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Syngas production in dry reforming of methane using phosphate-based and conventional catalysts

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OUTLINE

I. Introduction

Worldwide challenge about climate change

Synthetic gas (syngas) from biomass, bio-waste and residues

From greenhouse gases to fuel and biocommodities

Syngas Composition and end-use

II. State-of-the-art – Catalysts development

III. Phosphate catalysts production

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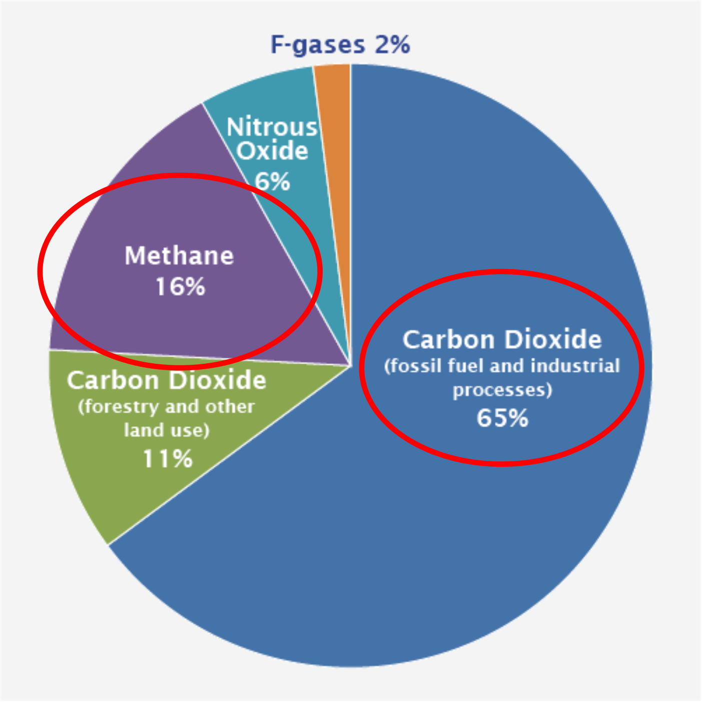
I. Introduction

Worldwide challenge about climate change

Global warming:

Main cause: Increase in greenhouse gases (GHGs) emissions due to fossil fuel combustion and industrial activities

Global greenhouse gas emissions by gas



CO_2, CH_4, NO_x, H_2O vapor, O_3

Combustion of hydrocarbons and biomass, natural gas, biogas

- CO_2 waste streams (flare, purge gas…)
- Hydrocarbons with high CO_2 contents

Dry reforming of methane (DRM)

