

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 CH_4 , reducing required reformation temperature
- ▶ Potential reduction in steam requirement due to H_2O generated by electrochemical oxidation of H_2
- ▶ 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 reformation.
 - 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 CH_4 —first order (general agreement)
 - Dependency on H_2O —zero to negative order
 - Dependency on H_2 —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

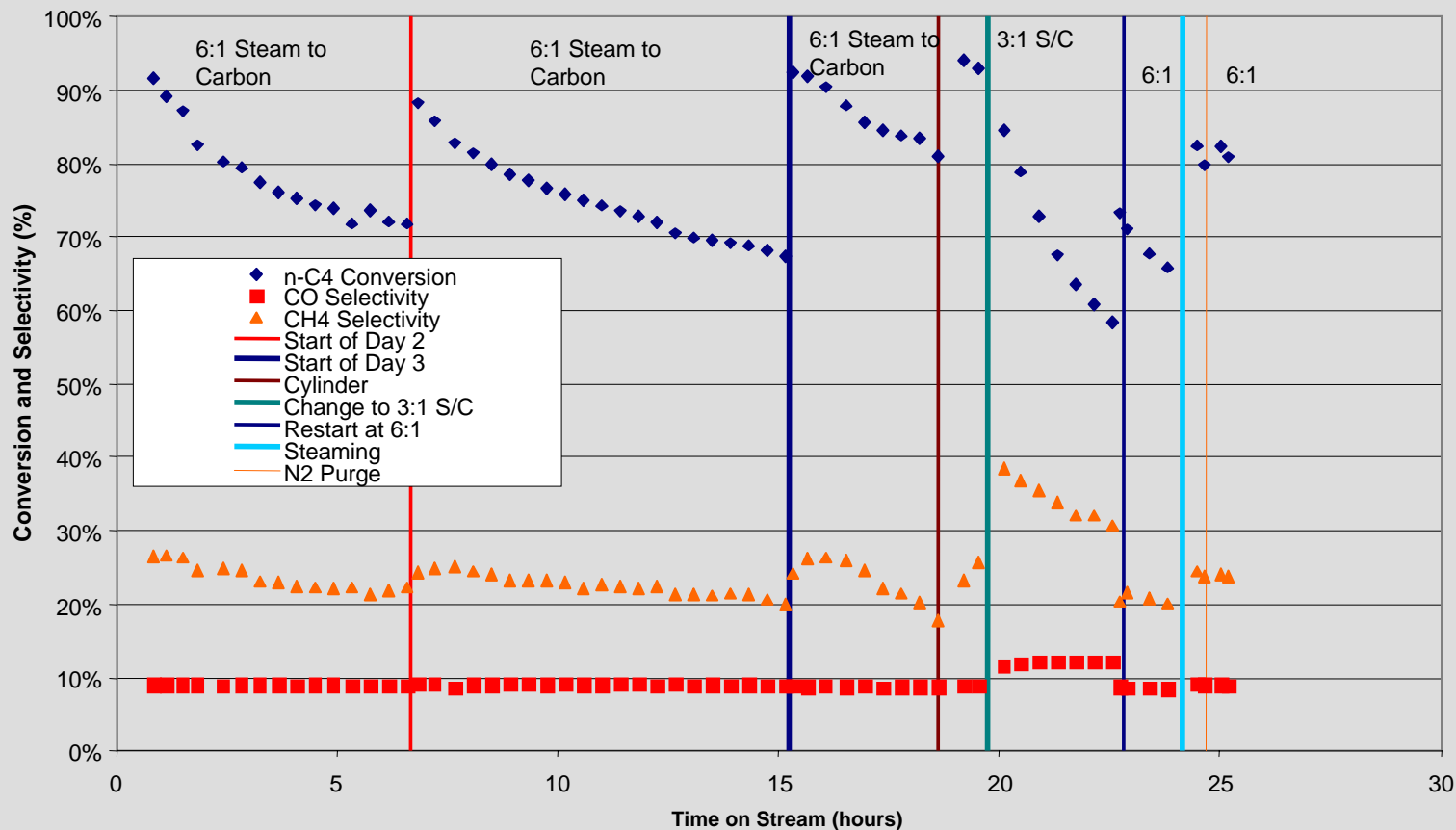
On-Anode Reforming

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; 550C Reactor Temperature
165,000 GHSV based on previous powder



