Controlling Activity and Stability of Ni-YSZ Catalysts for On-Anode Reforming

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Outline of Presentation

- Background and Issues Regarding On-anode Reforming
- Preliminary study of steam methane reforming with Ni-YSZ and Ni-YSZ + Au anode substrates
- Ni-YSZ catalytic powder tests
- Effect of MgO on stabilizing Ni-YSZ methane steam reforming relative to Ni surface restructuring
- Effect of Cu and Au on Ni anode activity
- Future work
Project Objectives

- Develop effective Ni-YSZ-based anode for on-anode reforming of methane and natural gas
  - Resistant to carbon formation
  - Stable operation at steam-to-carbon ratio (S/C) at or below 2
- Develop methods to control endothermic steam reforming activity
  - Provide acceptable thermal gradient along cell
  - Minimize thermal stresses leading to failure of cell or other components
Advantages of On-Anode Reforming

- Heat required for methane steam reforming can be supplied by heat generated during fuel cell operation
  - Energy and efficiency savings
  - Significant reduction in quantity of cathode air required for cooling
- Consumption of hydrogen increases equilibrium conversion of CH₄, reducing required reformation temperature
- Potential reduction in steam requirement due to H₂O generated by electrochemical oxidation of H₂
- Potential to downsize or eliminate external reformer
Disadvantages of On-Anode Reforming

- Carbon formation may deactivate anode
- Strong thermal gradients may damage cell or other components
- Loss of process flexibility
Technical Approach

- Work in conjunction with computational modeling to predict thermal profile of anode during direct methane reforming.
  - Provide kinetic data with Ni-YSZ to support model development
    - Activity as function of Ni weight and surface area
    - Rate dependence on CH₄, H₂O, CO₂, H₂ concentrations
    - Activation energy
  - Determine S/C ratio necessary to maintain catalyst activity
- Use model to predict anode thermal profile on active cell with methane feedstock
  - Determine steam reforming activity required for acceptable thermal gradients
- Modify anode composition to control activity and carbon formation
On-Anode Reforming
Other Work

Review of open literature indicates large disparity in results:
- Dependency on CH₄—first order (general agreement)
- Dependency on H₂O—zero to negative order
- Dependency on H₂—zero to positive order
- Activation energy variation from 100-300 kJ/mol
  - 100 kJ/mol consistent with other Ni-based reforming results
  - 300 kJ/mol possibly suggests increased Ni reduction at elevated T

Generally unclear whether kinetics were obtained under absence of heat and mass transport limitations

Inconsistent results on presence of carbon on anode
On-Anode Reforming
Other Work

Achenbach et. al., J. Power Sources 52 (1994) 283-288
- Reforming rate much faster than H₂ electrochemical oxidation rate
  - 42 @ 900°C
  - 81 @ 1000°C
  - 7.4 @ 700°C
- Leads to strong endotherm at front end of cell absent anode modification

Dicks et. al., J Power Sources 86 (2000) 523-530
- Non-Arrhenius behavior—suggests heat transfer issues
- Very low conversion with H₂O/CH₄ only—H₂ necessary for good CH₄ conversion

Clarke et. al., Catalysis Today 38 (1997) 411-423
- “…recent work by British Gas has shown that operation of a cell on steam/methane rather than hydrogen results in an increase in sintering of the nickel.”
Butane Rapidly Deactivates Anode But Activity Recovers With Steam Treatment

Anode Catalyst Material
Varying Steam to Carbon; 550°C Reactor Temperature
165,000 GHSV based on previous powder

Conversion and Selectivity (%)

- n-C4 Conversion
- CO Selectivity
- CH4 Selectivity
- Start of Day 2
- Start of Day 3
- Cylinder
- Change to 3:1 S/C
- Restart at 6:1
- Steaming
- N2 Purge

Time on Stream (hours)

0 5 10 15 20 25 30
Anode Catalyst
Post Reaction with n-Butane

Carbon readily wipes off surface of anode
Testing of Formed Ni/YSZ Anode

3:1 Steam to Carbon; 10:1 CH₄ to H₂, 700°C

0.02%Au on anode is equivalent to 0.8%Au on supported Ni catalyst; no deactivation observed with either material.
Anode SEM After CH$_4$ Reforming
Tests for Heat and Mass Transfer Limitations