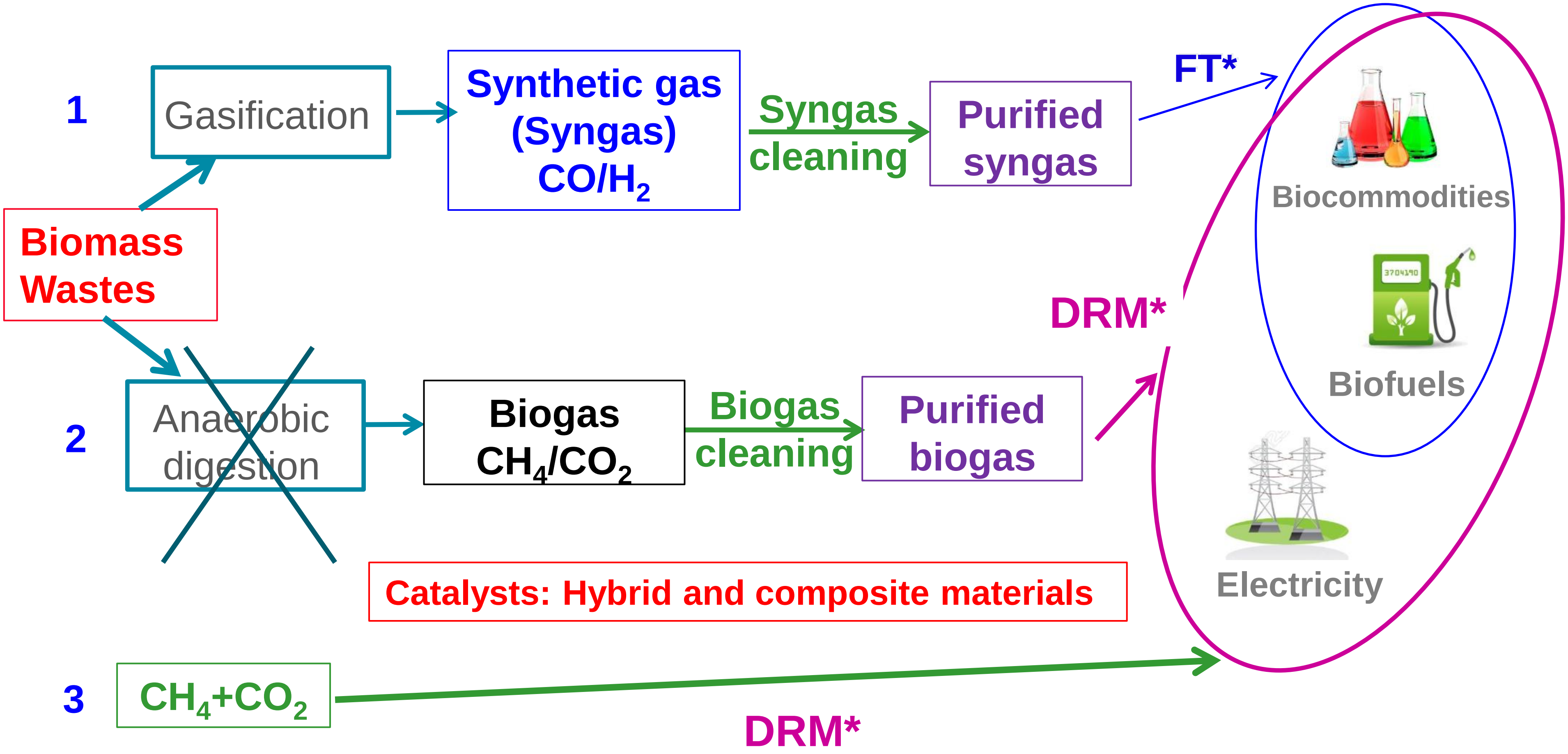
Valorization

Mitigate and/or get ride of GHGs

P. M. Mortensen *et al*, Appl. Cat. A Gen., vol. 495, pp. 141-151, 2015.
http://www3.epa.gov/climatechange/ghgemissions/global.html

I. Introduction

Synthetic gas (syngas) from biomass, bio-waste and residues



1

Gasification

Synthetic gas (Syngas) CO/H_2

Syngas cleaning

Purified syngas

FT*

Biomass Wastes

2

~~Anaerobic digestion~~

Biogas CH_4/CO_2

Biogas cleaning

Purified biogas

DRM*

Biocommodities

Biofuels

Electricity

Catalysts: Hybrid and composite materials

3

CH_4+CO_2

DRM*

FT*: Fisher Tropsch

DRM*: Dry Reforming of Methane

I. Introduction

From greenhouse gases to fuel and biocommodities

$$CH_4 + CO_2 \xrightarrow[\text{Catalysts}]{\text{DRM}} 2CO + 2H_2 \xrightarrow[\text{Catalysts}]{\text{FT}} \text{Fuels, Biocommodities}$$