Anode Catalyst Post Reaction with n-Butane

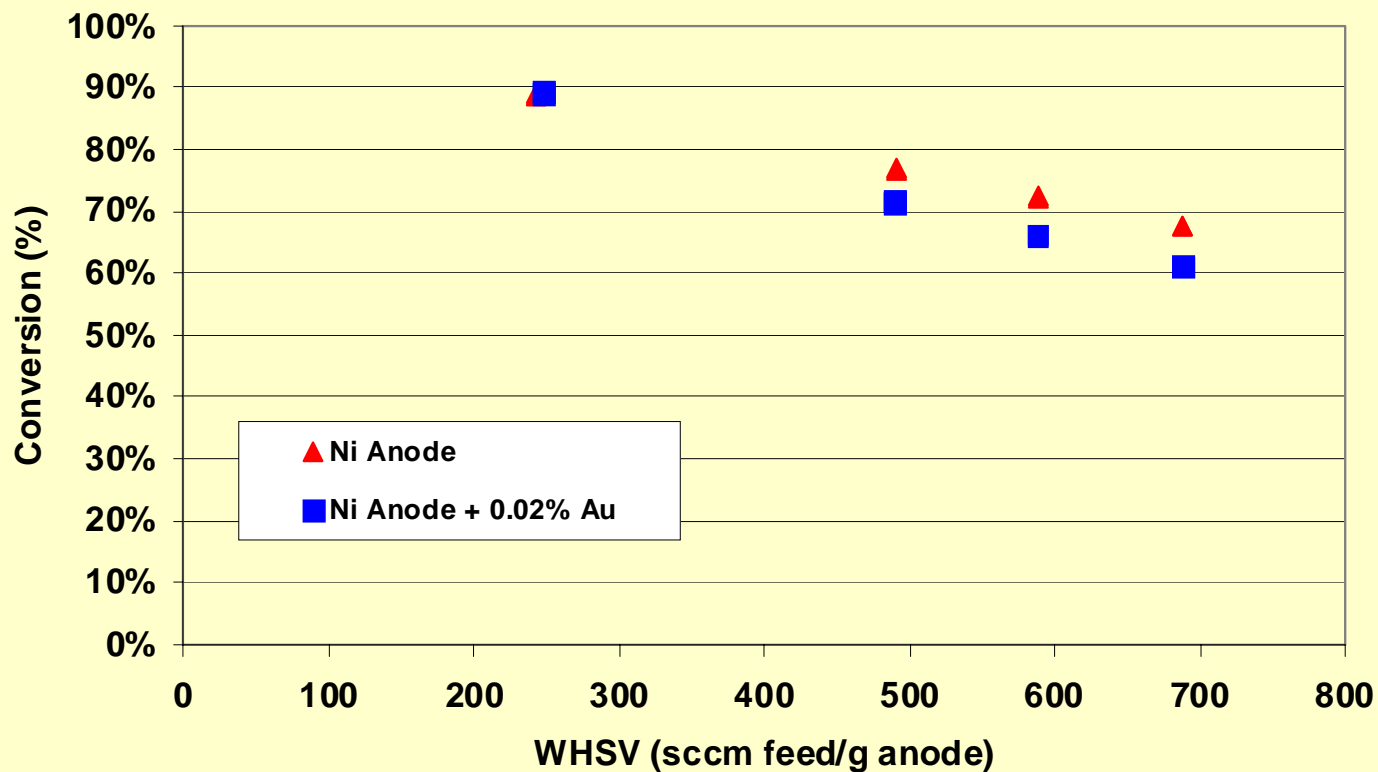


Carbon readily wipes off surface of anode

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 CH₄ Reforming

REDUCED ANODE MATERIAL

FRESH



SPENT



ANODE w/ 0.02 wt% Au

FRESH



SPENT

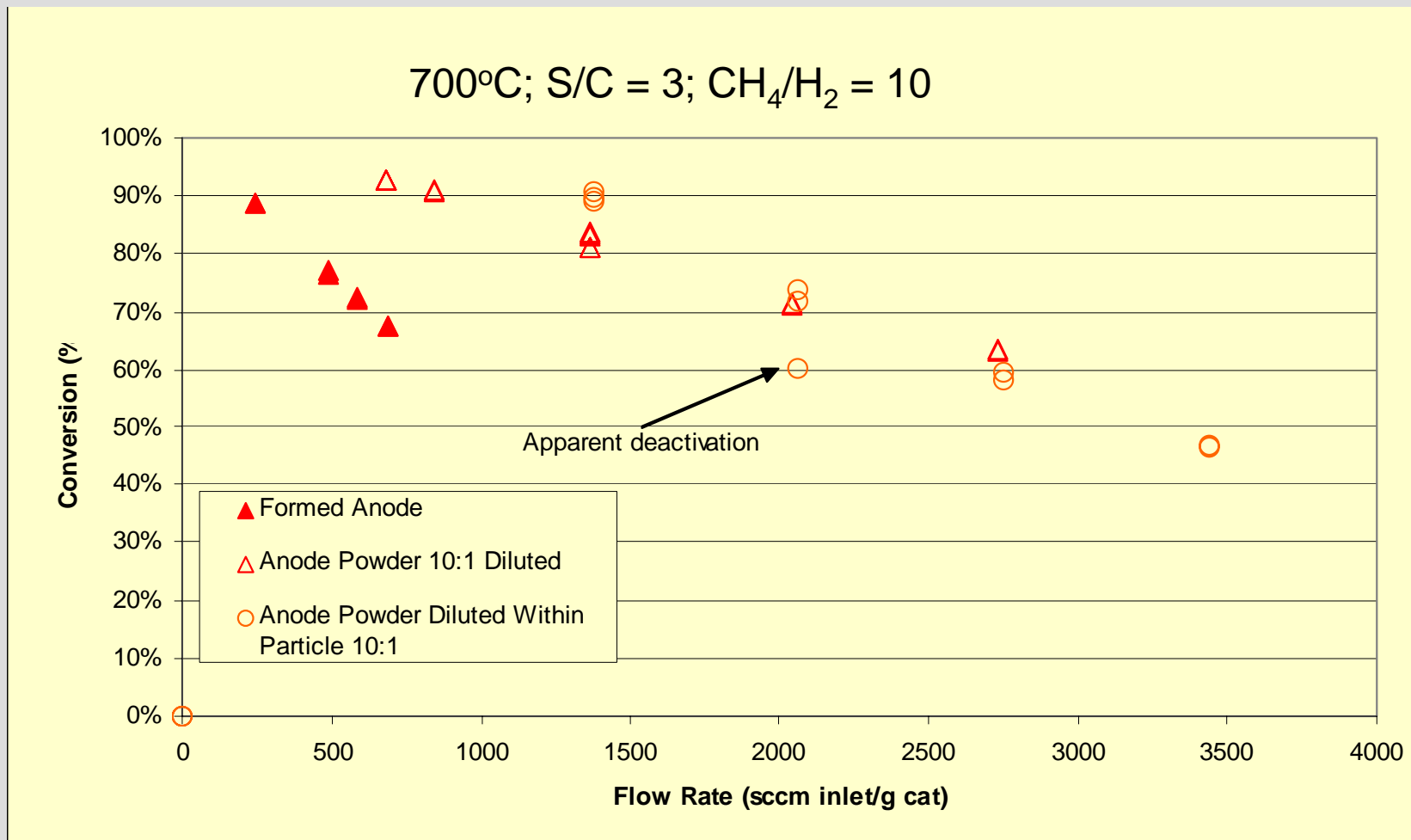


Tests for Heat and Mass Transfer Limitations

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

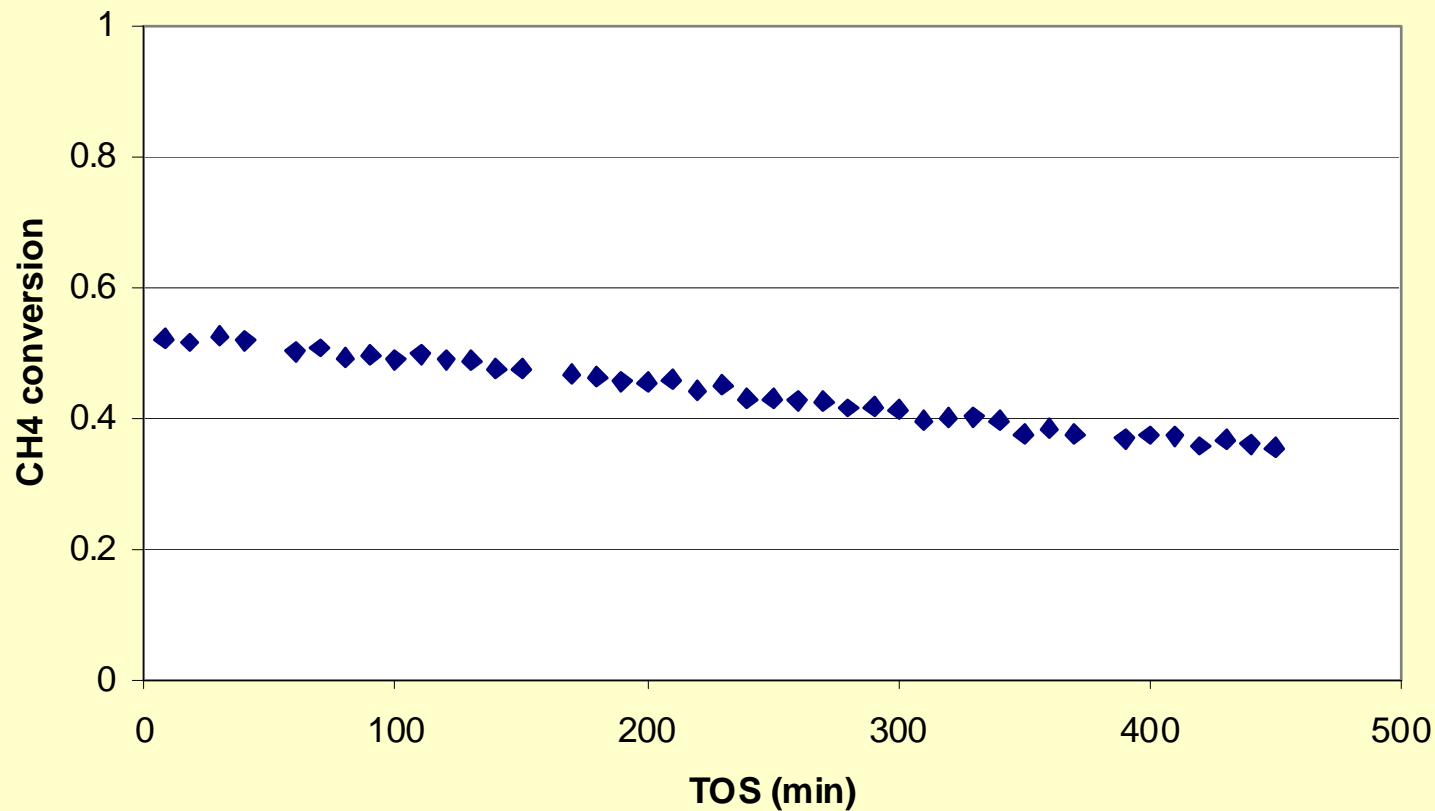
Testing of Diluted Anode Powders

Activity Comparison Ni-YSZ Anode vs. Anode Powder Indicates Heat and/or Mass Transfer Limitations Must Be Considered



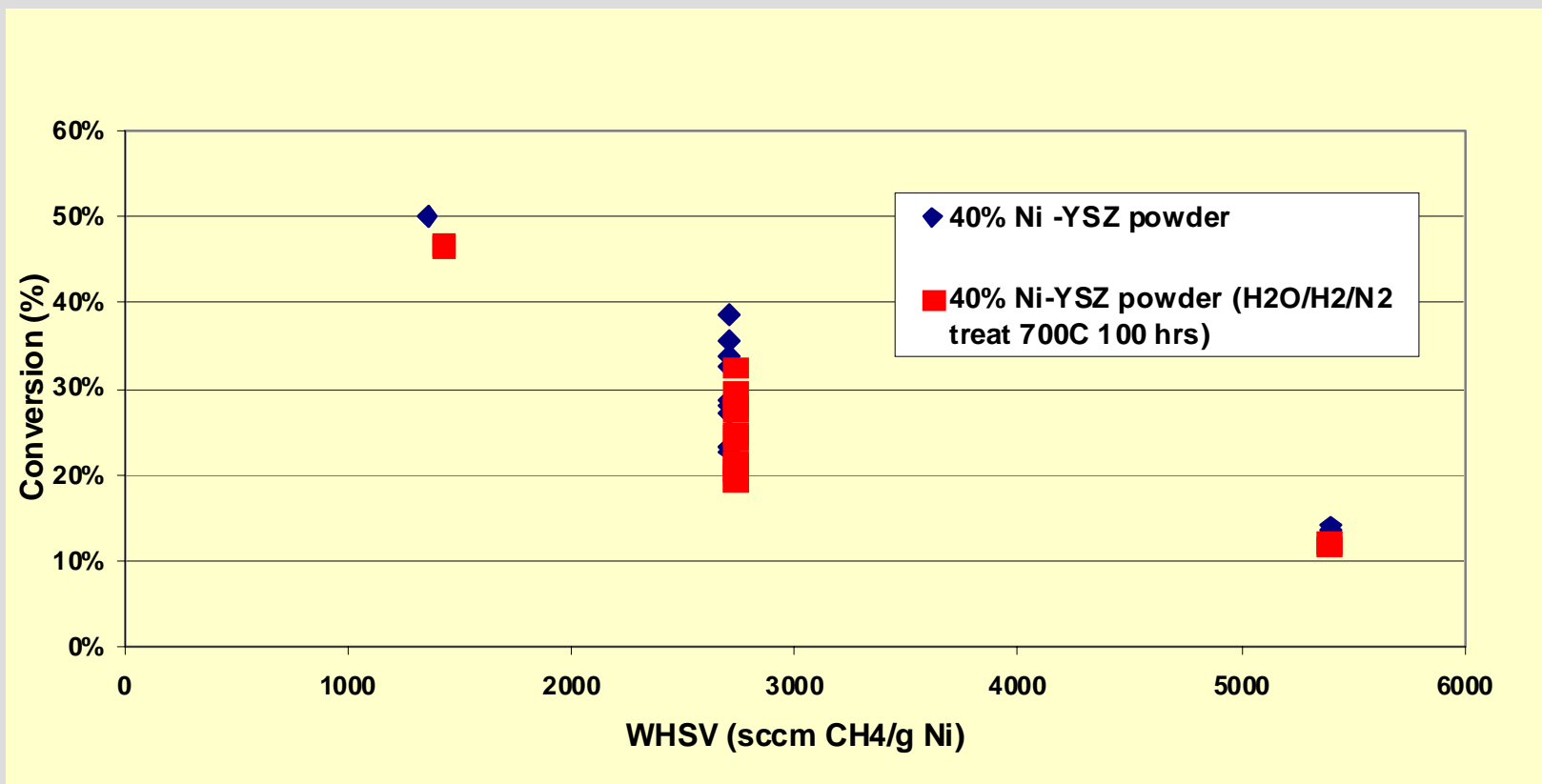
Initial Tests Indicate Deactivation of Ni-YSZ Complicates Gathering Kinetic Data

