preparation procedures and many others

CO_2 Conversion to Liquid Hydrocarbons

Scale up Processes

✓First demonstration plant producing gasoline range HCs of around 1000 tons/year capacity has been successfully developed in China in March 2022.



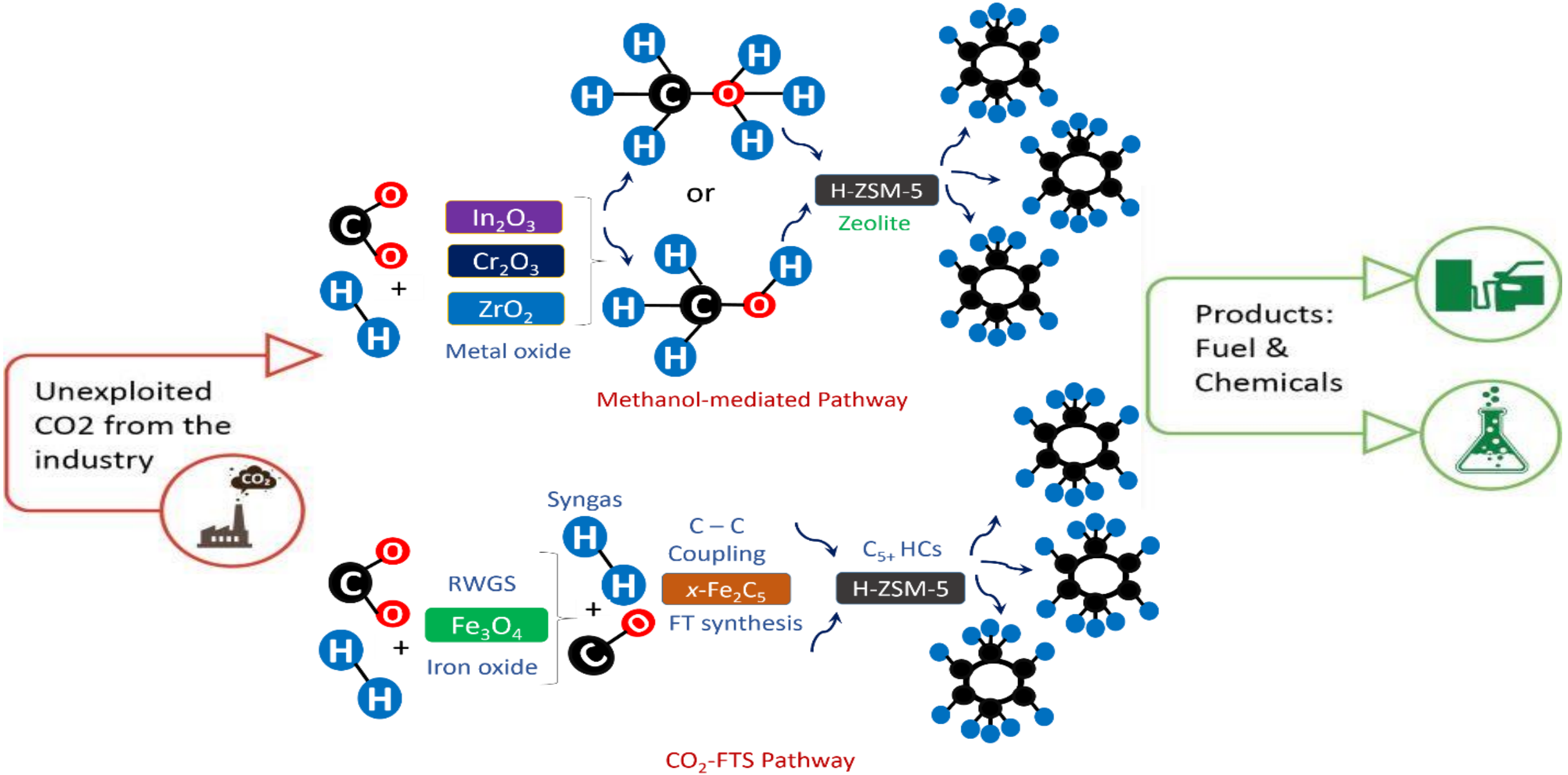
A pilot-scale demonstration of kiloton gasoline-ranged hydro-carbons synthesis represented by aromatics and isoparaffins per year via CO_2 hydrogenation.

Table 1: Recent studies with catalyst systems for conversion of CO_2 to C_{5+} hydrocarbons.

