Supported Iron-based Nano-materials for the Valorization of Carbon Dioxide

A. Bakratsa[1*], G. Kastrinaki[1], V. Zacharopoulou[1], G. Karagiannakis[1], V. Zaspalis[1,2]
[1]Chemical Process & Energy Resources Institute, CERTH, Thessaloniki, Greece
[2]Department of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki, Greece
* abakratsa@certh.gr

Introduction

Increased CO_2 emissions → **Global Warming** → **Solutions for reduction of CO_2 emissions** → **CO_2 Valorization** / **High added value products**

Reactions for CO_2 hydrogenation to H/C:

- Through the **Reverse Water-Gas Shift (RWGS)** CO_2 is converted into CO and then the latter is hydrogenated to (H/C) via **Fischer–Tropsch** reactions in the presence of a suitable **multifunctional catalyst**[1,2].
- In this work, supported and unsupported **iron based nanoparticles** were synthesized and characterized.
- **Iron based nanoparticles** catalyze the RWGS and the synthesis of olefins and the **acid cites** of **HZSM-5** promote the selectivity towards higher H/Cs[2].

Main CO_2 Valorization Routes (products):

CH_4 | C_2H_6 | C_3H_8 | C_3H_6 | Higher H/Cs

1.M.Liu,Y.Yi,L.Wang,H.Guo,A.Bogaerts,Catal.9275(2019).
2.Wei,Q.Ge,R.Yao,Z.Wen,C.Fang,L.Guo,H.Xu,J.Sun,Nat.Commun.816170(2017).

Methodology

SYNTHESIS PROCEDURE

Iron Based Nanoparticles

- Method: **Co-Precipitation**
- Precursors: $FeCl_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$
- Alkali promoters: **Na, K**
- Substrate: Zeolites **HZSM-5**

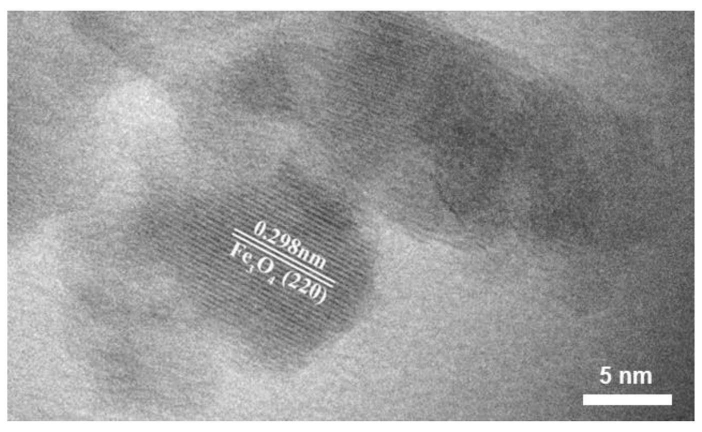

Figure 1. TEM image of a monocrystalline $Na\text{-}Fe_3O_4$ (1:1) NP.

PHYSICOCHEMICAL CHARACTERIZATION VIA: XRD, FT-IR, BET, SEM, TPD-NH_3, TEM

CATALYTIC EVALUATION:

- Continuous flow reactor
- $H_2/CO_2 = 3$
- T=320°C, P=3 MPa
- Online GC monitoring of the produced gas phase