Ni (40 vol%)/YSZ Anode Powder, 620°C
Diluted 10x With YSZ; WHSV=340,000 ml/h-g, S/C=3
Quartz Tubular Reactor



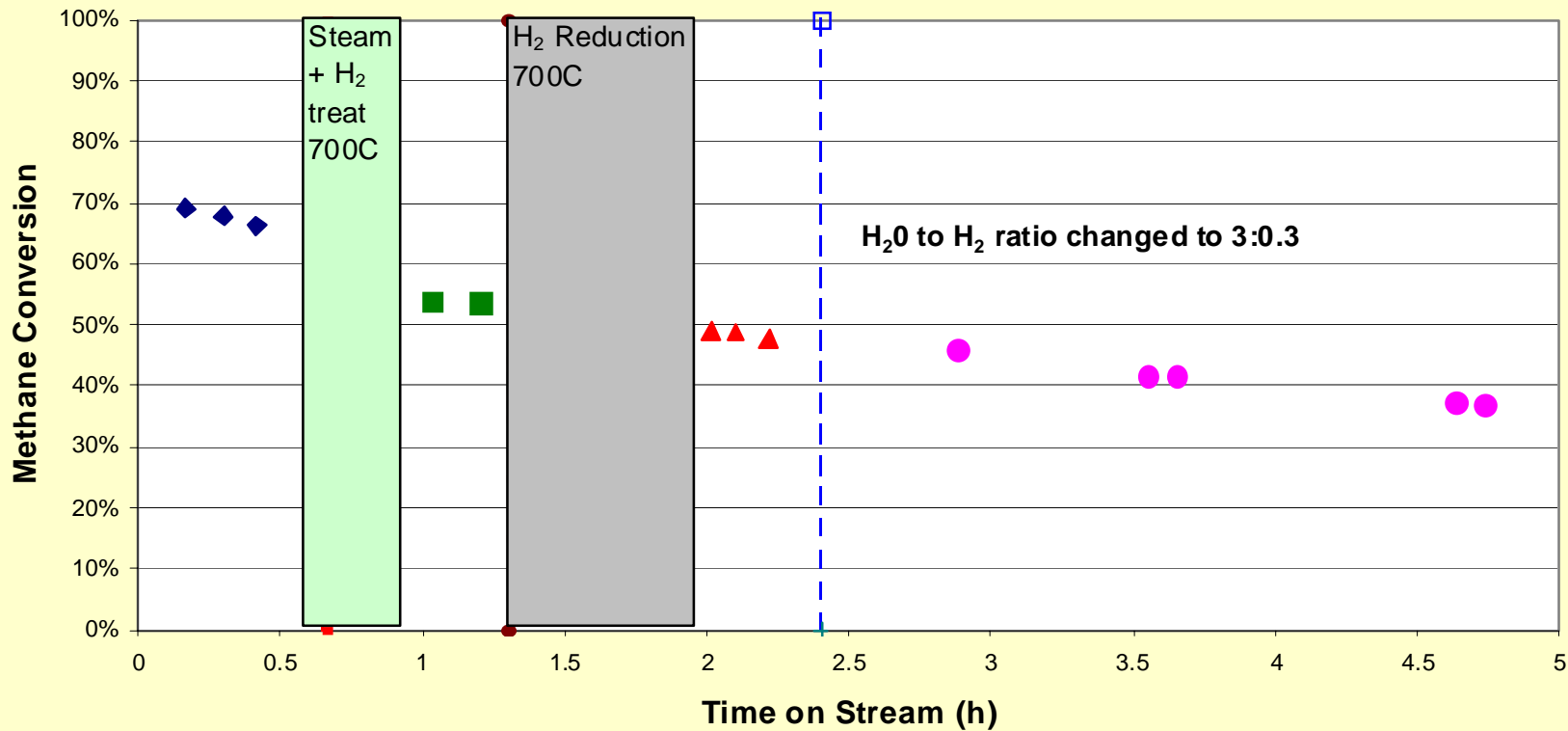
Pre-Steamming of Anode Powder Does Not Eliminate Deactivation Under Reforming Conditions

700°C, S/C/H = 3/3/0.1

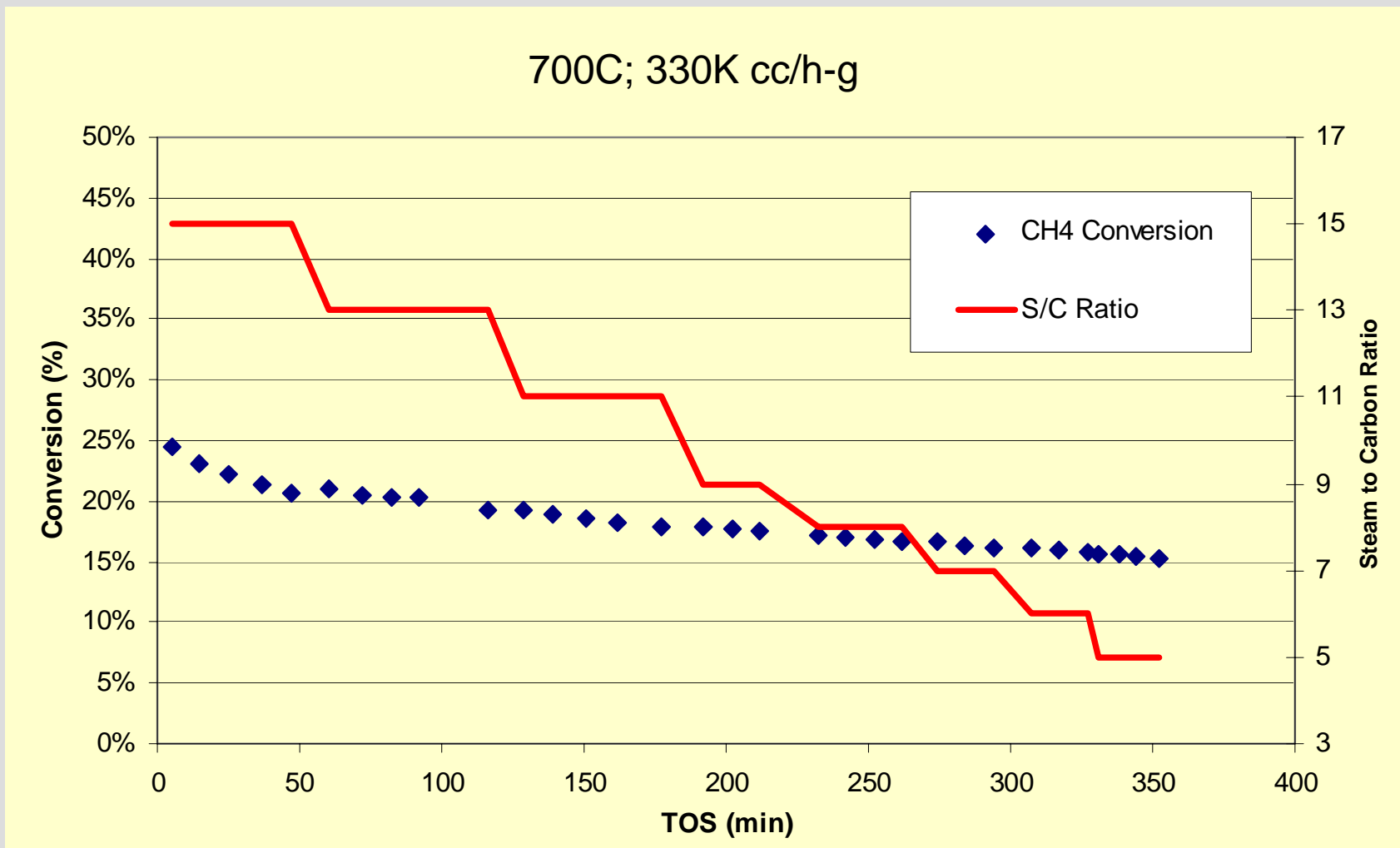


Activity Loss During Ni-YSZ Methane Reforming is Not Reversible

700C, S/C/H = 3/1/0.1



Ni-YSZ Powder Shows Deactivation Even at High S/C Ratio



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 H_2O or H_2/H_2O

Preparation of Anode Composition Catalysts By Glycine Nitrate (GN) Method

Metal Nitrates + Glycine

(Ni, Mg)

