Development of Modified Nickel-Based Compositions For On-Anode Reforming

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Outline of Presentation

- On-anode reforming—incentives and challenges
- FY05 areas of research
- Review and analysis of recent progress
- Conclusions
- Future work
Incentives for On-Anode Reforming

- **Increase efficiency**
  - Utilize heat generated from fuel cell energy losses
  - Reduce cell cooling requirements—less excess cathode air
- **Reduce system steam requirements**
  - Utilize $H_2O$ generated from electrochemical oxidation of $H_2$
- **Use synergy of electrochemical oxidation of $H_2$ and CO with CH$_4$ reforming**
  - Increase methane conversion by shift of equilibrium
  - Reduce reforming temperature
- **Eliminate or reduce size of high temperature external reformer**
  - Reduce capital investment and operating costs
Challenges in On-Anode Reforming

- Deactivation through carbon formation
  - Hinders operation at desired low steam-to-carbon (S/C) ratios
- Kinetic mismatch of Ni-YSZ reforming and electrochemical oxidation
  - Reforming rate fast relative to electrochemical oxidation
    - Possible large endotherm at leading edge of cell
    - Potential for warping or cracking cell

Our work is aimed at finding solutions for above challenges
FY05 Research Accomplishments

- Obtained baseline data on Ni-YSZ for methane and synthetic natural gas steam reforming
  - Activity, activation energy, feed component dependence
  - Activity maintenance—identified sintering effects from H₂O/CH₄ feed
- Evaluated modified Ni-YSZ for reduced carbon susceptibility and low S/C operation
  - Identified MgO modification of Ni-YSZ as stabilizer to Ni sintering and to carbon susceptibility
  - Continuing to assess need for pre-reforming of natural gas feedstock
- Evaluated Cu-modified Ni-YSZ for methane steam reforming activity reduction
  - Achieved activity reduction by more than one order of magnitude compared with Ni-YSZ at 700°C
Catalyst Testing Procedures

- **Reactor**
  - Tubular quartz, 4mm i.d.

- **Catalyst**
  - Typical charge 30 mg, 80-100 mesh
  - Dilution with 300 mg YSZ to minimize bed temperature endotherm
  - Pretreatment: typically 700°C for 1 hour in pure H₂

- **Feed**
  - Typically 3:1 S/C with variable H₂
  - N₂ or He diluent included to allow feed flexibility
    - Maintain constant residence time regardless of feed ratio
  - Natural gas: 96% CH₄, 3% C₂H₆, 1% C₃-C₄
  - Space velocity (GHSV): cc feed/g cat-h
Catalyst Preparation Methods

- Ni-YSZ
  - Standard material: NiO milled with YSZ and calcined at 1375°C

- Ni-MgO and Ni-Cu
  - Standard material: glycine nitrate preparation
    - Nitrate salts admixed followed by GN combustion, 800°C calcination
    - Alternate: milling of separately GN nitrate prepared NiO, MgO
    - For Ni-Cu: generally tested without added YSZ
  - Alternate preparations: impregnation of Ni (GN) by Cu or Mg nitrate
  - Modified materials: vary post-calcination temperature, up to 1375°C
Ni-YSZ Powder Catalyst Testing
Ni-MgO-YSZ Powder Catalyst Testing
Ni-Cu Powder Catalyst Testing
Ni-YSZ Exhibits Initial Deactivation But Activity Eventually Stabilizes

GHSV = 667K; S/C/H₂/He = 3/1/1/5; T=700°C

CH₄ Conversion vs. TOS (h)
Deactivation of Ni-YSZ is Reproducible

Methanation Activity Comparison

- Run 2 (XCH4)
- Increase SV to 667 K
- Run 1 (XCH4)

GHSV = 167K
GHSV = 667K
CO Methanation Provides Quantification of Activity Loss

Activation Energy
NiO-YSZ (Baker) 98.06 kJ/mol
NiO-YSZ spent 75.5 kJ/mol (deactivated)

