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

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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

IV. Materials and Methods

V. Results and discussion

VI. Conclusions
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$_2$O 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

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/H₂
   - Syngas cleaning
   - Purified syngas

2. Anaerobic digestion
   - Biogas CH₄/CO₂
   - Biogas cleaning
   - Purified biogas

3. CH₄+CO₂
   - Catalysts: Hybrid and composite materials

FT*: Fisher Tropsch
DRM*: Dry Reforming of Methane

[Diagram showing various processes and outputs related to biomass and biogas conversion, including electricity, biofuels, and biocommodities.]
I. Introduction

From greenhouse gases to fuel and biocommodities

\[ \text{CH}_4 + \text{CO}_2 \xrightarrow{\text{Catalysts}} 2\text{CO} + 2\text{H}_2 \]

Greenhouse gases as feedstock

Dry Reforming of Methane (DRM)

Advantages:
- Greenhouse gases as feedstock
- CH\(_4\): natural gas
- Biomass/Waste Biogas:
  - %CH\(_4\) = 50-75%
  - %CO\(_2\) = 30-40%
- Syngas production
- H\(_2\)/CO ratio suitable for GTL processes

Iron reduction
- Synthesis of natural gas
- Methanol
- Ethanol

Fischer-Tropsch (fuels)
- Syngas
- Hydrogen

Energy production

Carbon looping

Biomass and Waste

Thermochemical transformation

Energy, fuels and Chemicals

\(\uparrow\text{CO}_2\) atmosphere

\(\uparrow\text{CO}_2\) waste streams

Biocommodities

Electricity
I. Introduction
Syngas Composition and end-use

- **Choice for Syngas End-use**
  - H₂/CO ratio

- **Factors influencing H₂/CO ratio**
  - Gasifying agent (O₂, H₂O, CO₂)
  - Temperature
  - Catalyst
  - Feedstock properties
    - (-) Heterogeneous

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

Cat (Co, Fe, Ni, Ru)

\[(2n+1) \text{H}_2 + n \text{CO} \rightarrow C_n \text{H}_{(2n+2)} + n\text{H}_2\text{O}\]

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**SOFC: Solid Oxide Fuel Cells**

- Beachgrass, 540°C, S/C = 5.5
- Beachgrass, 570°C, S/C = 18
- Beachgrass, 640°C, S/C = 18
- Poplar, 680°C, S/C = 21
- Douglas Fir, 680°C, S/C = 48
- Douglas Fir, 720°C, S/C = 48

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**Gas Turbine Combustion**
(Cow NOₓ operation/good stability)

**Fischer Tropsch (diesel fuels)**

**Fischer Tropsch - Fe & Co-based Catalyst processes**

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**Specialty Chemicals**

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**% CO₂ added to gasification influent**

Source: Buttermán 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...
  - Transition metals: Ni, Co, Fe ...

- **Support:**
  - Well-established supports used for similar reactions (SRM): Al₂O₃, SiO₂, ...
  - Oxygen storage capacity (OSC): CeO₂, ZrO₂, rare-earth metal oxides...

- **Current research:**
  - Metal-organic frameworks (MOFs), bi and three metallic catalysts, etc ...

- **This work:**
  - Active phase: Ni
  - Support: Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂)
OUTLINE

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III. Phosphate catalysts production

Why hydroxyapatite (CaHA) for energy?

- Ion exchange and solid solutions

\[ M_{10}(ZO_4)_6X_2 \]

\[ \text{Ca, Sr, Ba, Cd, Pb, Mg, Na, K, H, D, ...} \]

\[ \text{OH, OD, CO_3, O, BO_2, F, Br, vacancies, ...} \]

\[ \text{P, CO_3, V, As, S, Si, Ge, Cr, B, ...} \]

- Chemical stability:
  - Low solubility in water, solubility product of the order of $10^{-59}$

- Thermal stability:
  - Transformation into oxy-hydroxyapatite at $T > 1000^\circ$C
  - No sintering below 700°C

- Presence of acid and basic sites = $f(\text{Ca/P})$

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1University of Liverpool, [http://www.chemtube3d.com/solidstate/SShydroxyapatite.htm](http://www.chemtube3d.com/solidstate/SShydroxyapatite.htm)
III. Phosphate catalysts production

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<table>
<thead>
<tr>
<th>Acid</th>
<th>Acid + basic</th>
<th>Basic</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ca/P &lt; 1.5$</td>
<td>$1.5 &lt; Ca/P &lt; 1.67$</td>
<td>$Ca/P &gt; 1.67$</td>
</tr>
</tbody>
</table>