Catalysts	CO_2 Conv. (%)	CO Sel. (%)	CH Sel. (%)	Hydrocarbon Distribution (%)[a] CH_4	C_2–C_4^0	C_2–$C_4^=$	C_{5+}	GHSV ml g^{-1} h^{-1}	T/°C	P/MPa	Ref.
C_{5+} hydrocarbons based on methanol reaction mechanism											
In_2O_3/HZSM-5	13.1	44.8	-	1.0	-	-	78.6	9000	340	3.0	26
InCo/Zn-HBeta	15.0	36.0	61.0	4.0	-	-	80.0	-	300	5.0	27
Ae–ZnO–ZrO_2(1:8)/Z5	16.0	34.3	65.7	0.3	12.8	6.6	80.3	7200	340	4.0	28
$ZnAlO_x$ and HZSM-5	9.1	57.4	42.6	0.5	6.7	10.7	80.3	2000	320	3.0	29
ZnZrO/HZSM-5	14.1	43.7	57.3	0.3	14.5	4.9	80.3	1200	320	4.0	16
Cr_2O_3/HZSM-5	33.6	41.2	-	3.0	15.7	3.1	78.2	1200	350	3.0	30
Fe–Zn–Zr@HZSM–5–HY	14.2	40.5	59.3	1.8	55.5		33.7	3000	340	5.0	31
Cr_2O_3/Zn-H-ZSM-5@SiO_2	22.1	35.1	-	2.9	19.1	8.0	70.0	1200	350	3.0	32
ZnCrOx/ZnZSM-5	30.5	60.8	39.2	-	-	-	58.0	2000	350	5.0	33
C_{5+} hydrocarbons based on CO_2 modified FTS mechanism											
FeZnK – NC	34.6	21.2	78.8	24.2	7.1	40.6	28.1	7200	320	3.0	34
Fe – 2K	30.0	22.0	74.0	31.1	14.9	32.4	21.6	-	320	2.0	35
$CuFeO_2$ − 24	16.7	31.4	-	2.4	-	-	64.9	1800	300	1.0	36
Na – CoCu/TiO_2	18.4	30.2	-	26.1	-	-	42.1	3000	250	5.0	37
10Fe0.8K0.53Co	54.6	2.0	98.0	19.3	7.8	24.9	48.0	560	300	2.5	38
Na – Fe_3O_4/HZSM-5	22.0	20.1	-	4.0	-	-	79.4	4000	320	3.0	41
10Fe4.8K	35.2	9.0	91.0	8.1	4.3	16.4	71.2	560	300	2.5	38
Fe – Cu-K – La/TiO_2	23.1	33.0	67.0	19.4	-	-	67.2	3600	300	1.1	42
92.6Fe7.4K	41.7	6.0	94.0	10.9	23.0	6.5	59.6	560	300	2.5	43
ZnFeOx–4.25Na/S–HZSM	36.2	11.0	89.0	8.2	13.3	3.2	75.4	4000	320	3.0	44
Fe_5C_2–10K/a–Al_2O_3	43.9	17.2	-	38.6	38.2		23.2	4000	320	3.0	45
Fe – Zn – Zr@HZSM	21.5	42.4	52.4	1.4	42.8		55.8	3000	340	5.0	46
15Fe–10K/Al_2O_3/P–HZSM	36.4	10.2	-	10.9	39.6		49.5	3000	400	3.0	47
Na–Fe@C/H–ZSM–5–0.2	33.3	13.3	86.7	4.8	10.4		84.8	-	320	3.0	48
1Na – Fe/HZSM-5-150	47.4	10.1	89.9	8.2	21.8		70.0	4000	340	3.0	49
FeK1.5/HSG|HZSM – 5(50)	45.0	20.0	80.0	2.8	4.2		93.0	14000	340	3.0	50

[a] The hydrocarbon distribution was calculated without CO

CO_2 Conversion to Liquid Hydrocarbons



Research Work

Catalytic Conversion of CO2 to liquid hydrocarbons via efficient catalyst design and development

Purpose of Research

Novel Catalyst Design
Improvement in CO2 conversion and selectivity
Contribution to the scientific knowledge in the area of nanocatalysis and its applications in CO2 hydrogenation process
Identification of reaction mechanism

Industrial Significance

Economic and Global Impact
Cheap Energy and Transportation Fuels
Minimizing dependence on fossil fuels
Utilizing Current Industry Infrastructure

Research Introduction

CO2 as Primary Feedstock
Catalyst development for direct CO2 conversion to liquid
Scale up of Operation

Current Research

FeZnCe Project

NaFe Project
Fe Carbide Project

1

High performance catalyst screening

- In-depth literature review
- Fe-based catalyst are superior
- Great potential for scale up

2

Catalyst Synthesis

- 1g to 20g catalyst was successfully prepared via Co-precipitation/sol gel method