Issues to consider with small test reactors and strongly endothermic reactions (integral conditions):
- Radial temperature gradients
- Intra-particle concentration gradients

Macrosopic dilution of bed with inerts—assess intra-reactor and inter-phase gradients
- Dilute until conversion at fixed space velocity is constant

Intra-particle mass transfer tests
- Change particle size of catalyst—constant activity at constant space velocity indicates absence of mass transfer (P drop concerns)
- Vary amount of catalyst and inert within the catalyst particle or dilute catalyst (Koros-Nowak-Madon-Boudart)—observed reaction rate proportional to amount of active catalyst
Testing of Diluted Anode Powders
Activity Comparison Ni-YSZ Anode vs. Anode Powder Indicates Heat and/or Mass Transfer Limitations Must Be Considered

700°C; S/C = 3; CH₄/H₂ = 10

Flow Rate (sccm inlet/g cat)

Conversion (%)
Initial Tests Indicate Deactivation of Ni-YSZ Complicates Gathering Kinetic Data

Ni (40 vol%)/YSZ Anode Powder, 620°C
Diluted 10x With YSZ; WHSV=340,000 ml/h-g, S/C=3
Quartz Tubular Reactor
Pre-Steaming of Anode Powder Does Not Eliminate Deactivation Under Reforming Conditions

700°C, S/C/H = 3/3/0.1

Conversion (%)

40% Ni - YSZ powder
40% Ni-YSZ powder (H2O/H2/N2 treat 700°C 100 hrs)

WHSV (sccm CH4/g Ni)
Activity Loss During Ni-YSZ Methane Reforming is Not Reversible

700°C, S/C/H = 3/1/0.1

Methane Conversion

Time on Stream (h)

H₂ Reduction 700°C

H₂₀ to H₂ ratio changed to 3:0.3

Steam + H₂ treat 700°C
Ni-YSZ Powder Shows Deactivation Even at High S/C Ratio

700C; 330K cc/h-g

- CH4 Conversion
- S/C Ratio

Conversion (%) vs. TOS (min)

Steam to Carbon Ratio

0% 5% 10% 15% 20% 25% 30% 35% 40% 45% 50%

0 50 100 150 200 250 300 350 400

700C; 330K cc/h-g
How Can We Explain Nickel-YSZ Deactivation?

- Ni-YSZ deactivation could be result of
  - Carbon formation
  - Nickel oxidation
  - Metal restructuring

- Deactivation by carbon formation unlikely
  - Deactivation even at very high S/C (15)
  - Activity not recoverable following treatment in H₂O or H₂/H₂O
Preparation of Anode Composition Catalysts By Glycine Nitrate (GN) Method

Metal Nitrates + Glycine
(Ni, Mg)

GN Synthesized Powder + Commerical YSZ (Daiichi)

Attrition milling
Calcination sieving
Testing

“Ash” calcined at 600°C to ensure homogeneity
Catalysts Prepared

Ni-YSZ 40 vol% Ni (conventional)

Ni-YSZ 40 vol% Ni (GN)
Ni-MgO-YSZ 40 vol% Ni (GN) 80:20 Ni/Mg mol/mol (various calcination T)
Ni-YSZ 40 vol% Ni (GN) + 20%MgO (impregnation)
Ni-YSZ 40 vol% Ni (GN) + 0.5% Au (impregnation)

Ni (GN)
Ni-MgO (GN) 80:20 and 90:10 Ni/Mg mol/mol
Ni-Cu (GN)

Calcination prior to testing generally at 800°C
Anode Powder Test Reactor
Ni-YSZ Deactivates Regardless of Preparation Method

700°C, 646K ml feed/h-g

Conversion (%) vs. Time (min)

Ni-YSZ gln method
Ni-YSZ (std prep)
Ni-YSZ Conventional Anode Powder Shows Deactivation Irrespective of H₂ Concentration

700°C, 648K ml/h-g

S/C/H/N=3:1:1:0 Initial

XCH4

- Restart change S:C:H:N to 3:1:0.5:0.5
- Change S:C:H:N to 3:1:0.1:0.9

CO Conversion

TOS (min)
Admixing NiO With 20% MgO Stabilizes CH₄ Conversion

Ni₀.₈ Mg₀.₂ (glycine nitrate; no YSZ) 706k ml/h-g, 650°C, S/C=3

Conversion

TOS (min)
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

Graph shows conversion (% vs time (min)) for Ni0.8Mg0.2O-YSZ (GN) Prepared together and Ni-YSZ (GN).
How Can We Explain The Effect of MgO on Ni-YSZ Anode Composition?