Based on methanation results, assuming all Ni sites has the same turnover number for 30 mg of NiO-YSZ:

~ 12.7 % surface Ni remained after deactivation

Loss of methanation activity parallels steam reforming deactivation
Typical Treatments for Carbon Removal Do Not Regain Activity

SV=667 k ml/g-h, T=700C, H₂O/CH₄/H₂/He=3/1/1/5
Lined-out Ni-YSZ Shows Temperature Dependence Typical of Ni Catalysts

Initial Conditions: \( T = 675^\circ C, \text{GHSV}=334K \text{ ml/(h*g)}, \text{S/C/H}=3:1:1 \)

\[ E_a = 26.93 \text{ kcal/mol} \]
## Pretreatment History Impacts on Ni-YSZ Lined Out Activity

<table>
<thead>
<tr>
<th>Catalyst Pretreatment</th>
<th>Gas composition S/C/H</th>
<th>GHSV (space velocity)</th>
<th>Lined-out conversion, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>700°C in H₂, 1h</td>
<td>3/1/6</td>
<td>326K</td>
<td>15</td>
</tr>
<tr>
<td>700°C in H₂, 1h</td>
<td>3/1/6</td>
<td>328K</td>
<td>12.5</td>
</tr>
<tr>
<td>700°C in H₂, 1h</td>
<td>3/1/3</td>
<td>328K</td>
<td>14.0</td>
</tr>
<tr>
<td>700°C in H₂, 1h</td>
<td>3/1/1</td>
<td>334K</td>
<td>12.7</td>
</tr>
<tr>
<td>700°C in H₂/H₂O, 7h; 700°C in H₂, 1h</td>
<td>3/1/6</td>
<td>334K</td>
<td>&lt;11</td>
</tr>
</tbody>
</table>

**S/H₂ ratio has little impact on lined out conversion**

**H₂O/H₂ treatment has greater effect**

Average turnover rate = 0.194 moles CH₄/g cat-h at 700°C
(exceeds literature value 0.02 moles CH₄/g cat-h at 700°C (Lee et. al., I&EC Research 1990, 29(5), 766-773))
Equilibrated Ni-YSZ Shows Stability Toward Synthetic Natural Gas

Initial GHSV = 667 K, S/C/H_2/He = 3/1/1/6, 700°C

No carbon observed in catalyst bed at end of run
Ni-YSZ Methane Steam Reforming Powder Tests--Conclusions

- Initial activity decline, possibly due to sintering or restructuring facilitated by H₂O/H₂*
- Catalyst achieves stable activity (equilibrates) after several to 10’s of hours
- Kinetic parameters for lined-out Ni-YSZ consistent with results from supported Ni catalysts
  - Activation energy ~27 kcal/mol
  - First order in CH₄; zero order in H₂O for S/C>1

Ni-YSZ Powder Catalyst Testing
Ni-MgO-YSZ Powder Catalyst Testing
Ni-Cu Powder Catalyst Testing
Effect of Addition of MgO on Stability of Ni-YSZ Anode Catalyst (GN Method)

800°C Calcination, 700°C, 646K ml/h-g, S/C/H = 3/1/0.1

The diagram shows the conversion (%) over time (min) for Ni0.8Mg0.2O-YSZ (GN) Prepared together and Ni-YSZ (GN).
CH₄ Conversion Over 0.8Ni 0.2MgO-YSZ
Shows Stability at S/C = 1
WHSV = 701K, S/C/H (Initial) = 3/1/0.1, 670°C,

Equilibrium conversion

- Change to 2:1 S/C
- Change to 1:1 S/C
- Shutdown/Restart
- Change to 0.5:1 S/C
Method of Addition of MgO to Ni-YSZ Affects Catalyst Activity and Stability