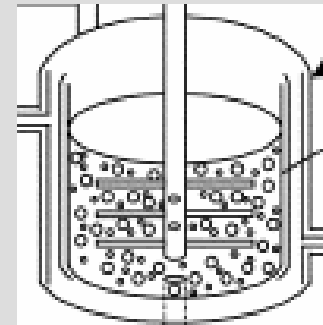


“Ash” calcined at 600°C to ensure homogeneity

GN Synthesized Powder

+

Commerical YSZ (Daiichi)



Attrition milling



Calcination sieving



Testing

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

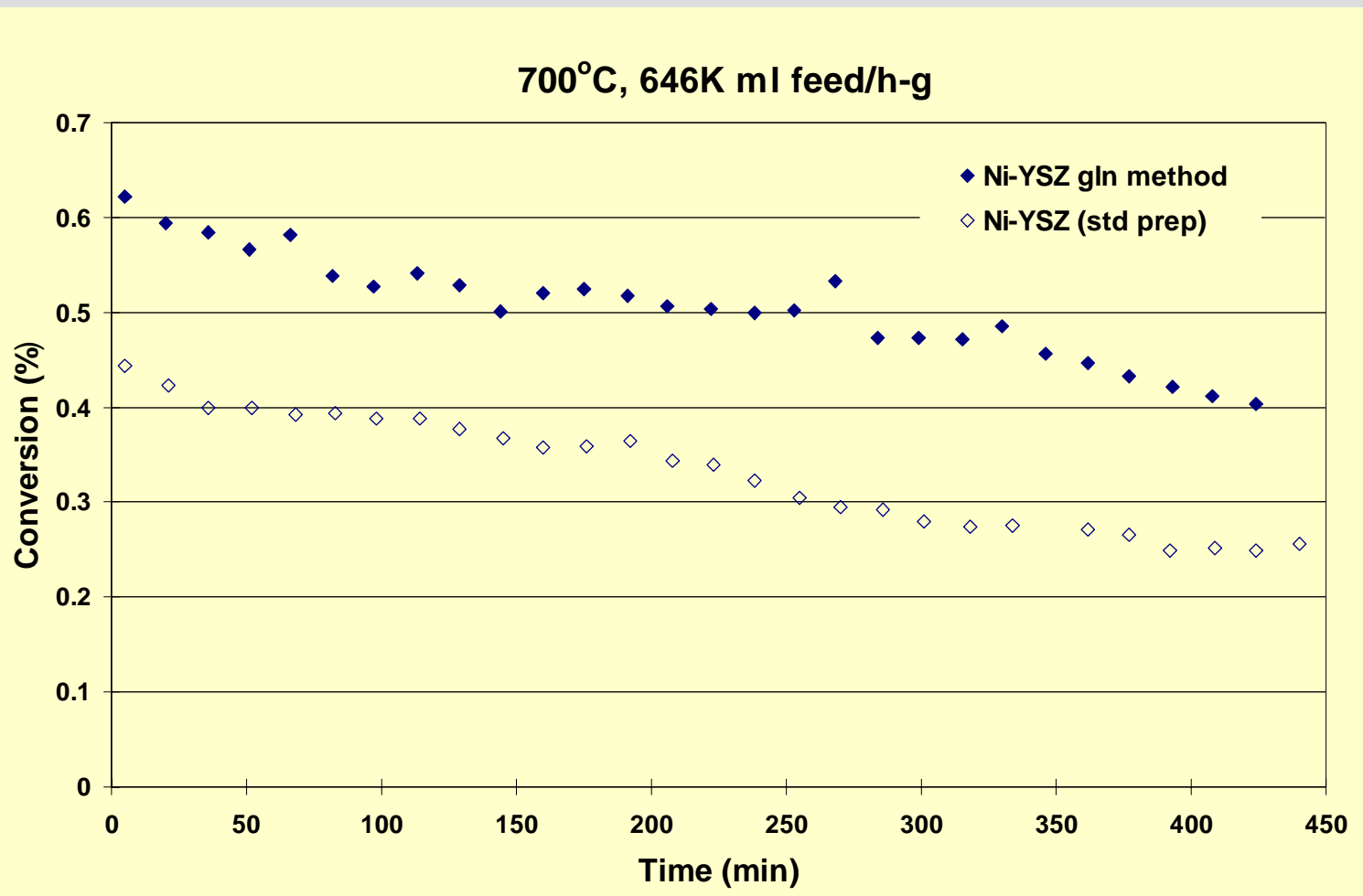
Ni-Cu (GN)