3

Evaluation of Operating Conditions

- Temperature and Pressure
- Flowrate, GHSV
- Catalyst weight, mesh size and bed configuration

4

Statistical Design of Experiment

- Based on the upper and lower limit of operating conditions statistical design of experiments will be generated

5

Catalyst Performance evaluation

- Experiments will be conducted over a wide range of operating conditions based on SDE and data will be gathered and analyzed

6

Optimization of the operating conditions to maximize yield

- Data of SDE will be analyzed and based on that product yield will be maximized

Catalyst Design and Selection of Active Component

Active Component

Fe was chosen as an active component as both of its oxides Fe_2O_3 and Fe_3O_4 are found to be very active for CO_2 conversion to higher HCs

Promoters

- Zn and K were chosen as promoters owing to their excellent contribution to Fe-based catalyst for CO_2 conversion.
- Addition of zinc to iron matrix forms $ZnFe_2O_4$ spinel phase and ZnO phase, increasing of the surface area and enhances the interaction between iron and zinc thereby altering the reduction and CO_2 adsorption behaviors.
- Potassium, on the other hand, improves the product distribution of higher hydrocarbons.

Support

CeO_2 as a support was selected based on its excellent CO_2 adsorption and activation affinity and ability to generate oxygen vacancies which improves the CO_2 conversion

Catalyst Synthesis and Pretreatment

A series of FeZn and K-promoted FeZn catalysts supported over mesoporous CeO_2 were prepared via Sol-gel Chelatization method using citric acid as a chelating agent

Catalyst	Fe (wt. %)	Zn (wt. %)	K (wt. %)	CeO_2 (wt. %)
$20F/CeO_2$	20.0	0.0	0.0	80.0
$20Fe5Zn/CeO_2$	20.0	5.0	0.0	75.0
$20Fe10Zn/CeO_2$	20.0	10.0	0.0	70.0
$1K20Fe5Zn/CeO_2$	20.0	5.0	1.0	74.0
$3K20Fe5Zn/CeO_2$	20.0	5.0	3.0	72.0
$5K20Fe5Zn/CeO_2$	20.0	5.0	5.0	70.0

Synthesis

- Calculated amount of metal salts solution were prepared and mixed with citric acid solution, heated at 110 ^oC with continuous stirring to form a yellow color Gel. Later dried in an oven overnight at 80 ^oC