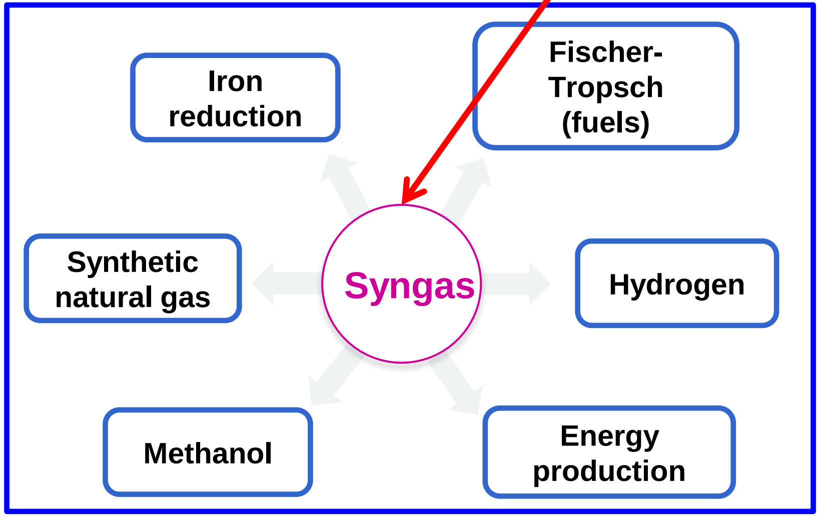
Syngas

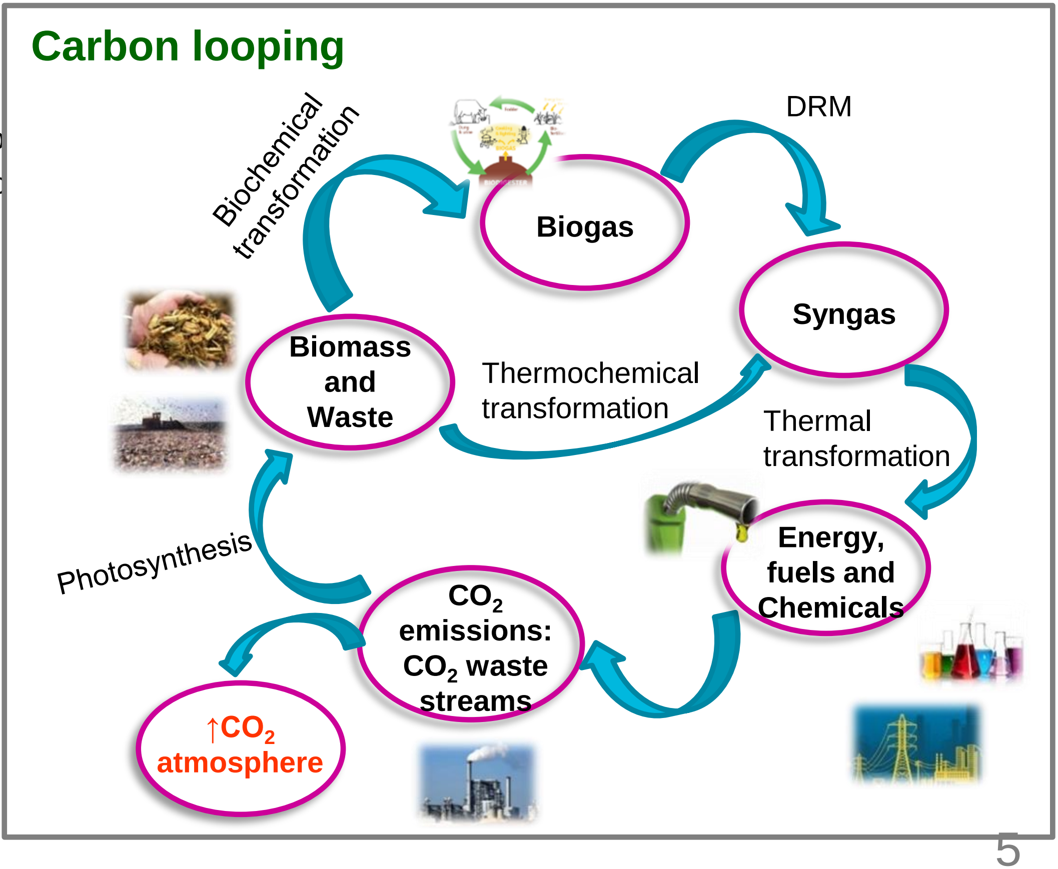
Greenhouse gases as feedstock

Dry Reforming of Methane (DRM)

Advantages:

- ✓ Greenhouse gases as feedstock
- ✓ CH_4: natural gas
- ✓ Biomass/Waste $\xrightarrow[\text{methanation}]{}$ **Biogas:** $\%CH_4 = 50\text{-}75\%$, $\%CO_2 = 30\text{-}40\%$
- ✓ Syngas production
- ✓ H_2/CO ratio suitable for GTL processes





