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Compelling in terms of CO$_2$ conversion into value-added chemicals and CO$_2$ abatement

**RWGS:** $CO_2 + H_2 \leftrightarrow CO + H_2O \quad \Delta H = 41.3 \text{ kJ mol}^{-1}$

Side reactions:

- **Sabatier reaction:** $CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad \Delta H = -165.0 \text{ kJ mol}^{-1}$
- CO methanation: $CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \Delta H = -206.0 \text{ kJ mol}^{-1}$

Catalysts used: precious metals, Pt, Pd, Ru and Au catalysts; transitional metals, Cu, Fe, Co and Ni catalysts, good alternatives for precious metals.

Applications:

- **Syngas (CO and H$_2$)**
  - FTS
  - IGCC
  - Methanol
  - Sabatier
  - Liquid fuels
  - Power
  - Chemicals
  - Artificial natural gas
<table>
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<tr>
<th>Challenges</th>
<th>Cause</th>
<th>Example</th>
<th>Solution</th>
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<tbody>
<tr>
<td>Selectivity to CO</td>
<td>Side reactions, CO\textsubscript{2} and CO methanation</td>
<td>Ni catalyst shows high CH\textsubscript{4} selectivity</td>
<td>Promoters as alkali metals, or changing particle size etc.</td>
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<tr>
<td>Stability</td>
<td>Metal sintering, carbon formation, sulfur poisoning</td>
<td>Cu catalysts tend to sinter at high T, and carbon formation tend to happen for Ni</td>
<td>Usage of bimetallic material, creating more O vacancies, use sulfur adsorption materials</td>
</tr>
<tr>
<td>Activity (CO\textsubscript{2} conversion)</td>
<td>Catalysts deactivation, high activation energy</td>
<td>As mentioned in the second column</td>
<td>As mentioned in the second column</td>
</tr>
</tbody>
</table>
Challenge:
High loading of Co tends to lose activity due to agglomeration and structure degradation.

Proposed solution:

1. Co catalyst stability can be improved by using porous ZSM-5 material as a constraint material due to the high temperature robustness of ZSM-5.
2. RWGS activity can be improved by combining Co and ZSM-5 components with in-situ CO$_2$ trap and conversion.

Metal-oxide nanoarray based monolithic catalysts:

- Sufficient Low Temperature Catalytic Activities
- Enhanced Materials Utilization Efficiency
- Improved Mass Transport
- Tunable Catalytic Performance
- Excellent hydrothermal-aging stability
- Excellent thermal and mechanical stability

low price, high selectivity to CO and easy accessibility.

Co$_3$O$_4$

Cordierite

Highly porous and heat resistant

ZSM-5 nanoarray

Cordierite
Materials synthesis

![Diagram of materials synthesis process]

<table>
<thead>
<tr>
<th>Catalyst name</th>
<th>Co LR (wt%)</th>
<th>ZSM-5 LR (wt%)</th>
<th>Total weight</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cor-CC</td>
<td>10.5</td>
<td>0</td>
<td>0.4964</td>
<td>Co nanowire</td>
</tr>
<tr>
<td>Cor-CC-HZA</td>
<td>11.2</td>
<td>16.4</td>
<td>0.4398</td>
<td>ZSM-5 grown on Co nanowire</td>
</tr>
</tbody>
</table>

Test protocol:
- Weight hour space velocity (WHSV) of 12 L/g h\(^{-1}\), Pressure: 1 bar
- Keep at each temperature for 1 h to achieve a steady state, sweep from 250-600 °C.
- Carbon balance is calculated for each test. Only tests with more than 95% of CB is valid and presented.

H\(_2\) reduction 400°C/1h

RWGS

Temperature-sweeping @ 250-600°C at 50°C interval
- \(\text{H}_2/\text{CO}_2\) ratio
- \(\text{CO}_2\) percentage

Long-term stability @ 600°C
RWGS with different \( \text{H}_2/\text{CO}_2 \) ratio

**Summary:**

1. CC-HZA catalyst shows better \( \text{CO}_2 \) conversion with 1:1 and 2:1 \( \text{H}_2/\text{CO}_2 \) ratio.
2. With 3:1 \( \text{H}_2/\text{CO}_2 \) ratio, CC-HZA sample shows much better CO selectivity at low temperature range, while it is mainly \( \text{CH}_4 \) for CC catalyst.
3. CC-HZA sample shows good stability in terms of \( \text{H}_2/\text{CO}_2 \) ratio variation.