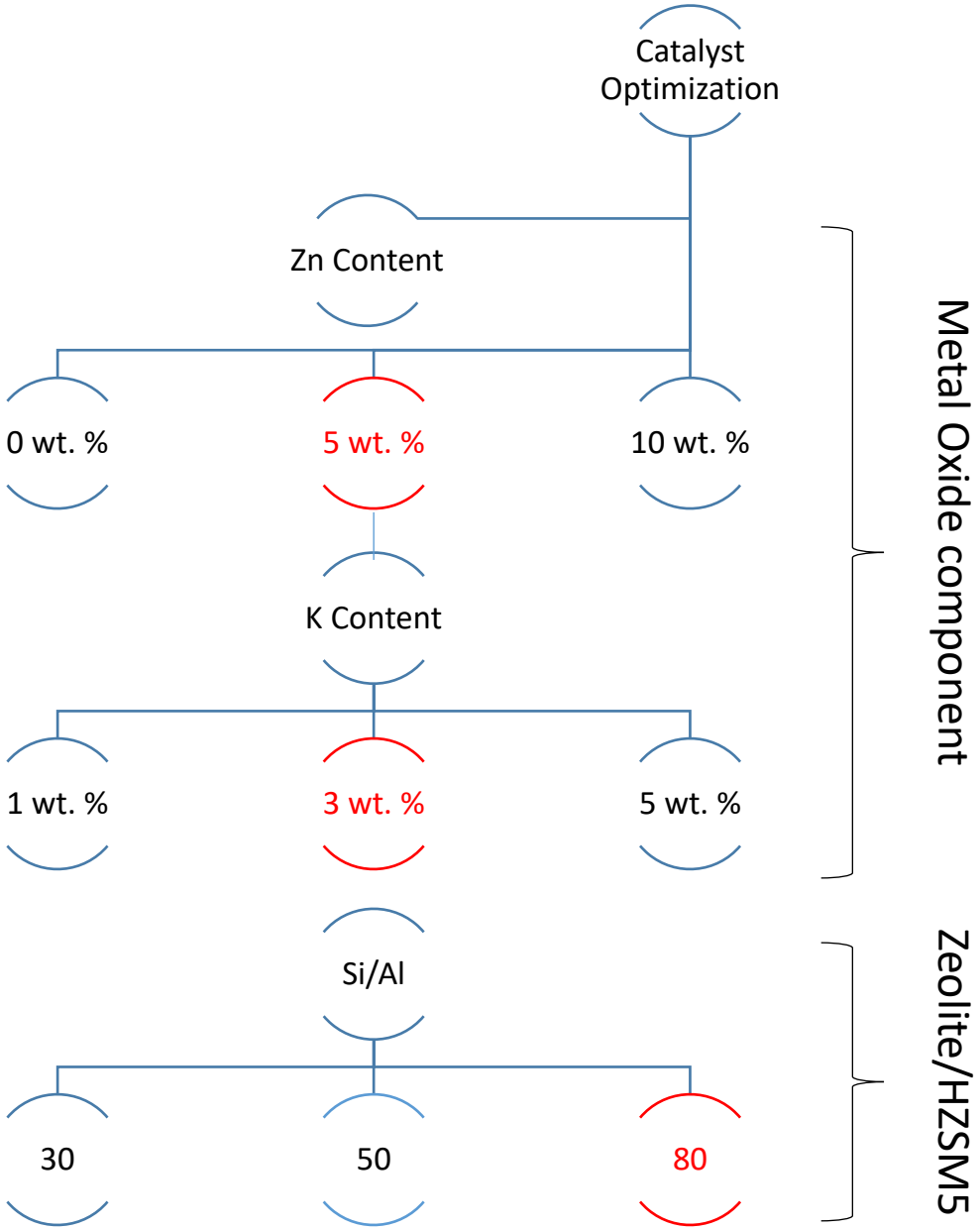
Calcination

- Catalyst samples were calcined in dry air at 500 ^oC for 5 hrs

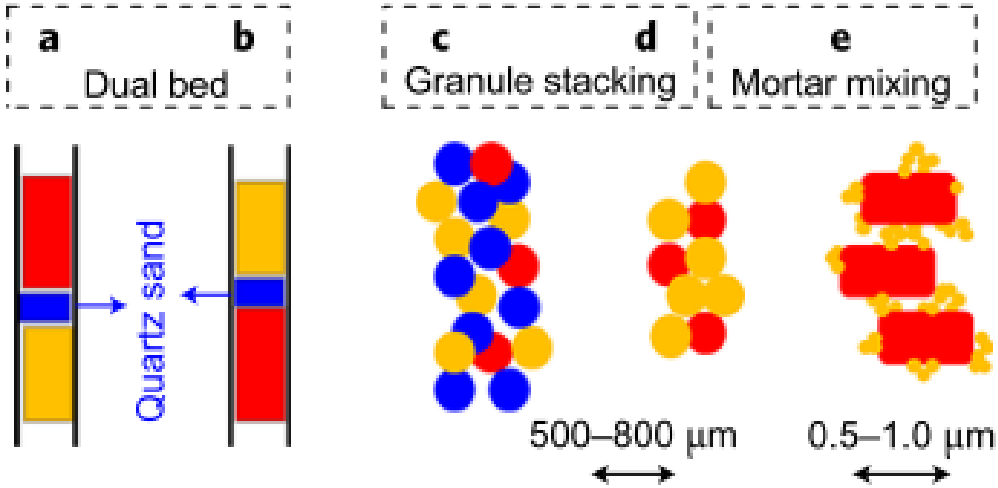
Pretreatment

- 180 mg of catalyst weight was loaded into fixed-bed reactor and reduced at 450 ^oC under pure H_2 atmosphere for 4 hrs prior reaction.