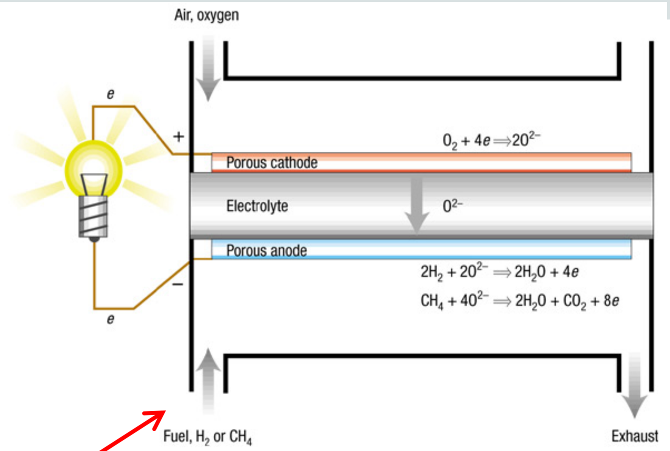
I. Introduction

Syngas Composition and end-use

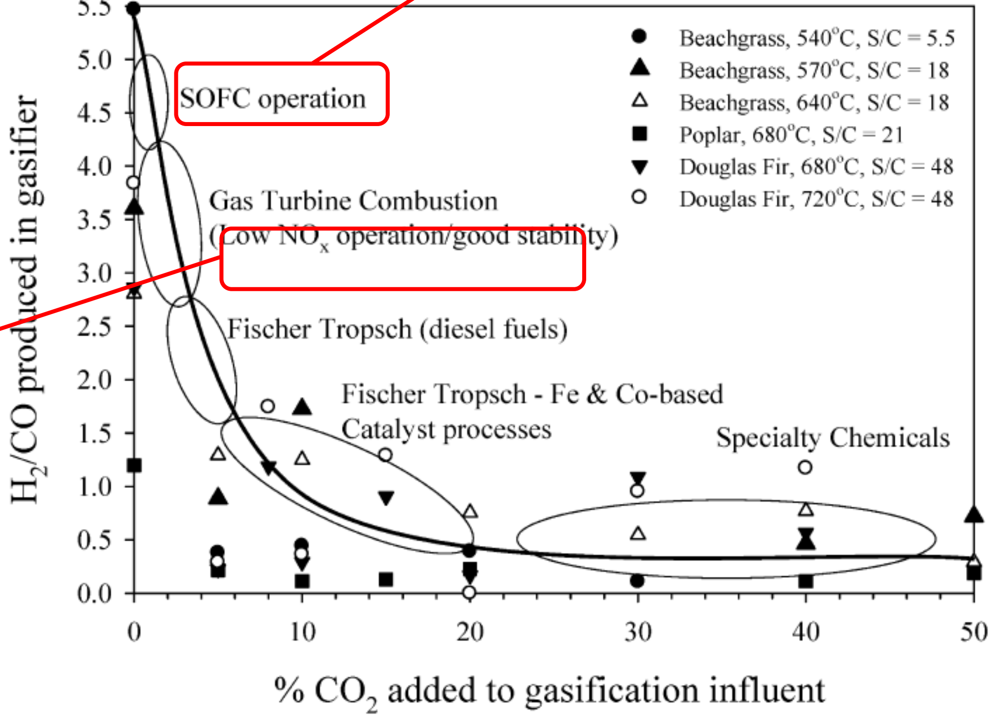
- **Choice for Syngas End-use**
  H_2/CO ratio

- **Factors influencing H_2/CO ratio**
  - Gasifying agent (O_2, H_2O, CO_2)
  - Temperature
  - Catalyst
  - Feedstock properties

    (-) Heterogeneous



SOFC: Solid Oxide Fuel Cells



FT
GTL (gas to liquid (olefins, alcohols))
CTL (coal to liquid)

$$(2n+1)\ H_2 + n\ CO \xrightarrow{\text{Cat (Co,Fe, Ni, Ru)}} C_nH_{(2n+2)} + nH_2O$$

Source : Butterman HC, Castaldi MJ; Environ. Sci. Technol. 2009 43, 9030-9037

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II. State-of-the-art – Catalysts development

- **Active phase:**
  - Noble metals : Ru, Pd, Pt… ⬆ **Catalytic performance** ⬆ **Cost**
  - Transition metals : Ni, Co, Fe … ⬆ **Catalytic performance** ⬇ **Cost** ⬆ **Coke deposition**
- **Support:**
  - Well-established supports used for similar reactions (SRM): Al_2O_3, SiO_2, …
  - Oxygen storage capacity (OSC): CeO_2, ZrO_2 , rare-earth metal oxides…

⬆ **OSC** ⬆ **Oxidation of coke**

  - Increased basicity

⬆ **Basicity** ⬆ **CO_2 adsorption** ⬆ **removal of coke**

Mg, K, Ca…

- **Current research:**
  - Metal-organic frameworks (MOFs), bi and three metallic catalysts, etc …
- **This work:**
  - Active phase: Ni
  - Support: Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$)