RWGS temperature sweep for CC and CC-HZA catalysts with different \( \text{H}_2/\text{CO}_2 \) ratios: (a) \( \text{H}_2/\text{CO}_2=1:1 \), (b) \( \text{H}_2/\text{CO}_2=2:1 \) and (c) \( \text{H}_2/\text{CO}_2=3:1 \). ○: \( \text{CO}_2 \) conversion for CC-HZA, ●: \( \text{CO}_2 \) conversion for CC, □: CO selectivity for CC-HZA and ■: CO selectivity for CC, dashed line: thermal equilibrium \( \text{CO}_2 \) conversion of RWGS reaction. Total gas flowrate is kept at 120 sccm for all the tests.
Summary:
1. CC-HZA catalyst shows superior stability for RWGS even at 600 °C for 68 h.
2. CC catalyst deactivates vary fast under the reaction condition.
CC-HZA sample with varied CO$_2$ conc

RWGS CO$_2$ conversion and CO selectivity for CC-HZA catalyst with CO$_2$ molar concentrations of 4% and 21%. ○: CO selectivity, ●: CO$_2$ conversion.

Red color for 4% of CO$_2$, while blue for 21% of CO$_2$. Total gas flowrate is kept at 120 sccm and H$_2$/CO$_2$ ratio is 3:1 for all the tests.

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Summary:
1. 100% of CO selectivity for 4% of CO$_2$ flue gas, while CO$_2$ conversion remains high of 58%.
2. Potential application for the direction conversion of CO$_2$ to CO for NGCC flue gas.
Summary:
1. 400 C is enough to reduce Co$_3$O$_4$, while after RWGS reaction, most of the Co stays in Co metallic form.
2. Co tends to agglomerate. Co crystallite size increases from 31.3 nm to 36.4 nm then to 72.2 nm. While for CC-HZA sample, crystallite size of Co and ZSM-5 stays almost the same.

<table>
<thead>
<tr>
<th>Condition</th>
<th>CC</th>
<th></th>
<th>CC-HZA</th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co$_3$O$_4$</td>
<td>Co</td>
<td>Co$_3$O$_4$</td>
<td>Co</td>
</tr>
<tr>
<td>Fresh</td>
<td>31.3</td>
<td>-</td>
<td>37.9</td>
<td>-</td>
</tr>
<tr>
<td>Reduced</td>
<td>-</td>
<td>36.4</td>
<td>-</td>
<td>39.5</td>
</tr>
<tr>
<td>Used</td>
<td>-</td>
<td>72.2</td>
<td>-</td>
<td>34.1</td>
</tr>
</tbody>
</table>
Top-view SEM images of (a,d) CC-fresh, (b,e) CC-reduced, (c,f) CC-used, (g) CC-HZA-fresh, (h) CC-HZA-reduced, and (i) CC-HZA-RWGS-used, respectively.

Summary:
1. Fresh CC shows nano needle structure.
2. H$_2$ reduction at 400°C results partial collapse of the CC nano needle structure.
3. Under 600°C RWGS condition, severe Co agglomeration can be observed.
4. Morphology of CC-HZA (fresh, reduced and used) stays almost unchanged.
5. Highly agrees with XRD characterization.
Summary:
1. Co encapsulated inside ZSM-5 structure. CC nano array is composed of many Co particles.
2. CC-HZA shows very rigid structure (a,b,c), no obvious sintering.
3. Particle size stays almost not changed.