Calcination prior to testing generally at 800°C

Anode Powder Test Reactor

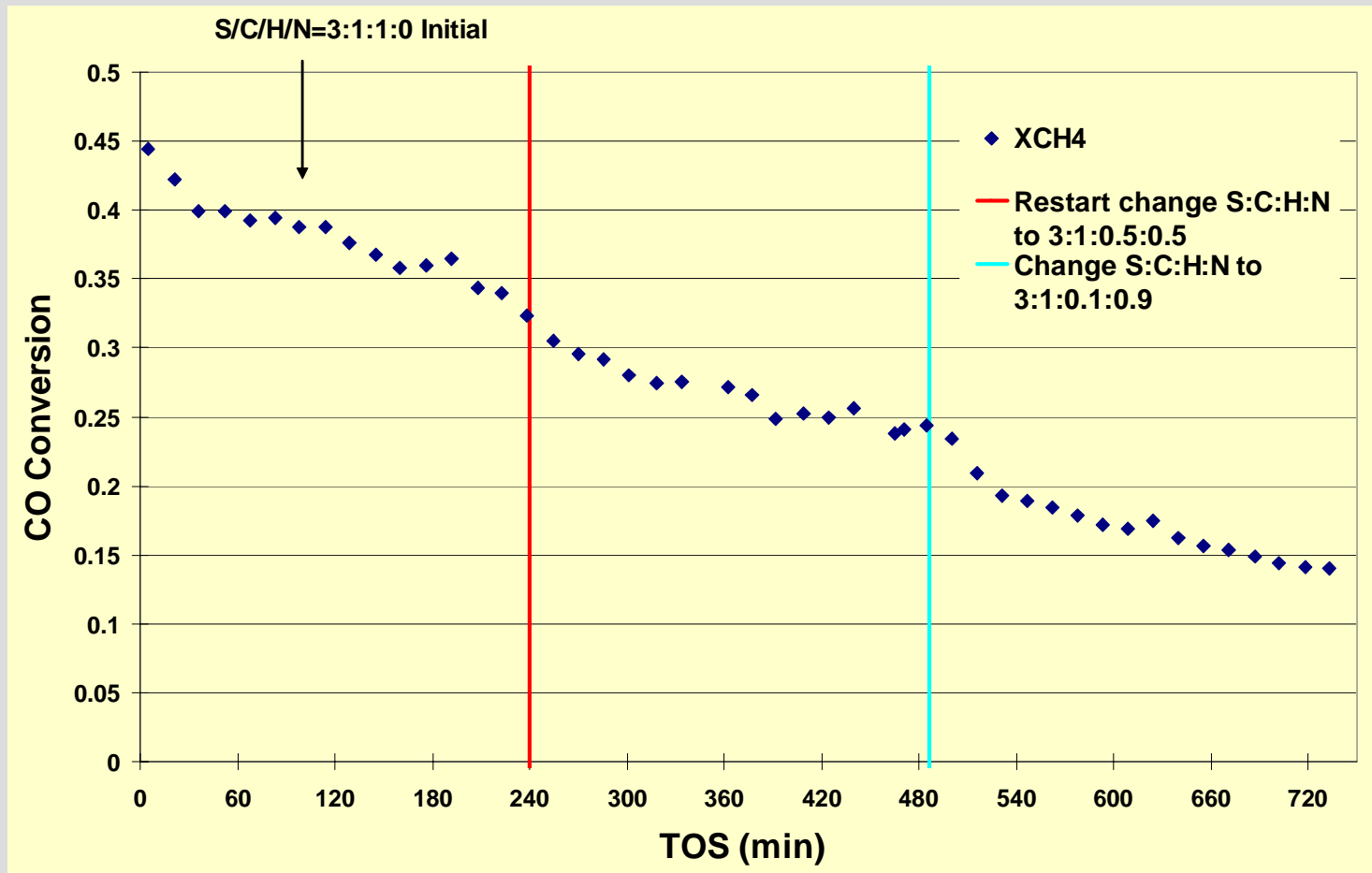


Ni-YSZ Deactivates Regardless of Preparation Method



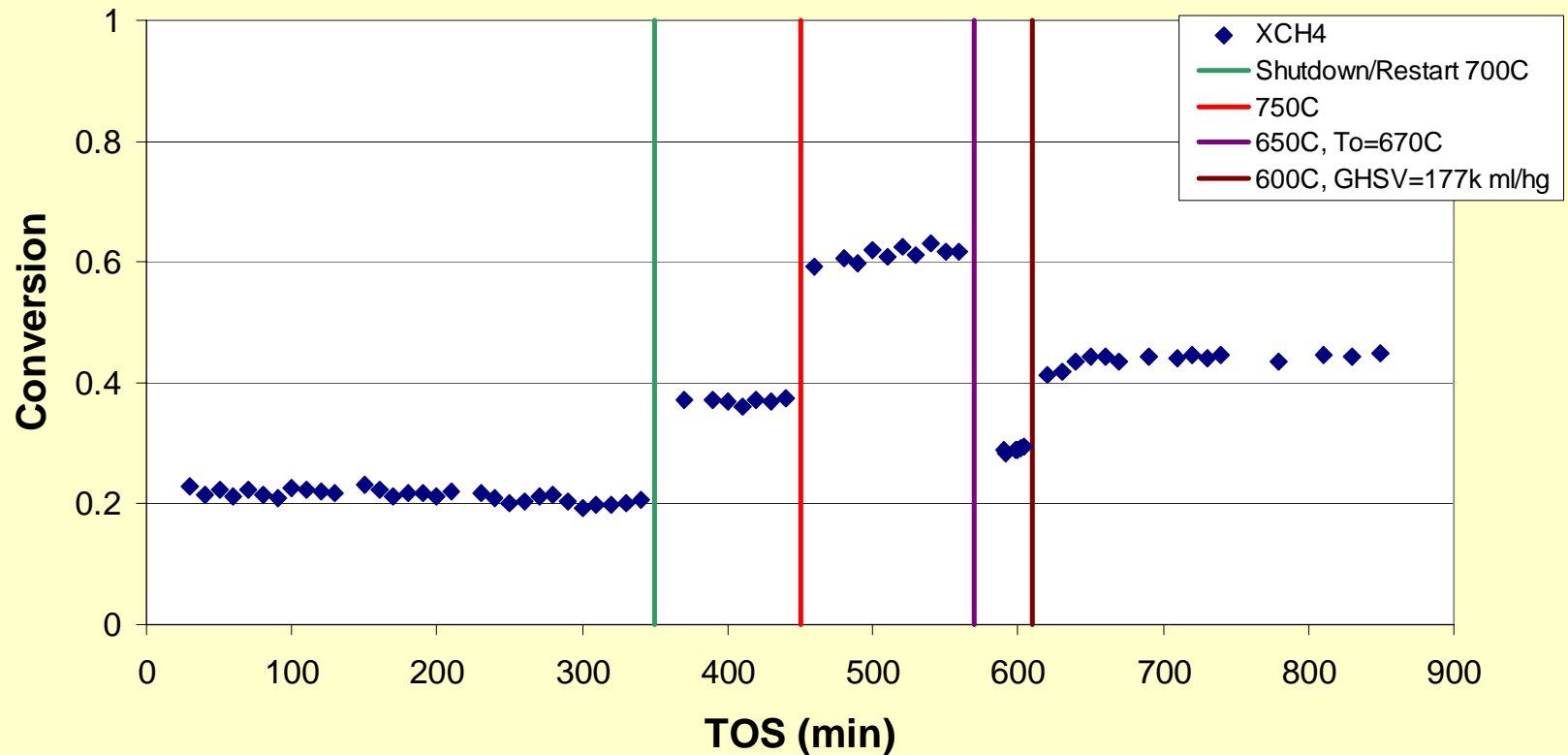
Ni-YSZ Conventional Anode Powder Shows Deactivation Irrespective of H₂ Concentration

700°C, 648K ml/h-g



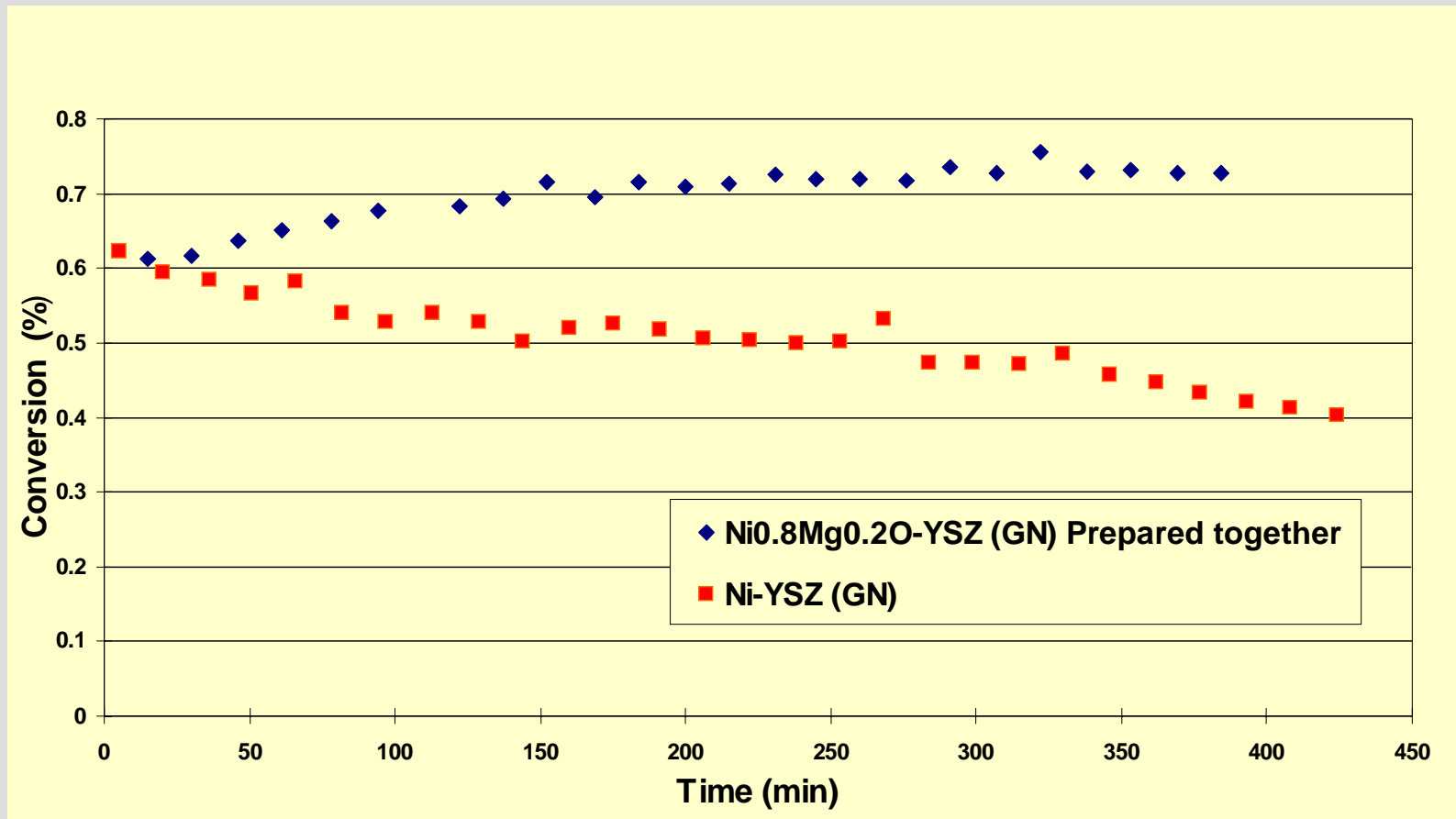
Admixing NiO With 20% MgO Stabilizes CH₄ Conversion

Ni_{0.8} Mg_{0.2} (glycine nitrate; no YSZ) 706k ml/h-g, 650C, S/C=3



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



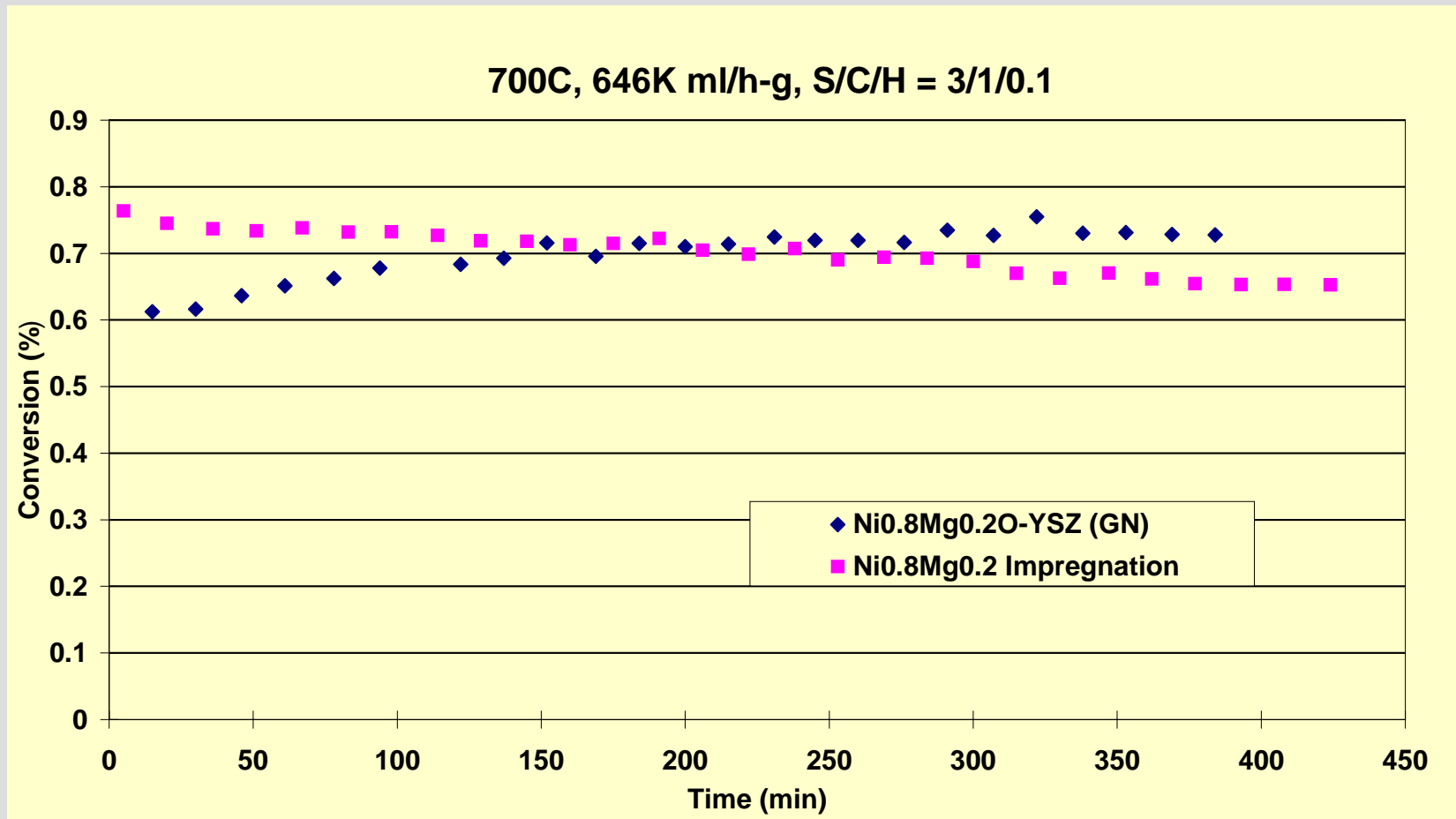
How Can We Explain The Effect of MgO on Ni-YSZ Anode Composition?