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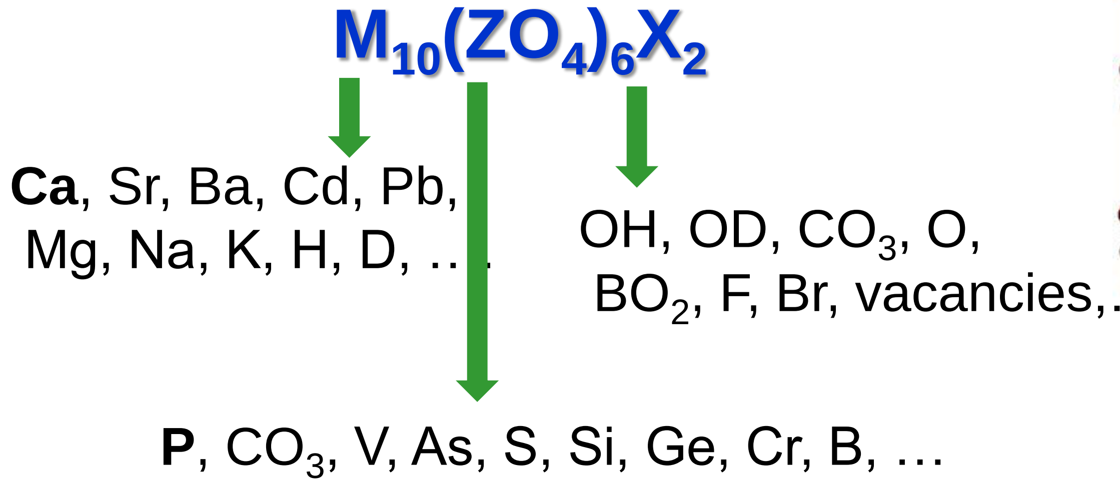
III. Phosphate catalysts production

Why hydroxyapatite (CaHA) for energy?

- **Ion exchange and solid solutions**

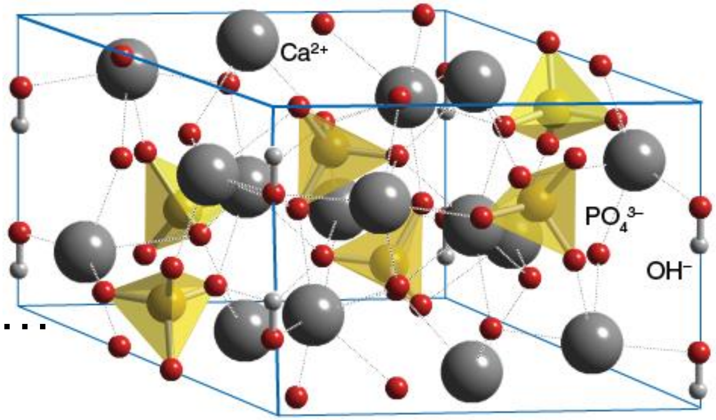


$M_{10}(ZO_4)_6X_2$

Ca, Sr, Ba, Cd, Pb, Mg, Na, K, H, D, …

OH, OD, CO_3, O, BO_2, F, Br, vacancies,…

P, CO_3, V, As, S, Si, Ge, Cr, B, …



Hydroxyapatite structure[1]

Cristalline structure : hexagonal
Gaps in cationic sites and OH

- **Chemical stability:**
  - Low solubility in water, solubility product of the order of 10^{-59}
- **Thermal stability:**
  - Transformation into oxy-hydroxyapatite at T > 1000°C
  - No sintering below 700°C
- **Presence of acid and basic sites = f(Ca/P)**

[1] University of Liverpool, http://www.chemtube3d.com/solidstate/SShydroxyapatite.htm

III. Phosphate catalysts production

Why hydroxyapatite (CaHA) for energy?

Competitive materials:
- ✓ Zeolites
- ✓ Catalysts
- ✓ Sorbents

- **Ion exchange**
- **Chemical stability:**
  - Low solubility in water, solubility product of the order of 10^{-59}
- **Thermal stability:**
  - Transformation into oxy-hydroxyapatite at T > 1000°C
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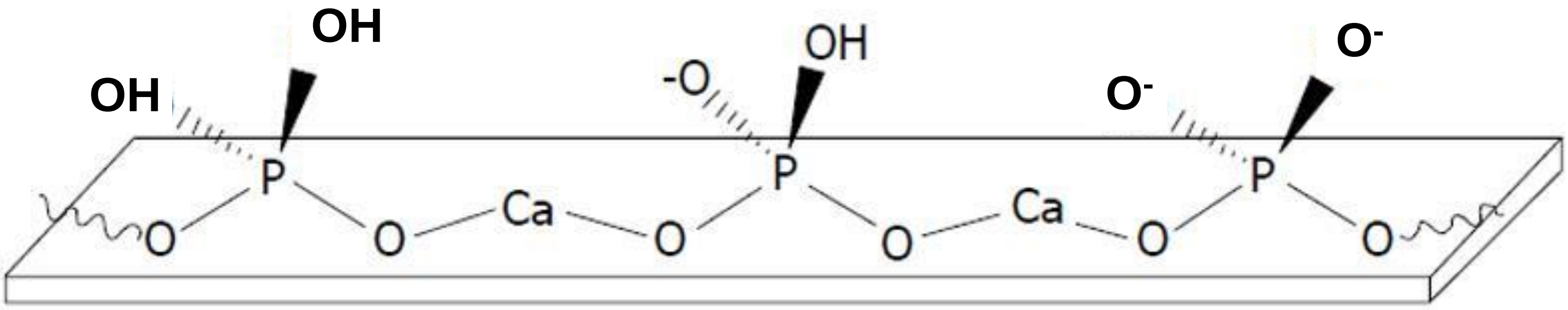
- **Presence of acid and basic sites = f(Ca/P)**