Experimental Design

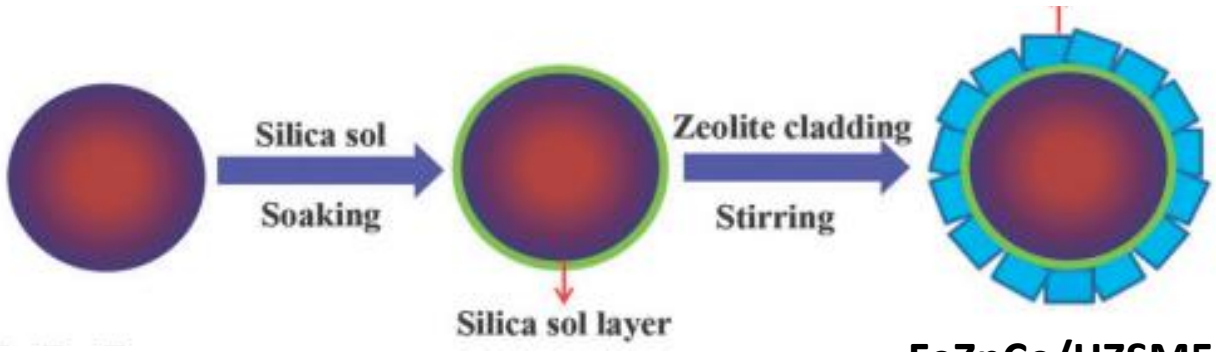


Catalyst Bed Configuration



Core-shell Configuration

ZSM-5 Crystal



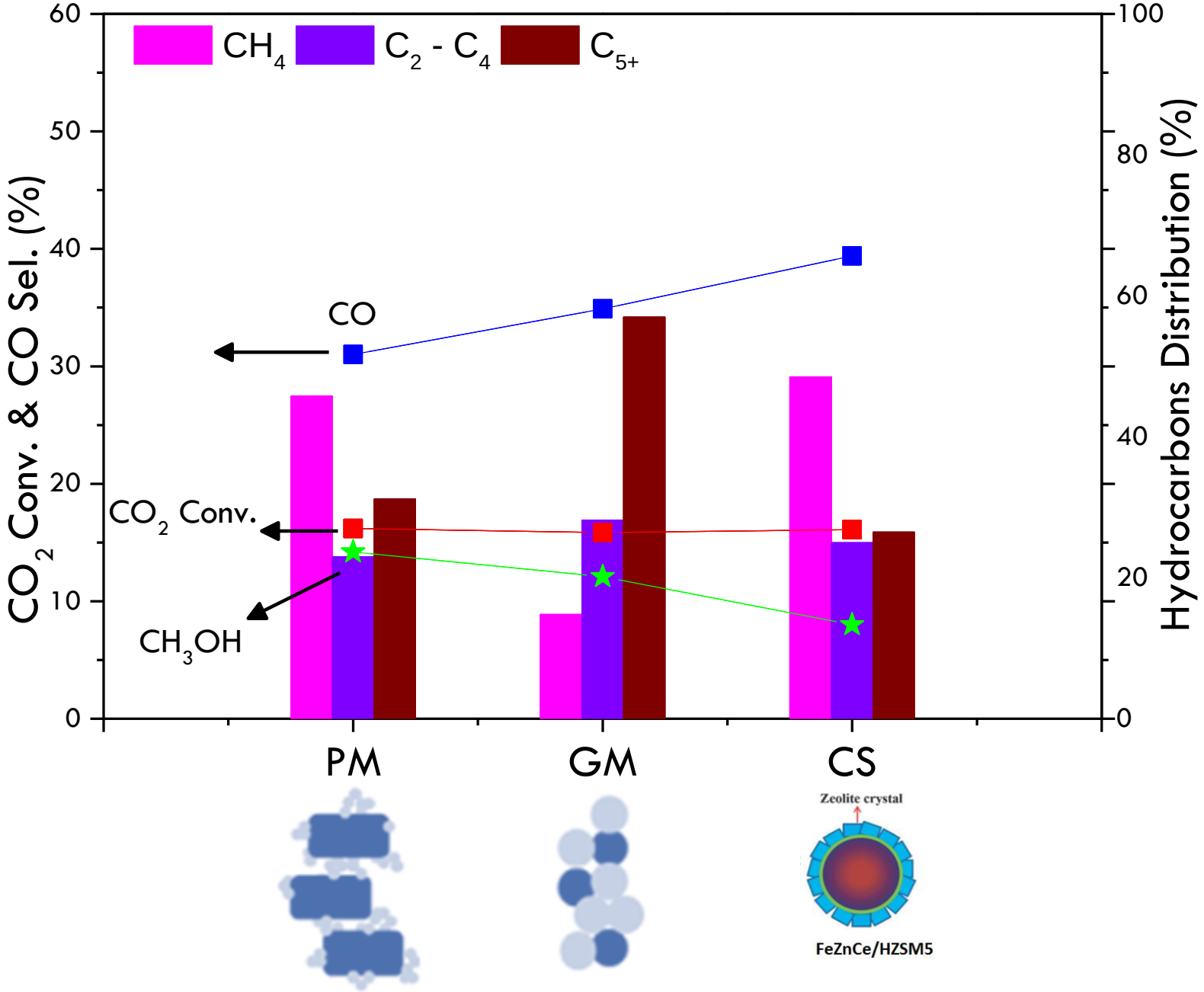
Catalyst Performance Evaluation

Catalyst	Si/Al	Configuration	T (°C)/P (bar)	X_{CO2} %	S_{CO} %	S_{CH3OH} %	S_{CH} %	Hydrocarbon Selectivity (%)		
								C_1	$C_2 - C_4$	C_{5+}
Fe/Ce	-	Pellets	340/50	16.5	48.0	0.0	52.0	42.4	9.6	0.0
Fe5Zn/Ce	-	Pellets	340/50	16.68	28.4	15.9	55.69	30.9	23.5	1.3
Fe10Zn/Ce	-	Pellets	340/50	16.14	49.0	8.01	42.99	28.6	13.4	0.79