- ▶ 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



SMR Kinetics Over Ni-MgO (GN) Catalyst

$$(-r_{CH_4})(mol / g_{cat} / s) = 2.188 \times 10^8 e^{-\frac{94.95 \times 10^3}{RT}} C_{CH_4} C_{CO_2}^{-0.0134}$$

Conversion as Function of Calcination Temperature Ni-MgO-YSZ Catalyst (GN) 700°C, 646K ml/h-g, S/C/H = 3/1/0.1

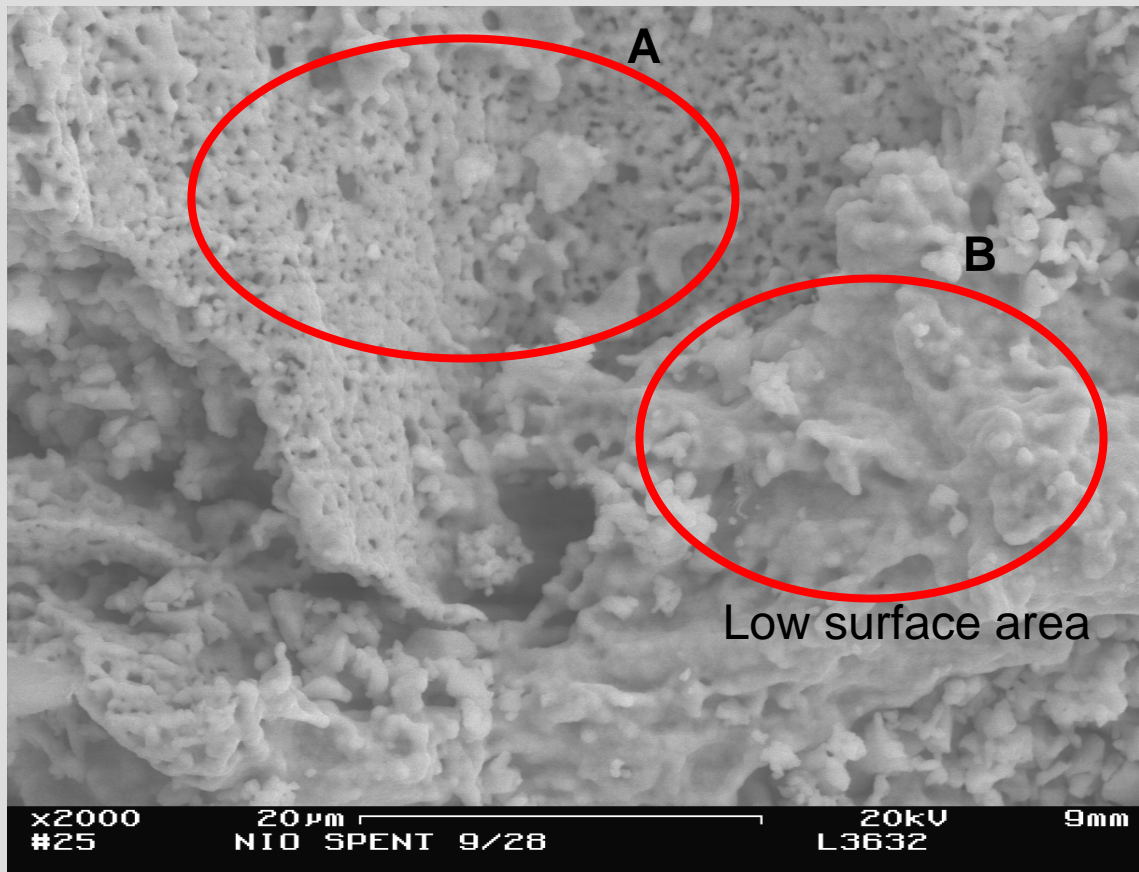
Calcination Temperature	Reduction Temperature	CH ₄ Conversion
800C	700C	72%
1100C	700C	< 3%
1400C	700C	< 3%
1100C	900C	< 3%

Surface Area of Ni Anode Catalysts

Sample	Treatment	Surface Area m ² /g
NiO-YSZ (std prep)	Calcine 1375°C	0.45
NiO-YSZ (GN)	Calcine 800°C 1h	3.97
NiO-YSZ (GN)	Calcine 1100°C 1h	2.04
NiO-YSZ (GN)	Calcine 1400°C 1h	0.42
NiO-MgO-YSZ (GN)	Calcine 800°C 1h	8.09
NiO-MgO-YSZ (GN)	Calcine 1100°C 1h	2.06
NiO-MgO-YSZ (GN)	Calcine 1400°C 1h	0.2
NiO (GN)	Calcine 800°C 4h	1.15
NiO-MgO (GN)	Calcine 800°C 4h	4.17
NiO-CuO (GN)	Calcine 800°C 4h	0.30

SEM of spent GN synthesized NiO

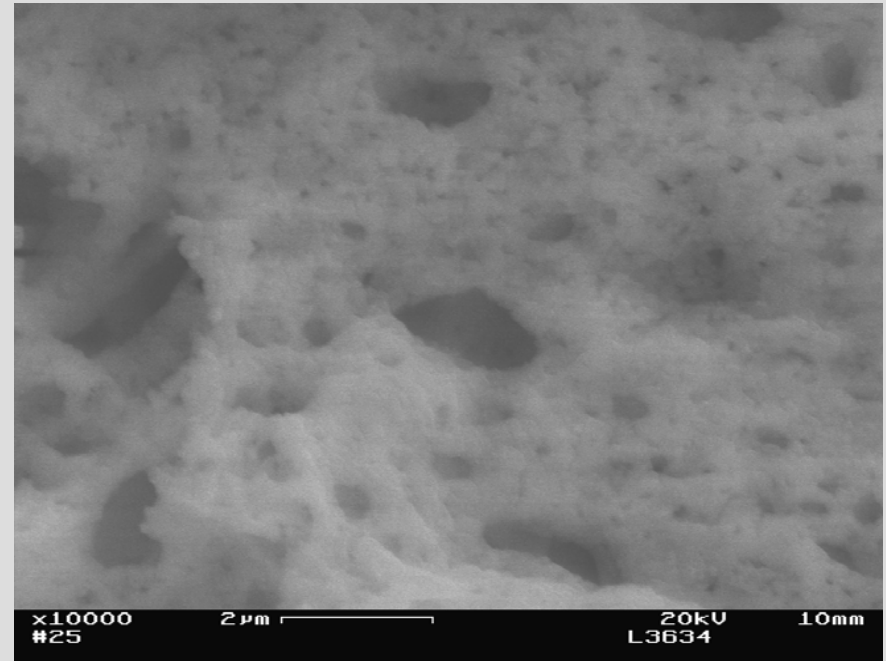
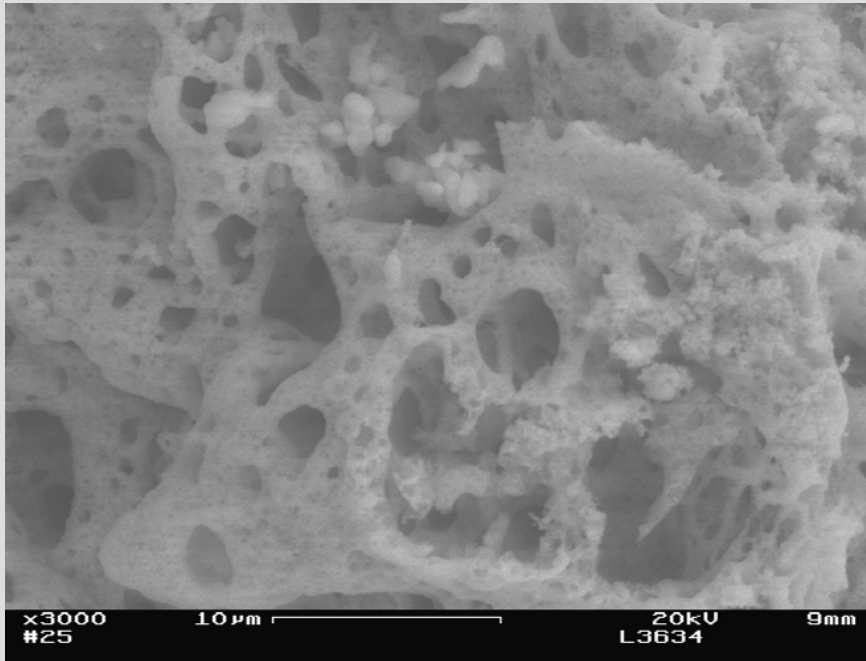
Image after 1h SMR at 700°C, S/C = 3