Acid	Acid + basic	Basic
Ca/P < 1,5	1,5 < Ca/P < 1,67	Ca/P > 1,67



Acidic ← **Neutral** → **Basic**

[1]Chap1: Biological Apatites in Bone and Teeth, in Nanoceramics in Clinical Use: From Materials to Applications (2), 2015, 1-29; ISBN:978-1-78262-255-0

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Catalysts preparation

⇒ **Support :**

$Ca_{10}(PO_4)_6(OH)_2$: **CaHA**

- CaHA1 (S_{BET} = 7m²/g, V_p = nd)
- CaHA2 (S_{BET} = 60m²/g, V_p = 0.07cm³/g)
- Al_2O_3(S_{BET} = 170m²/g, V_p = 0.42cm³/g)
- PuralMG30 (Sasol): MgO:Al_2O_3

  (wt%) = 30:70

  (S_{BET} = 148m²/g, V_p = 0.17cm³/g)

Catalysts preparation:

1°) Doping of support with $Ni(NO_3)_2$: 5wt%Ni

Incipient wetness impregnation (IWI)

→

2°) Drying :

T = 105°C

↓

3°) Calcination :

T = 500°C, t = 2h

4°) Characterization :

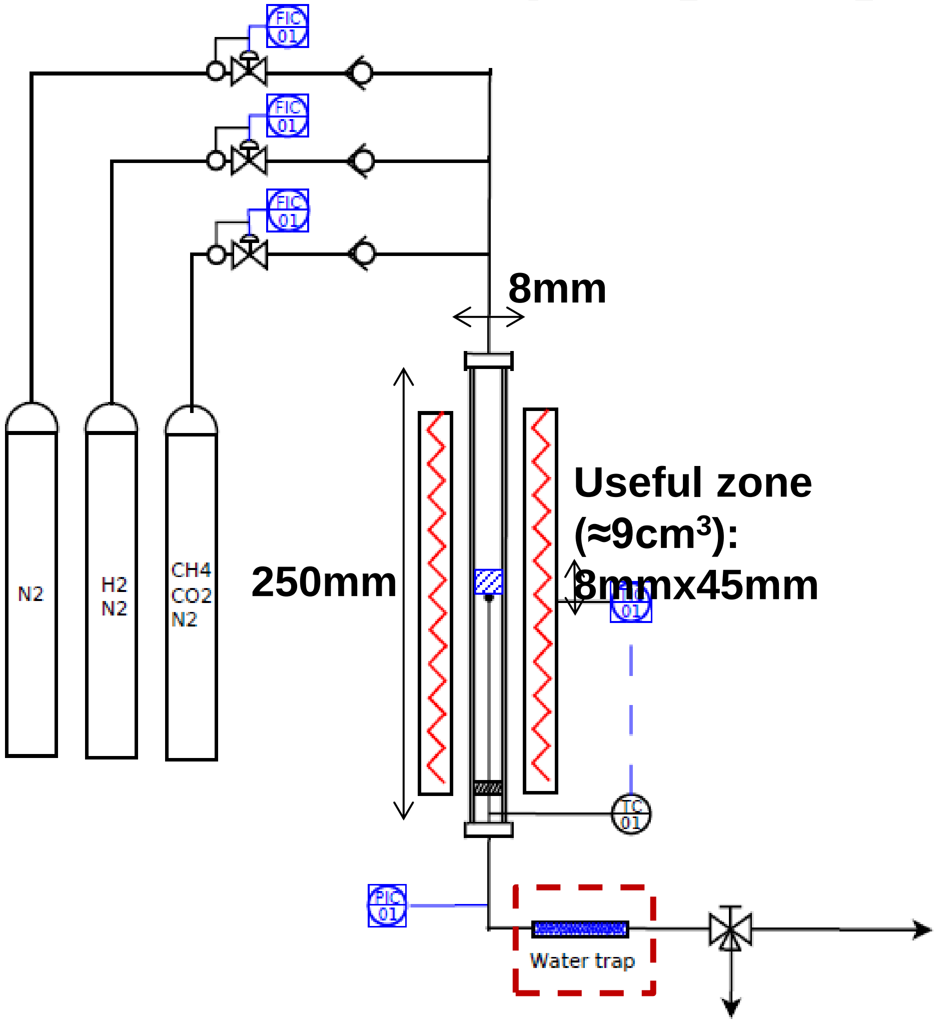
- **XRD**
- **SEM, TEM**
- **TGA**
- **TPX, x being:**