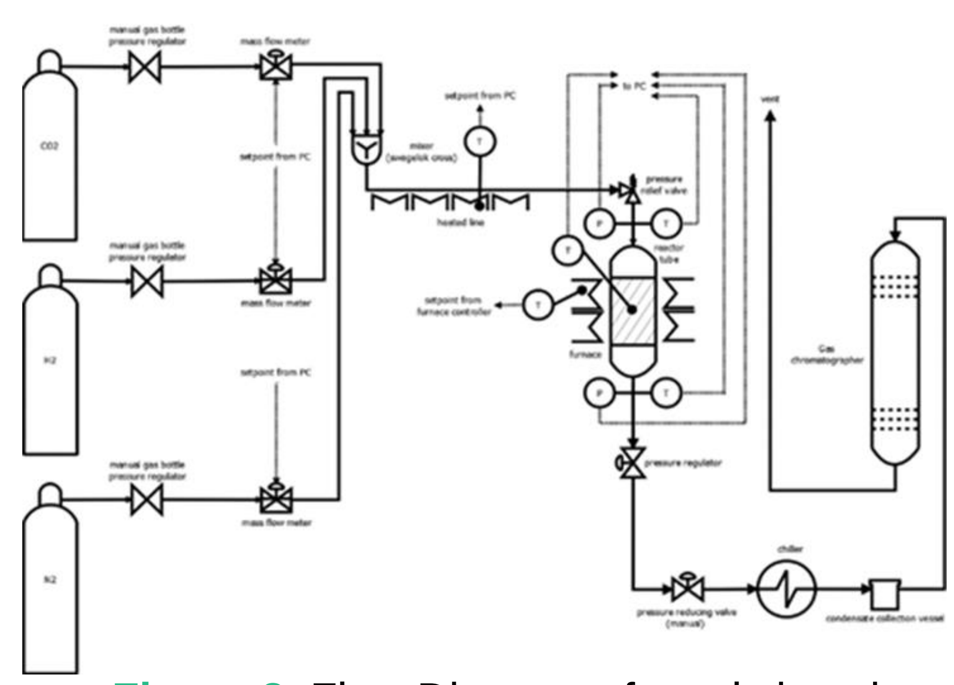

Figure 2. Flow Diagram of catalytic unit.

Physicochemical Results

BET

- The **BET surface** is **145.6**, **145.2/136.1**, **148.3/151.3** m^2/g for Fe_3O_4, $Na\text{-}Fe_3O_4$ **(1:1/1:2)** and $K\text{-}Fe_3O_4$ **(1:1/1:2)** respectively, and 409.4, **423.1** m^2/g for HZSM-5 80 SAR and **140-160 SAR**, accordingly.
- **BET analyses** indicate that the synthesized iron oxide nanoparticles obtained a surface area with values from 136 to151 m^2/g.

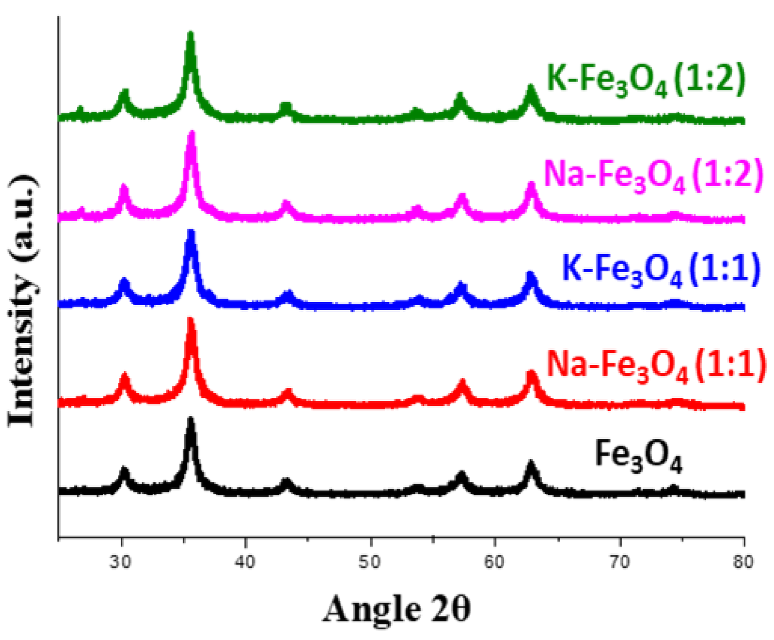

Figure 3. XRD Diffractograms of unsupported nanoparticles.

XRD

- XRD patterns confirm the crystalline structure of the iron based nanoparticles.
- Crystallite size was calculated from the Scherrer equation and found equal to 11 nm.
- The particle size calculated by TEM analysis show that the nanoparticles are monocrystalline.