Fe5Zn/Ce/HZSM5	150	Granule Mixing	340/50	16.20	37.5	9.4	53.1	22.6	10.7	19.8
Fe5Zn/Ce/HZSM5	80	Granule Mixing	340/50	15.85	34.9	12.1	53.0	18.3	4.3	30.4
Fe5Zn/Ce/HZSM5	50	Granule Mixing	340/50	15.35	54.7	10.4	34.9	11.7	4.1	19.1
Fe5Zn/Ce/HZSM5	30	Granule Mixing	340/50	15.2	60.1	11.1	28.8	8.52	3.6	16.6

Reaction Conditions: GHSV: 3300 mL/g.hr; Reaction Time; 3 hrs

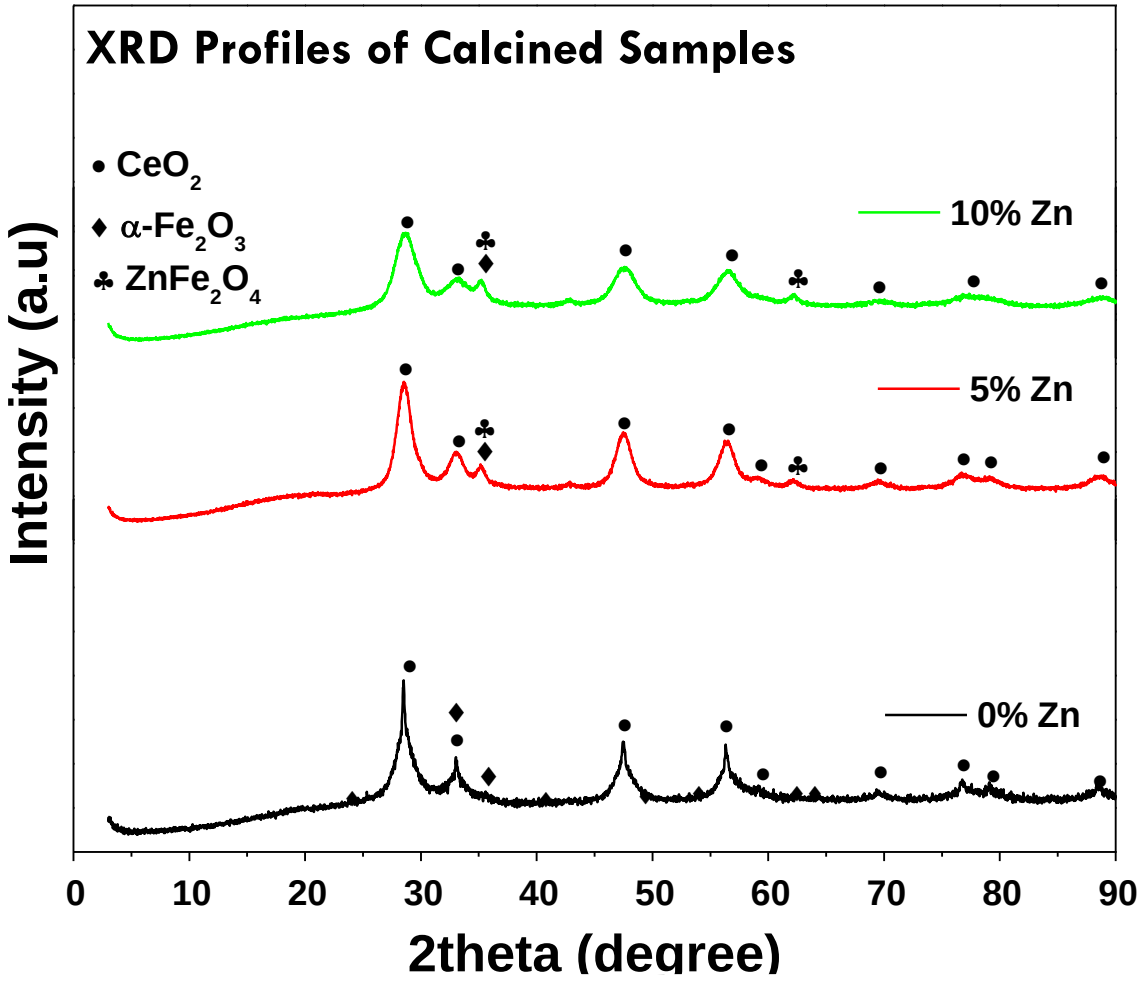
- RWGS is dominant > 300 °C; Methanol synthesis is dominant at < 300 °C
- Formed methanol further converted to hydrocarbons with zeolite addition, suppressing CO and CH_4.