R (reduction), O (oxidation), D (desorption)…

IV. Materials and Methods

Experimental apparatus

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO$$



Testing conditions:

Reduction in-situ :

T = 700°C

t = 2h

Catalytic evaluation:

T = 700°C

P = 1.6 bar

WHSV* = 15882 $mLh^{-1}g_{cat}^{-1}$

t = 50h-300h

Maximum operating conditions:

T_{max} = 850°C

P_{max} = 30 bar

*Weight hourly space velocity (WHSV = Mass Flow/*Catalyst* Mass).

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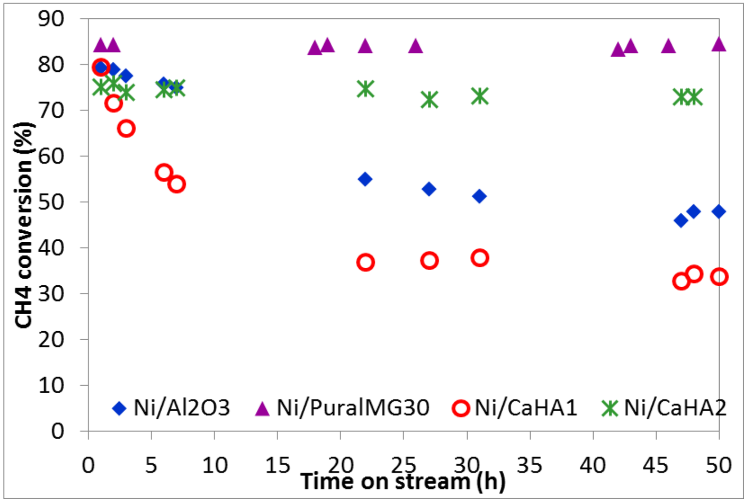
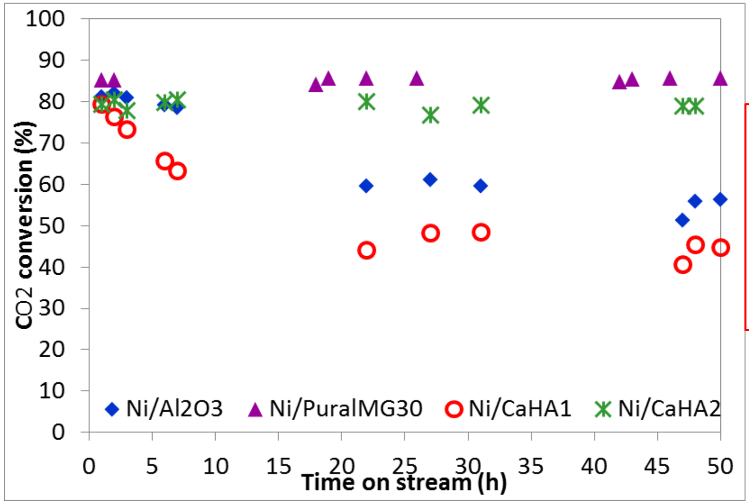
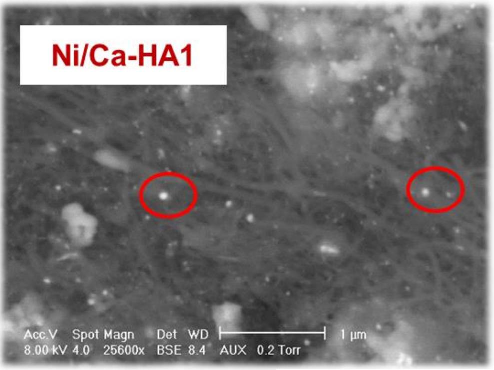
$$CH_4 + CO_2 \xleftrightarrow{\text{Catalyst}} 2H_2 + 2CO$$