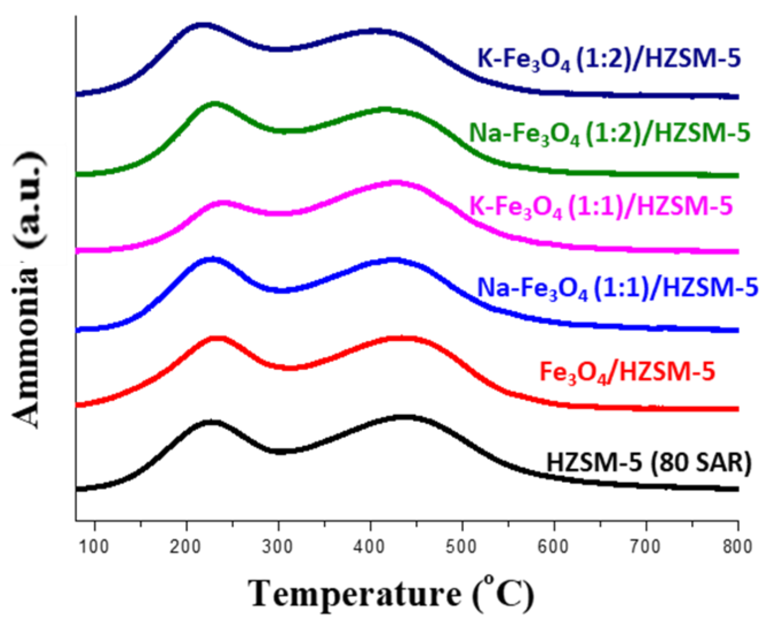

Figure 4. TPD-NH_3 Diagrams for supported nanoparticles.

TPD-NH_3

- HZSM-5 (80 SAR) show weak and strong acid sites.
- The dispersion of the nanoparticles on the HZSM-5 (80 SAR) does not affect the strength of the acid sites.
- The acidity of supported iron based nanoparticles is higher than that of the unsupported iron based nanoparticles.

Catalytic Performance

Table1. Catalytic results-Preliminary experiments*.

Catalyst	CO_2 conversion (%)	Selectivity(%)				
		CO	CH_4	C_2H_6	C_3H_6	C_3H_8
$Na\text{-}Fe_3O_4$ /HZSM-5 (80 SAR) – as synthesized	5.1	100.0	-	-	-	-
$Na\text{-}Fe_3O_4$ /HZSM-5 (80 SAR)- (4 hrs)	7.7	39.1	58.3	0.1	1.0	1.5
$Na\text{-}Fe_3O_4$ /HZSM-5 (80 SAR)-reduced (8 hrs)	7.5	37.1	59.9	0.1	1.3	1.6
$Na\text{-}Fe_3O_4$ /HZSM-5 (140-160 SAR)-reduced (4 hrs)	9.3	16.4	81.1	0.2	0.3	1.9

- C_1-C_3 **deoxygenated products**, such as **methane**, **ethane**, **propylene**, and **propane** are produced only upon **reduction** of the catalyst.
- Further reduction (8 hrs) does not improve catalytic performance.
- Over reduced $Na\text{-}Fe_3O_4$ /HZSM-5 (140-160 SAR) **CO_2 conversion** and **selectivity into methane** are improved.

*Reaction conditions: 320°C, 3 MPa, H_2/CO_2=3/1
Reduction conditions: 350°C, under H_2 flow

Conclusions

- Synthesized iron based nanoparticles have relatively high specific surface area and small crystallite size.
- The acidity of the supported samples is mainly attributed to HZSM-5.
- Medium acidity (SAR) promotes selective conversion of CO_2 into deoxygenated H/Cs with three atoms of C only upon reduction.

Acknowledgments

COST EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY
Funded by the European Union
Co-financed by Greece and the European Union
We acknowledge the support of this work by the project "PROMETHEUS: A Research Infrastructure for the Integrated Energy Chain" (MIS 5002704) which is implemented under the Action "Reinforcement of the Research and Innovation Infrastructure", funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).