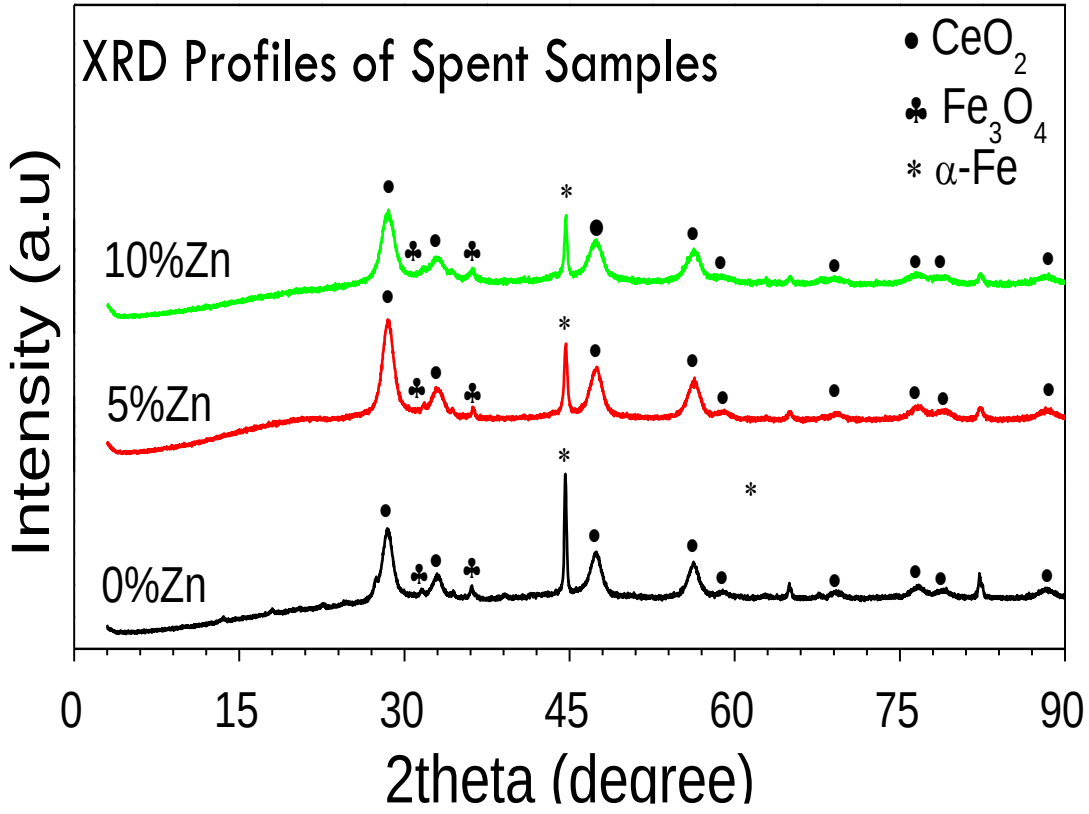
Catalyst Bed Configuration



Reaction Conditions: T: 340 °C, P: 50 bar
GHSV: 3300 mL/g.hr;
Reaction Time; 3 hrs