- Ni-YSZ deactivation could be result of:
  - Carbon formation
  - Nickel oxidation
  - Metal restructuring

- Role of MgO is to stabilize reduced Ni crystallites:
  - Solid solution formation between NiO and MgO
  - Reducibility and migration of Ni is affected
MgO Addition By GN Method Gives Better Results Than By Impregnation

800°C Calcination

700°C, 646K ml/h-g, S/C/H = 3/1/0.1

Conversion (%)

Time (min)

Ni0.8Mg0.2O-YSZ (GN)
Ni0.8Mg0.2 Impregnation
SMR Kinetics Over Ni-MgO (GN) Catalyst

\[ (-r_{CH_4})(mol / g_{\text{cat}} / s) = 2.188 \times 10^8 e^{-\frac{94.95 \times 10^3}{RT}} C_{CH_4} C_{CO_2}^{-0.0134} \]
### Conversion as Function of Calcination Temperature

**Ni-MgO-YSZ Catalyst (GN)**

700°C, 646K ml/h-g, S/C/H = 3/1/0.1

<table>
<thead>
<tr>
<th>Calcination Temperature</th>
<th>Reduction Temperature</th>
<th>CH₄ Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>800°C</td>
<td>700°C</td>
<td>72%</td>
</tr>
<tr>
<td>1100°C</td>
<td>700°C</td>
<td>&lt; 3%</td>
</tr>
<tr>
<td>1400°C</td>
<td>700°C</td>
<td>&lt; 3%</td>
</tr>
<tr>
<td>1100°C</td>
<td>900°C</td>
<td>&lt; 3%</td>
</tr>
</tbody>
</table>
## Surface Area of Ni Anode Catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Surface Area $m^2/g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO-YSZ (std prep)</td>
<td>Calcine 1375°C</td>
<td>0.45</td>
</tr>
<tr>
<td>NiO-YSZ (GN)</td>
<td>Calcine 800°C 1h</td>
<td>3.97</td>
</tr>
<tr>
<td>NiO-YSZ (GN)</td>
<td>Calcine 1100°C 1h</td>
<td>2.04</td>
</tr>
<tr>
<td>NiO-YSZ (GN)</td>
<td>Calcine 1400°C 1h</td>
<td>0.42</td>
</tr>
<tr>
<td>NiO-MgO-YSZ (GN)</td>
<td>Calcine 800°C 1h</td>
<td>8.09</td>
</tr>
<tr>
<td>NiO-MgO-YSZ (GN)</td>
<td>Calcine 1100°C 1h</td>
<td>2.06</td>
</tr>
<tr>
<td>NiO-MgO-YSZ (GN)</td>
<td>Calcine 1400°C 1h</td>
<td>0.2</td>
</tr>
<tr>
<td>NiO (GN)</td>
<td>Calcine 800°C 4h</td>
<td>1.15</td>
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<tr>
<td>NiO-MgO (GN)</td>
<td>Calcine 800°C 4h</td>
<td>4.17</td>
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<tr>
<td>NiO-CuO (GN)</td>
<td>Calcine 800°C 4h</td>
<td>0.30</td>
</tr>
</tbody>
</table>
SEM of spent GN synthesized NiO

Image after 1h SMR at 700°C, S/C = 3

- No evidence of carbon deposition
- Evidence of metal restructuring

Low surface area
SEM of spent GN synthesized NiMgO

Images after 14h SMR at 600-750°C, S/C = 3

No evidence for coke formation or significant Ni restructuring
TPR of Ni-YSZ and Ni-MgO-YSZ

2% H₂/Ar, 5°C/min from RT to 1100°C

Increasing heat treatment temp of Mg-NiO-YSZ increases the Ni-Mg interaction and makes reduction more difficult.
Reducibility of NiO-MgO-YSZ Incomplete at 700°C Over Extended Time