<table>
<thead>
<tr>
<th>Catalyst Composition</th>
<th>Pretreatment</th>
<th>GHSV</th>
<th>Conversion, %</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-YSZ</td>
<td>1375C calcine; 700C in H₂, 1h</td>
<td>621K</td>
<td>12-15</td>
<td>Decrease to line out</td>
</tr>
<tr>
<td>NiO 0.8-MgO 0.2 GN-YSZ</td>
<td>800C calcine; 700C in H₂, 1h</td>
<td>646K</td>
<td>72</td>
<td>Increase to line out, stabilized high activity</td>
</tr>
<tr>
<td>NiO 0.8-MgO 0.2 GN-YSZ; Ni and Mg GN separately, mechanically mixed</td>
<td>800C calcine; 700C in H₂, 1h</td>
<td>626K</td>
<td>≤41</td>
<td>Decrease to line out, but not fully lined out at 13h</td>
</tr>
<tr>
<td>Ni-YSZ impregnated Mg nitrate</td>
<td>800C calcine; 700C in H₂, 1h</td>
<td>636K</td>
<td>&lt;15</td>
<td>Decrease to line out, similar to Ni-YSZ</td>
</tr>
<tr>
<td>NiO 0.8-MgO 0.2 GN-YSZ</td>
<td>1100C calcine; 700C in H₂, 1h</td>
<td>164K</td>
<td>9</td>
<td>Conversion increases to 45% at 655K at 800C</td>
</tr>
</tbody>
</table>
Ni-MgO-YSZ Methane Steam Reforming Powder Tests--Conclusions

- MgO shows promise as additive for activity stabilization and carbon control
  - Finely dispersed MgO (20%) in Ni shows stable (high initial) activity
    - Well-dispersed MgO retards Ni sintering/restructuring in H₂O/H₂
    - Stable CH₄ reforming obtained at S/C = 1 for ~20 hours
- Method of MgO introduction is important for catalytic performance
  - Activity and stability observed in the following order:
    \[ \text{NiO-MgO(GN)-YSZ} > \text{NiO (GN) + MgO (GN)-YSZ} > \text{Ni-YSZ + MgO (impreg)} \]
- Calcination temperature affects performance of Ni-MgO-YSZ
  - “NiMgO₂” solid solution forms at or below 1100°C
  - Activity slowly increases with time as Ni becomes reduced and available
Ni-YSZ Powder Catalyst Testing
Ni-MgO-YSZ Powder Catalyst Testing
Ni-Cu Powder Catalyst Testing
98%Ni-2%Cu (GN) After 1375°C Calcination Shows Loss of Cu Efficacy

\[ T_{\text{init}} = 750^\circ\text{C}; \text{S/C/H} = 3/1/1; \text{WHSV}_{\text{init}} = 81,700 \]

\[ \text{Ea} = 32 \text{ kcal/mol}; \text{compare with 12\% conversion at 667K GHSV for Ni-YSZ} \]

Loss of CuO by evaporation at 1375°C implicated
Catalyst with an initial composition of 80%Ni-20%Cu (GN) calcined at 1375°C maintains reduced activity. GHSV = 82,000; Tinit = 750°C; S/C/Hinit = 3/1/1

Ea = 36.3 kcal/mol; compare 700°C result with 12% conversion at 667K GHSV for Ni-YSZ. Some Cu retained following 1375°C calcination.
Cu Addition Method and Pretreatment Affect Ni Activity