TEM images of CC-reduced: Bright-field TEM image (a) CC-HZA-fresh, (b) CC-HZA-reduced, (c) CC-HZA-used; (d-f) corresponding enlarged image
Summary:
1. Low surface and meso pore volume for CC sample. No micropore.
2. High surface and micro, meso pores for CC-HZA sample.
3. CC nano array catalysts tend to collapse, resulting the decrease of pore size and meso pore volume.
4. Micro and meso pore remain for CC-HZA sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$</th>
<th>$S_{micro}$</th>
<th>$S_{ext}$</th>
<th>$V_{total}$</th>
<th>$V_{micro}$</th>
<th>$V_{meso}$</th>
<th>Pore Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC-Fresh</td>
<td>4</td>
<td>0</td>
<td>4</td>
<td>0.024</td>
<td>0</td>
<td>0.024</td>
<td>21.6</td>
</tr>
<tr>
<td>CC-Reduced</td>
<td>12</td>
<td>5</td>
<td>7</td>
<td>0.027</td>
<td>0</td>
<td>0.027</td>
<td>9.1</td>
</tr>
<tr>
<td>CC-Used</td>
<td>7</td>
<td>3</td>
<td>4</td>
<td>0.016</td>
<td>0</td>
<td>0.016</td>
<td>9.9</td>
</tr>
<tr>
<td>CC-HZA-Fresh</td>
<td>63</td>
<td>38</td>
<td>25</td>
<td>0.030</td>
<td>0.015</td>
<td>0.015</td>
<td>3.1</td>
</tr>
<tr>
<td>CC-HZA-Reduced</td>
<td>69</td>
<td>37</td>
<td>32</td>
<td>0.057</td>
<td>0.015</td>
<td>0.042</td>
<td>3.3</td>
</tr>
<tr>
<td>CC-HZA-Used</td>
<td>15</td>
<td>9</td>
<td>6</td>
<td>0.019</td>
<td>0.004</td>
<td>0.015</td>
<td>5.1</td>
</tr>
</tbody>
</table>
Proposed mechanism

- Easy sintering and structure collapse
- Minimum mass and heat transfer limitation; High sintering resistance; optimum material usage

Cordierite

Co$_3$O$_4$ nanoarray

ZSM-5 nanoarray

Co$_3$O$_4$ particle
By applying the hybrid CC-HZA structure for RWGS:

1. CO$_2$ conversion of 48% with 100% of CO selectivity under 600 °C with H$_2$/CO$_2$ ratio of 3:1, 1 bar.

2. Less sensitive to the variation of H$_2$/CO$_2$ ratios. 100% of CO selec for 4% CO$_2$ NGCC flue gas abatement with 58% CO$_2$ conv.

3. Excellent thermal stability at 600 °C during 66 h TOS, resulting from ZSM-5 confinement.

4. Less material usage with negligible mass and heat transfer.
Collaborators:
Prof. Jingyue Liu (Arizona State Univ.); Dr. Yong Ding (Georgia Tech), Dr. Tom Pauly (Umicore)

Funding sources:
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Department of Energy
University of Connecticut
Backup materials
Space velocity effect

Summary:
1. High CO$_2$ conversion of 45% and 95% of CO selectivity can be achieved at high WHSV of 36 L/g h$^{-1}$.
2. No obvious CO$_2$ conversion and CO selectivity decrease in T range of 250-500°C, indicating good mass and heat transfer.
RWGS SV effect of CC-HZF tested at 1 bar, and H₂/CO₂ of 3:1 in terms of (a) CO₂ conversion and (b) CO selectivity after H₂ reduction treatment

Summary:
1. CO₂ conv and CO selectivity varied significantly with SV.
1. TPR: 4 and 5% H2 to see the difference

2. CC washcoated with ZSM-5 to see its stability

3. CC coated with SiO2 seeding could do the trick maybe.
Summary:
1. Co sintering can be observed. Agrees with SEM and XRD characterization.
2. A $\text{Co}_3\text{O}_4$ layer can be observed for CC-used sample. This could be one of the reasons for the catalyst deactivation besides the Co particle sintering.
Summary:
1. Polycrystalline ZSM-5 and Co can be observed.
2. Co is encapsulated inside ZSM-5 nano branch structure with many meso pores in between.

TEM images of CC- HZA-fresh: (a) (b) Bright-field TEM image; (c) HRTEM images; and (d) Diffraction pattern.
Summary:
1. Two reduction peaks can be observed for CC, CC-HZF and CC-HZA catalysts, indicating a two-step reduction process of Co.
2. CC-HZA shows lower reduction peak compared with CC and CC-HZF. This could be due to the intact cobalt nanostructure during H₂ reduction.
1. TPR: 4 and 5% H2 to see the difference
2. CC washcoated with ZSM-5 to see its stability
3. CC coated with SiO2 seeding could do the trick maybe.