- No evidence of carbon deposition
- Evidence of metal restructuring

SEM of spent GN synthesized NiMgO

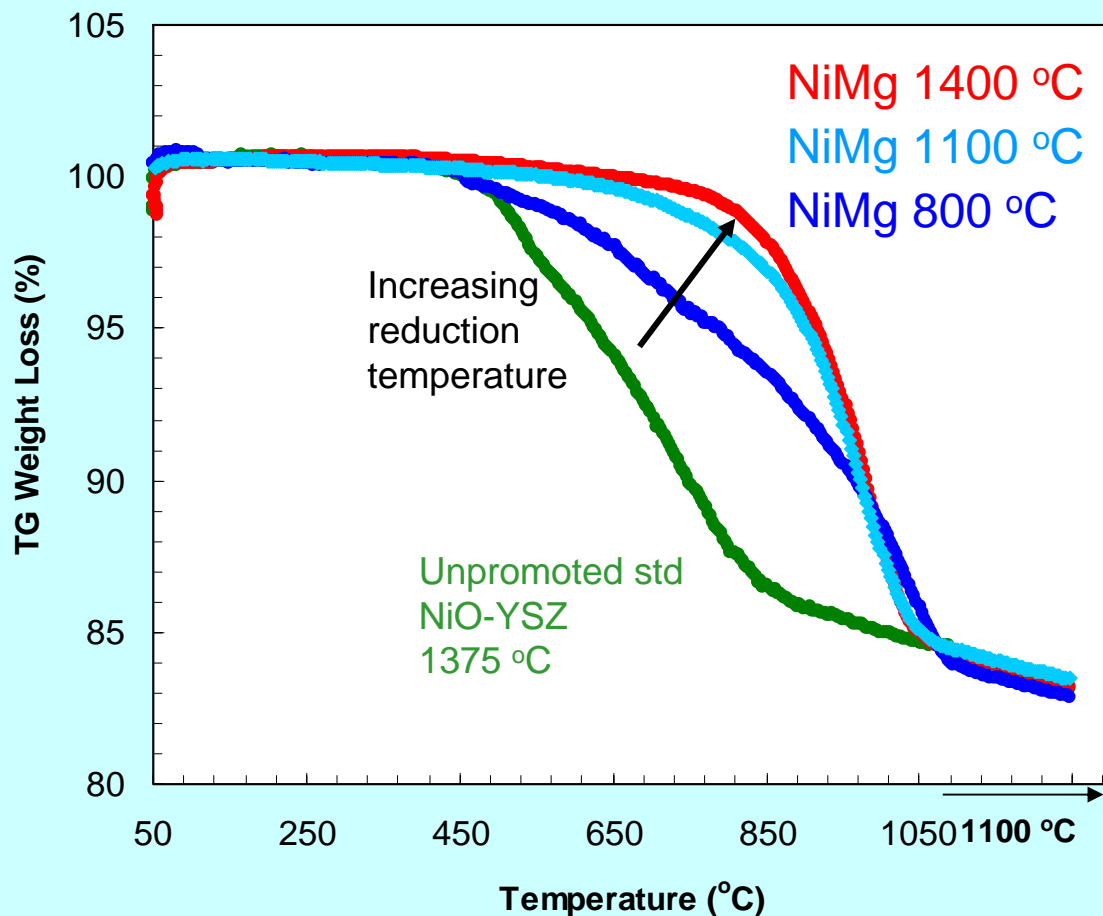
Images after 14h SMR at 600-750°C, S/C = 3