<table>
<thead>
<tr>
<th>Cu Content and Prep Method</th>
<th>Calcination-Reduction</th>
<th>Temp, C</th>
<th>Space Velocity, K</th>
<th>CH₄ Conversion, %</th>
<th>Normalized Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% Cu; GN</td>
<td>800C 4h-700C 1h</td>
<td>700</td>
<td>312</td>
<td>1.5</td>
<td>0.093</td>
</tr>
<tr>
<td>2% Cu; GN</td>
<td>800C 4h-900C 3h</td>
<td>700</td>
<td>83</td>
<td>12.5</td>
<td>0.21</td>
</tr>
<tr>
<td>2% Cu; GN</td>
<td>1375C 1h-700C 1h</td>
<td>700</td>
<td>163</td>
<td>23</td>
<td>0.81</td>
</tr>
<tr>
<td>20% Cu; GN</td>
<td>800C 4h-700C 1h</td>
<td>750</td>
<td>81</td>
<td>1.9</td>
<td>0.012</td>
</tr>
<tr>
<td>20% Cu; GN</td>
<td>1375C 1h-700C 1h</td>
<td>700</td>
<td>82</td>
<td>5.5</td>
<td>0.079</td>
</tr>
<tr>
<td>20% Cu impregnated on Ni-YSZ</td>
<td>800C 4h-700C 1h</td>
<td>700</td>
<td>166</td>
<td>20</td>
<td>0.69</td>
</tr>
<tr>
<td>Ni-YSZ</td>
<td>1375C 1h-700C 1h</td>
<td>700</td>
<td>328</td>
<td>15</td>
<td>1</td>
</tr>
</tbody>
</table>
Ni-Cu Methane Steam Reforming
Powder Tests--Conclusions

- Cu shows promise for decreasing activity of Ni-YSZ
  - Glycine nitrate synthesis
  - Activity decrease at 700°C nearly two order of magnitude with 20% Cu
- Effectiveness of Cu decreases with increasing temperature
  - Phase segregation and/or high mobility of Cu at higher temperatures implicated
  - Activation energy of Ni-Cu is higher than Ni-YSZ
- Developing realistic preparation method key to viable Ni-Cu-YSZ anode
  - Volatility of CuO at sintering temperatures requires post-addition of Cu or alternative method of synthesis
  - Simple Cu impregnation method inadequate
Future Work
Carbon Tolerance Studies

- Extended runs to determine Ni-YSZ susceptibility to carbon formation
  - S/C and conversion level effects for methane and natural gas reforming
  - Provide baseline data for comparison with alternate formulations

- Evaluate Ni-MgO-YSZ formulations for improved carbon tolerance
  - Determine effect of preparation and pretreatment on
    - Activity and lineout behavior
    - Carbon-free operation
  - Compare with Ni-YSZ baseline data

- Corroborate/correlate powder results with Ni-YSZ and Ni-MgO-YSZ anode strips
Future Work
Activity Modification Studies

- Determine limits to Ni-YSZ activity control through thermal steam/hydrogen pretreatment

- Extend studies of Ni-Cu-YSZ activity control
  - Cu concentration and pre-treatment effects
  - Temperature cycling studies 700-850°C for activity and stability
  - Stability to low S/C and natural gas
  - Effect of YSZ on Ni-Cu interaction
Future Work
Ni-Cu-YSZ Synthesis and Fabrication

- Evaluate preparation methods for Ni-YSZ-Cu
  - Infiltration or electrodeposition of Cu onto Ni-YSZ post-sintering
  - Other approaches including industry collaboration

- Tailored compositions that compensate for Cu loss during sintering

- Test compositions as powders and formed strips
  - Compare with GN results
  - Measure thermal axial profile and compare with model predictions

- Work with industry to evaluate Ni-Cu-YSZ in cell tests
Acknowledgements

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Additional PNNL contributor: V. Sprenkle provided anode compositions used in our tests.
Backup Slides
Ni0.98Cu0.02 Catalyst Shows Low Activity
GN, Calcined at 800°C/4hr,
WHSV = 312,400 S/C/H=3:1:0.1 T=700°C

Compare with 12-15% CH₄ conversion for Ni-YSZ
Conversion of Synthetic Natural Gas over Non-Equilibrated Ni-YSZ Shows Slow Deactivation

GHSV = 667K, S/C/H/He = 3/1/1/5, T=700°C

Carbon observed at front end of catalyst bed at end of run