Competitive materials:
- Zeolites
- Catalysts
- Sorbents

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Catalysts preparation

⇒ Support:

$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ : CaHA

- $\text{CaHA1} \quad (S_{\text{BET}} = 7 m^2/g, V_p = \text{nd})$
- $\text{CaHA2} \quad (S_{\text{BET}} = 60 m^2/g, V_p = 0.07 cm^3/g)$
- $\text{Al}_2\text{O}_3 (S_{\text{BET}} = 170 m^2/g, V_p = 0.42 cm^3/g)$
- $\text{PuralMG30 (Sasol)}: \text{MgO:Al}_2\text{O}_3$
  \((\text{wt\%}) = 30:70 \quad (S_{\text{BET}} = 148 m^2/g, V_p = 0.17 cm^3/g)\)

Catalysts preparation:

1°) Doping of support with Ni(NO$_3$)$_2$: 5wt%Ni

2°) Drying:

\[ T = 105^\circ C \]

3°) Calcination:

\[ T = 500^\circ C, t = 2h \]

4°) Characterization:

- XRD
- SEM, TEM
- TGA
- TPX, x being:
  \( R \) (reduction), \( O \) (oxidation), \( D \) (desorption)…
**IV. Materials and Methods**

**Experimental apparatus**

\[ \text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{H}_2 + 2\text{CO} \]

**Testing conditions:**

**Reduction in-situ:**
- \( T = 700^\circ\text{C} \)
- \( t = 2\text{h} \)

**Catalytic evaluation:**
- \( T = 700^\circ\text{C} \)
- \( P = 1.6\text{ bar} \)
- \( \text{WHSV}^* = 15882\ \text{mLh}^{-1}\text{g}_{\text{cat}}^{-1} \)
- \( t = 50\text{h}-300\text{h} \)

**Maximum operating conditions:**
- \( T_{\text{max}} = 850^\circ\text{C} \)
- \( P_{\text{max}} = 30\text{ bar} \)

*Weight hourly space velocity (WHSV = Mass Flow/Catalyst Mass).*
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\[ \text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{H}_2 + 2\text{CO} \]

Catalyst

Ni/PuralMG30

Ni/CaHA2

Ni/Al\(_2\)O\(_3\)

Ni/CaHA1

Carbon gasification:

\[ \text{H}_2\text{O} + \text{C}_\text{(s)} \leftrightarrow \text{CO} + \text{H}_2 \]

Ni particle size:

Ni/PuralMG30

100 – 200nm

Ni/Ca-HA1

Ni/Ca-HA2

Ni particle size < 50 nm

↑ Ni particle size ↑ Coke deposit

Ni particles are not discernable
V. Results and discussion
Comparative study: hydroxyapatite-based catalysts / commercial catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conditions</th>
<th>CH\textsubscript{4} Conversion</th>
<th>Bibliography</th>
</tr>
</thead>
</table>
| 5\%Ni/CaHA\textsubscript{2} \_S | T = 700°C  
P = 1,6bar  
WHSV = 12,3Lh\textsuperscript{-1}g\textsuperscript{cat}\textsuperscript{-1} | ≈80-60%  
H\textsubscript{2}/CO  
Reaction time: 0,7-1,0  
300h | This work |
| 5\%NiLa\textsubscript{2}O\textsubscript{3}/ZrO\textsubscript{2} | T = 700°C  
P = P\textsubscript{atm}  
GHSV = 15 | 70%  
0,95  
50h | Rezaei et al., App Cat B 77 (2008) 346-354 |
| 6\%NiK/Al\textsubscript{2}O\textsubscript{3} | T = 700°C  
P = P\textsubscript{atm}  
GHSV = 22,5 | 57%  
dl  
24h | Juan-Juan et al., App Cat A 301 (2006) 9-15 |
| 1\%Pd/Al\textsubscript{2}O\textsubscript{3} | T = 700°C  
P = P\textsubscript{atm}  
WHSV = 0,4Lh\textsuperscript{-1}g\textsuperscript{cat}\textsuperscript{-1} | 44%  
0,9  
6h | Shi et al., App Cat B 170-171 (2015) 43-52 |
| 1\%Pt/CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} | T = 700°C  
P = P\textsubscript{atm}  
GHSV = nd | 90%  
0,9  
6h | Carvalho et al., App Cat A 473 (2014) 132-145 |

Ni/CaHA\textsubscript{2} \_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**
  
  \[ \text{↑Conversion GHGs, ↓ Selectivity for side products} \]

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

**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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