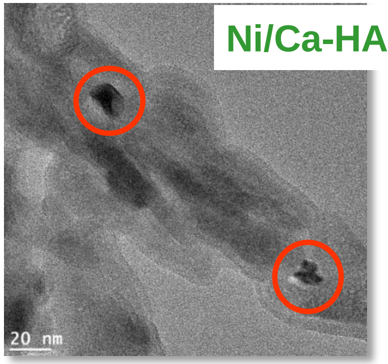




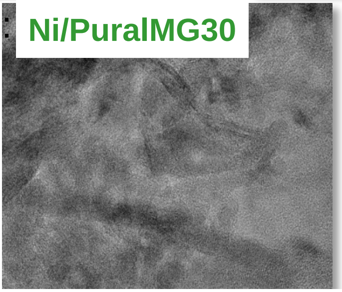
Ni/PuralMG30
$>$ **Ni/CaHA2**
$>>>$ **Ni/Al_2O_3**
$>$ **Ni/CaHA1**



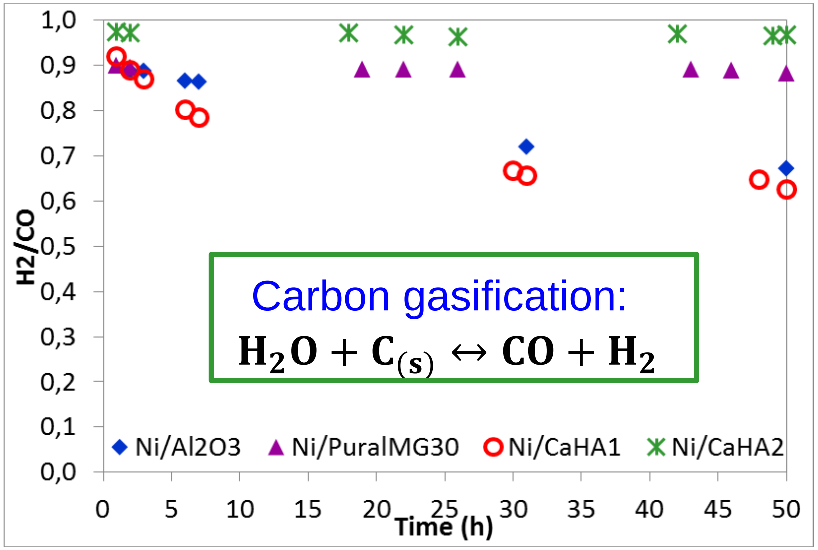
Ni particle size: 100 – 200nm



Ni particle size < 50 nm



Ni particles are not discernable



Carbon gasification:

$$H_2O + C_{(s)} \leftrightarrow CO + H_2$$

↑ Ni particle size ↑ Coke deposit

V. Results and discussion

Comparative study: hydroxyapatite-based catalysts / commercial catalysts

Catalyst	Conditions	CH_4 Conversion H_2/CO Reaction time	Bibliography
5%Ni/CaHA2_S	**T = 700°C** **P = 1,6bar** **WHSV = 12,3$Lh^{-1}g_{cat}^{-1}$**	**≈80-60%** **0,7-1,0** **300h**	**This work**
5%$NiLa_2O_3/ZrO_2$	T = 700°C P = P_{atm} GHSV = 15	**70%** 0,95 50h	Rezaei et al., App Cat B 77 (2008) 346-354
6%NiK/Al_2O_3	T = 700°C P = P_{atm} GHSV = 22,5	**57%** nd 24h	Juan-Juan et al., App Cat A 301 (2006) 9-15
1%Pd/Al_2O_3	T = 700°C P = P_{atm} WHSV = 0,4$Lh^{-1}g_{cat}^{-1}$	**44%** 0,9 6h	Shi et al., App Cat B 170-171 (2015) 43-52
1%Pt/CeO_2-Al_2O_3	T = 700°C P = P_{atm} GHSV = nd	**90%** 0,9 6h	Carvalho et al., App Cat A 473 (2014) 132-145

→ **Ni/CaHA2_S: promising catalyst for DRM**

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VI. Conclusions

- **Ni/CaHA2_S : active and stable** catalyst and **comparable** to commercial catalysts and results reported in the literature
- **Motivation for developing a novel P-based and efficient catalyst for DRM**

↑Conversion GHGs, ↓ Selectivity for side products

- ↑S_{BET}, V_p
- ↓ Size of Ni particles
- ↑ Metal-support interaction
- ↑ Support basicity

Future works

- **Bimetallic catalysts:** Expand the hydroxyapatite properties by adding two different metals in its structure (synergy between added metals)
- **Understanding the associated mechanisms**
- **Injection of a controlled amount of steam**
- **Energy Balance**

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My research team

Current academic collaborations

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1865

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NACIONAL
DE COLOMBIA
SEDE BOGOTÁ

Asia

ZHEJIANG UNIVERSITY
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MGU
MAHATMA GANDHI UNIVERSITY

Africa

UNIVERSITE ASSANE SECK
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