Catalyst Characterization

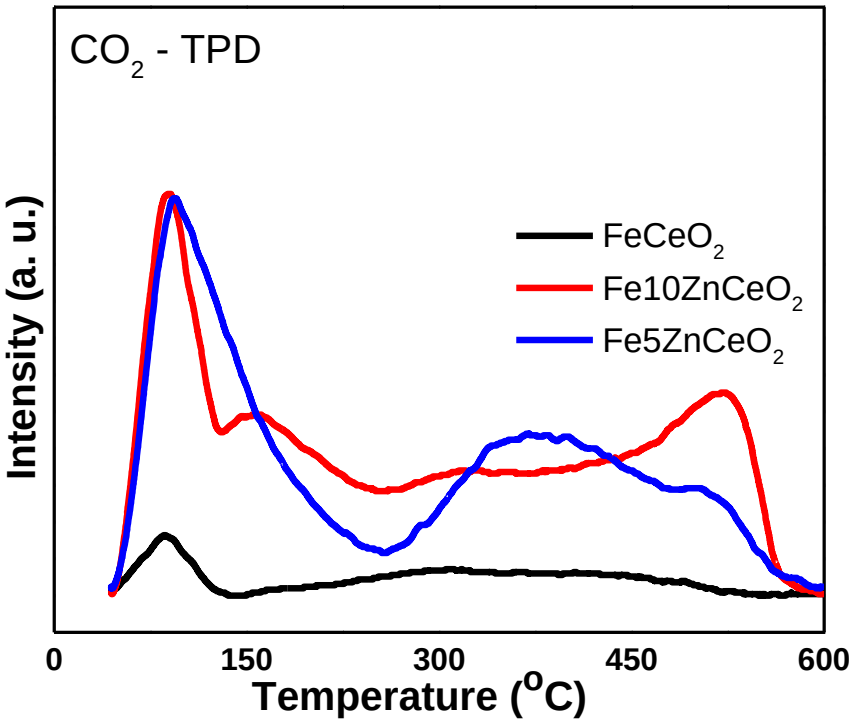


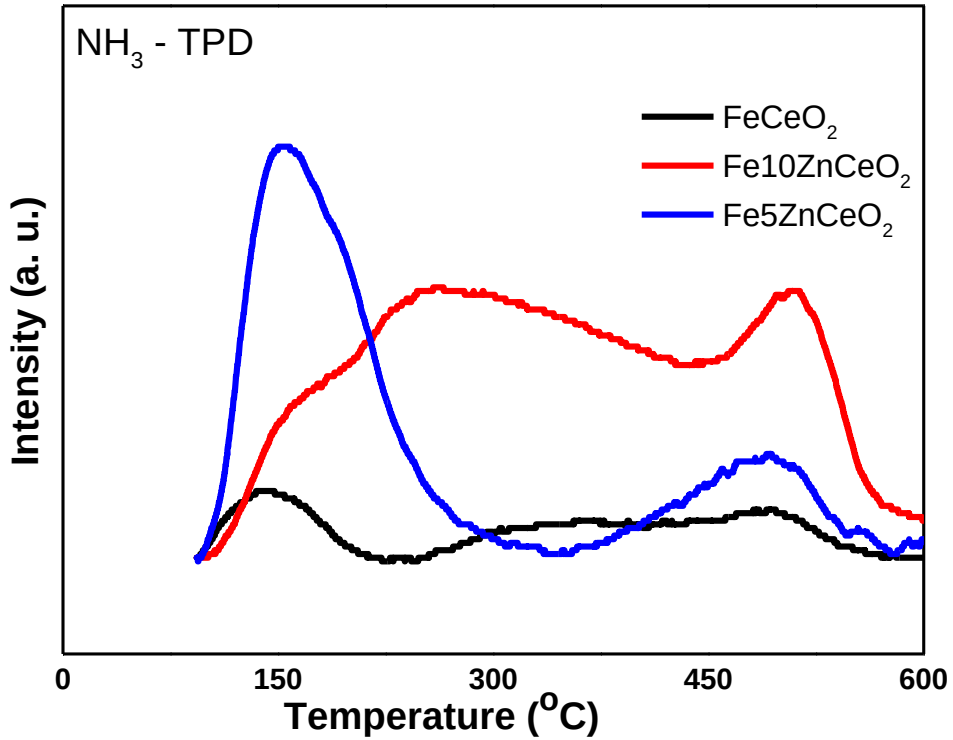


Catalyst Characterization

BET and TPD results

Catalyst	S_{BET} (m^2g^{-1})	V_p (mLg^{-1})	W_p (nm)	mmol NH_3/g	mmol CO_2/g
$20Fe/CeO_2$	51.3	0.14	11.2	0.02	0.023
$20Fe5Zn/CeO_2$	59.7	0.16	12.1	0.07	0.18
$20Fe10Zn/CeO_2$	63.34	0.17	9.9	0.13	0.15
$1K20Fe10Zn/CeO_2$	78.6	0.23	11.8		0.30
$3K20Fe10Zn/CeO_2$	70.5	0.19	10.8		0.35
$5K20Fe10Zn/CeO_2$	39.0	0.11	11.0		0.40





Research Vision & Future Plans

Short Term 1

Design and develop efficient catalytic materials and catalytic routes for highly efficient activation and conversion of CO_2 to valuable fuels and chemicals

Short Term 2

Understanding structure-performance relationships and role of active sites using advanced tools and computational modelling of energy catalysis systems to provide fundamental understandings of catalytic activation and reaction mechanism for catalyst optimization and development

Long Term 3

Explore novel reactions, approaches, and methodologies by catalysis, reaction engineering innovation, and green chemistry especially in areas of CO_2 conversion to liquid fuels

Long Term 4

Scale up the liquid fuel production process by addressing the engineering challenges associated with the process


Thank you!