**Graph**: Reduction at 700°C under 2% H₂/Ar

Ramp rate: 5°C/min to 700°C

Isothermal at 700°C for 17h

- NiMg 1100°C
- NiMg 800°C
- Ni-YSZ std 1375°C
### Summary of H$_2$ Chemisorption Results

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Ni Surface Area (m$^2$/g)</th>
<th>BET SA over Reduced Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO-YSZ std 1375 C</td>
<td>0.51</td>
<td>1.11</td>
</tr>
<tr>
<td>NiO-YSZ SMR 16h spent</td>
<td>0.34</td>
<td>0.97</td>
</tr>
<tr>
<td>NiO 0.8-Mg 0.2-YSZ 800 C</td>
<td>2.18</td>
<td>7.76</td>
</tr>
<tr>
<td>NiO 0.8 Mg 0.2-YSZ 1100 C</td>
<td>0.87</td>
<td></td>
</tr>
</tbody>
</table>

H$_2$ Chemisorption Does Not Correlate With Activity
Addition of Copper (2 mol%) to Nickel Decreases Methane Reforming Activity By Two Orders of Magnitude

Ni$_{0.98}$Cu$_{0.02}$ (GN), S/C/H$_2$ = 3:1:0.1; 700°C; Space Velocity = 154K
SEM of Ni0.8-Cu0.2O GN Reduced at 700°C Indicates Low Surface Area Material
SEM Micrograph of GN Prepared NiO

Ni0.8Cu0.2 O
0.3 m2/g

NiO
1.15 m2/g

Ni0.8Mg0.2O
4.17 m2/g
Gold Addition to Supported Nickel Catalyst Significantly Reduces Methane Steam Reforming Activity

247,500 GHSV; 485°C; 3:1 Steam to Carbon

![Graph showing CH4 conversion over time on stream for 8.8% Ni and 8.8% Ni 0.4% Au catalysts. The 8.8% Ni catalyst shows a higher CH4 conversion compared to the 8.8% Ni 0.4% Au catalyst.]
0.5% Gold Addition to Ni-YSZ (GN) Reduces Activity But Not Deactivation

Gold Addition by Impregnation

Conditions: 700°C, S/C/H = 3/1/0.1, 628K ml/g-h
Au K Edge EXAFS

0.2% Au/MgO-Al2O3 (oxidized)
0.2% Au/8.8% Ni/MgO-Al2O3 (oxidized)
0.2% Au/MgO-Al2O3 (reduced)

When supported over MgO-Al2O3 without Ni, Au present as metallic particles under both reducing and oxidizing conditions.

When Ni oxide present (no reduced Ni), no evidence for interaction between Au and Ni.
Au K Edge EXAFS over Ni-Au/MgO-Al₂O₃

Increasing Au concentration:
- 0.1% Au
- 0.2% Au
- 0.4% Au
- 1% Au

Oxidizing Conditions:
- Ni is in oxidic form
- Au is in metallic form

Reducing Conditions:
- Ni is in metallic form
- Au migrates onto Ni surface

When Ni is in reduced form, Au migrates onto Ni surface.
Summary and Conclusions

- On-anode reforming provides significant advantages in terms of efficiency and cost but poses technical challenges.
- Kinetic measurements of anode catalyst must be free of heat and mass transfer limitations—test as diluted powders.
- Testing of Ni-YSZ anode powders shows loss of activity with time due to nickel metal sintering under SMR conditions.
- Addition of MgO to nickel retards sintering and provides stable methane reforming operation; calcination temperature affects activity.
- Addition of copper shows promise in reducing Ni anode activity; gold less effective.
Future Work

- Extended reaction tests to further examine catalytic stability of
  - Ni-YSZ
  - Ni-Mg-YSZ
  - Ni-Cu-YSZ
- Determine stability of anode aged 1000h in H₂
- Develop practical synthesis methods for modified Ni-YSZ anode materials
- Evaluate modified Ni-YSZ anode powders (Mg, Cu, Au) for carbon resistance
  - Methane @ S/C = 1-2
  - Natural gas
- Continue anode modification studies to reduce activity and interface with modeling group
- Initiate studies of on-anode reforming with electrochemically active cell