No evidence for coke formation or significant Ni restructuring

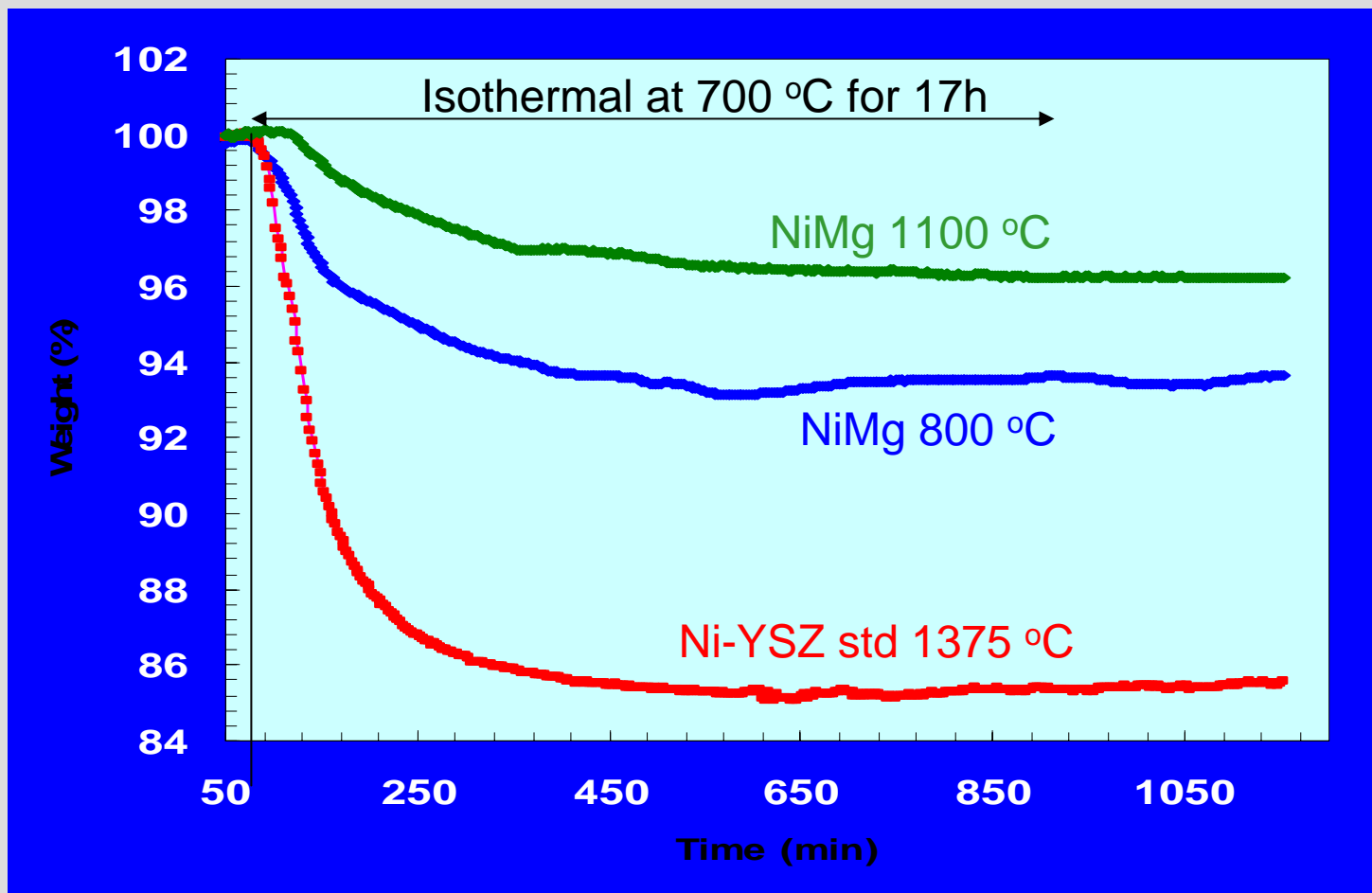
TPR of Ni-YSZ and Ni-MgO-YSZ

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



Ramp rate: 5°C/min to 700 °C
Reduction at 700 °C under 2% H₂/Ar

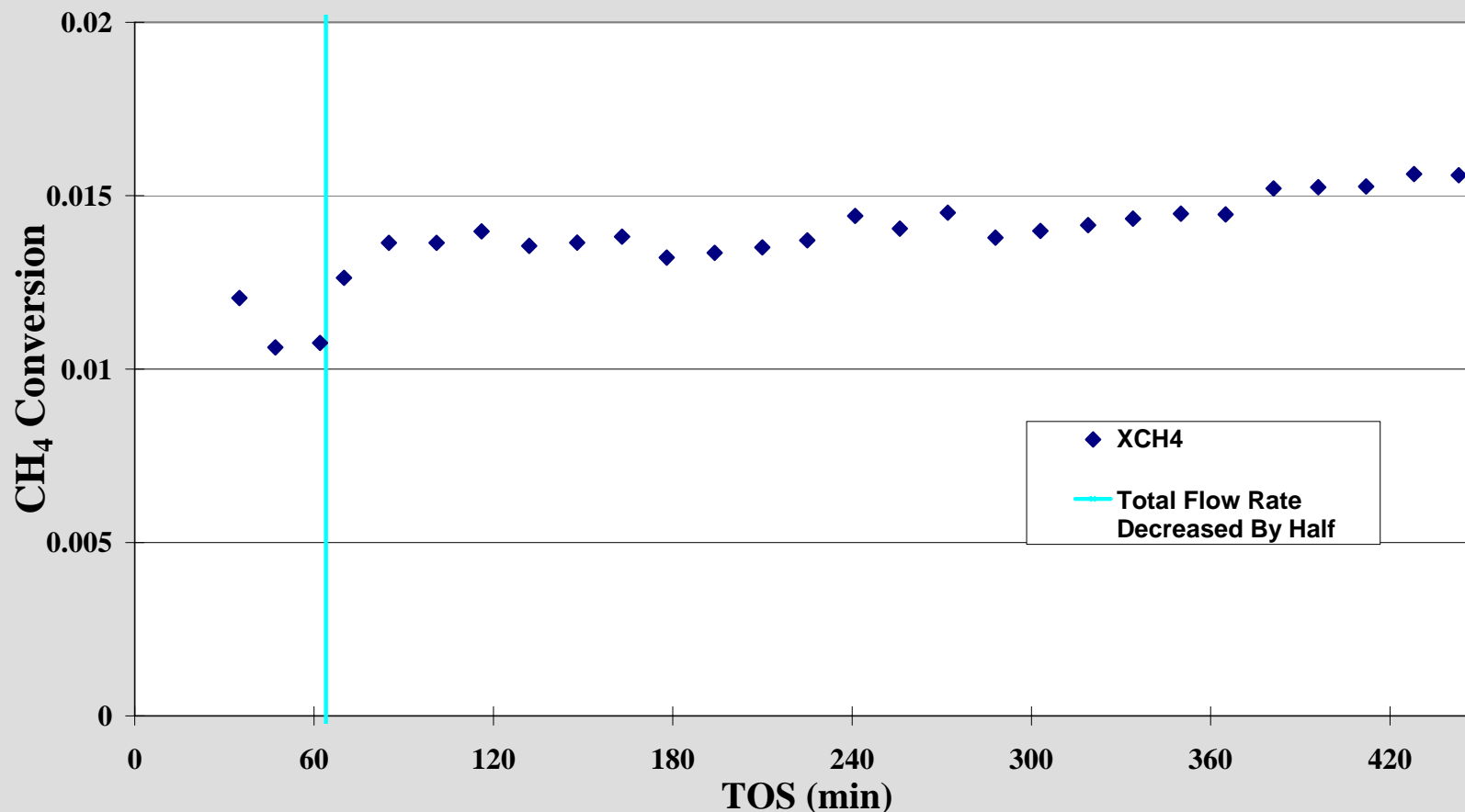
Summary of H₂ Chemisorption Results

	Ni surface area (m ² /g)	BET SA over Reduced sample
NiO-YSZ std 1375 C	0.51	1.11
NiO-YSZ SMR 16h spent	0.34	0.97
NiO 0.8-Mg 0.2-YSZ 800 C	2.18	7.76
NiO 0.8 Mg 0.2-YSZ 1100 C	0.87	

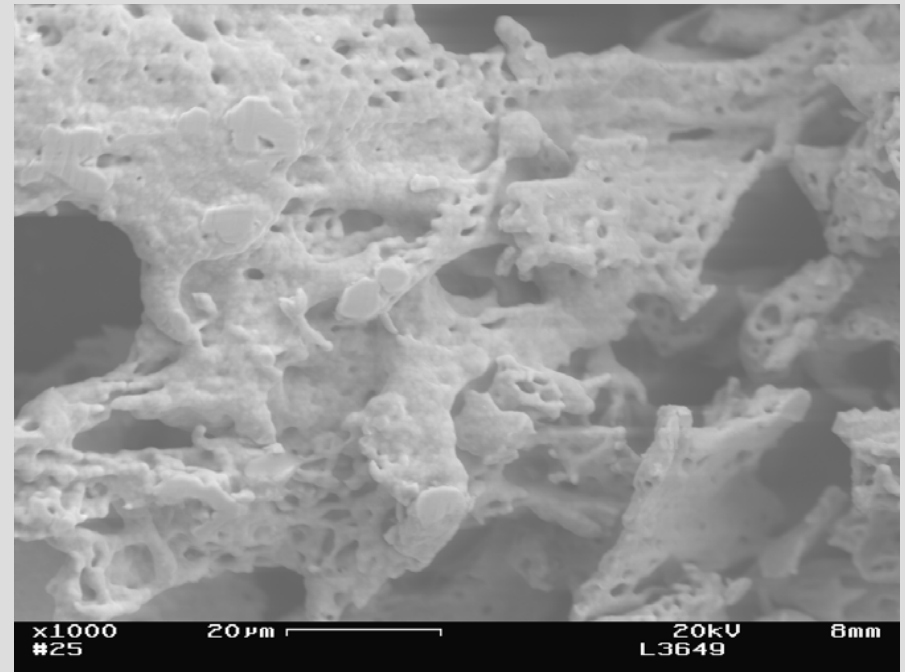
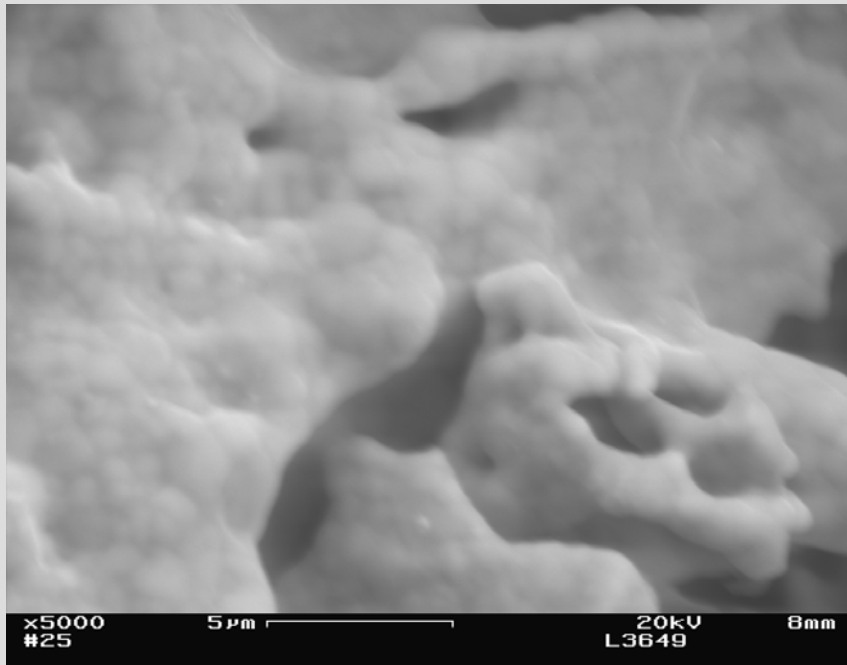
H₂ Chemisorption Does Not Correlate With Activity

Addition of Copper (2 mol%) to Nickel Decreases Methane Reforming Activity By Two Orders of Magnitude

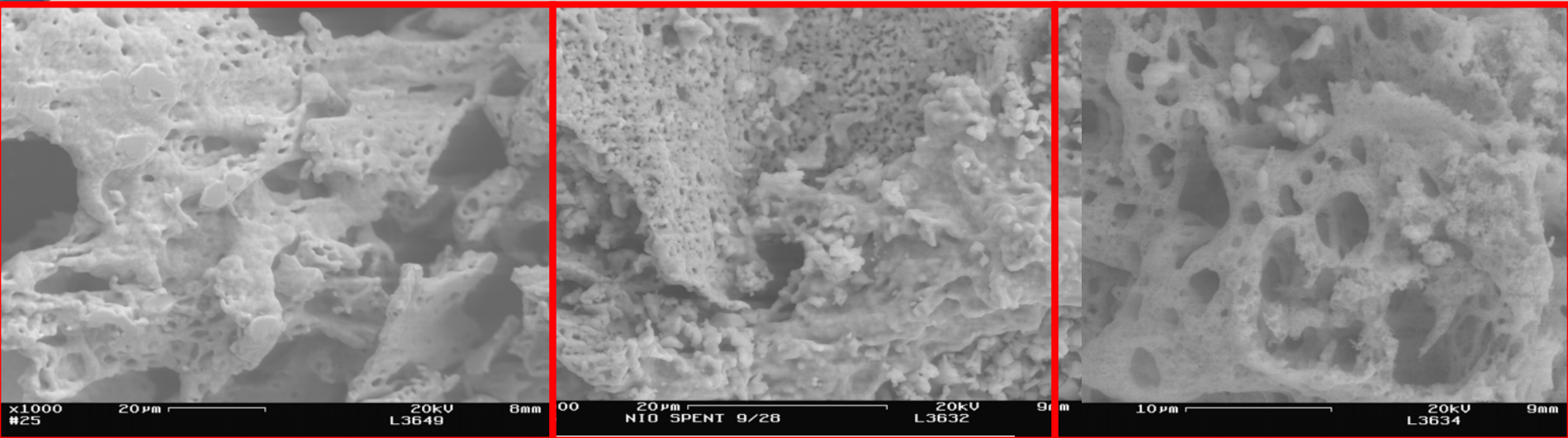
$\text{Ni}_{0.98}\text{Cu}_{0.02}$ (GN), S/C/ H_2 = 3:1:0.1; 700°C; Space Velocity = 154K



SEM of Ni_{0.8}-Cu_{0.2}O GN Reduced at 700°C Indicates Low Surface Area Material



SEM Micrograph of GN Prepared NiO



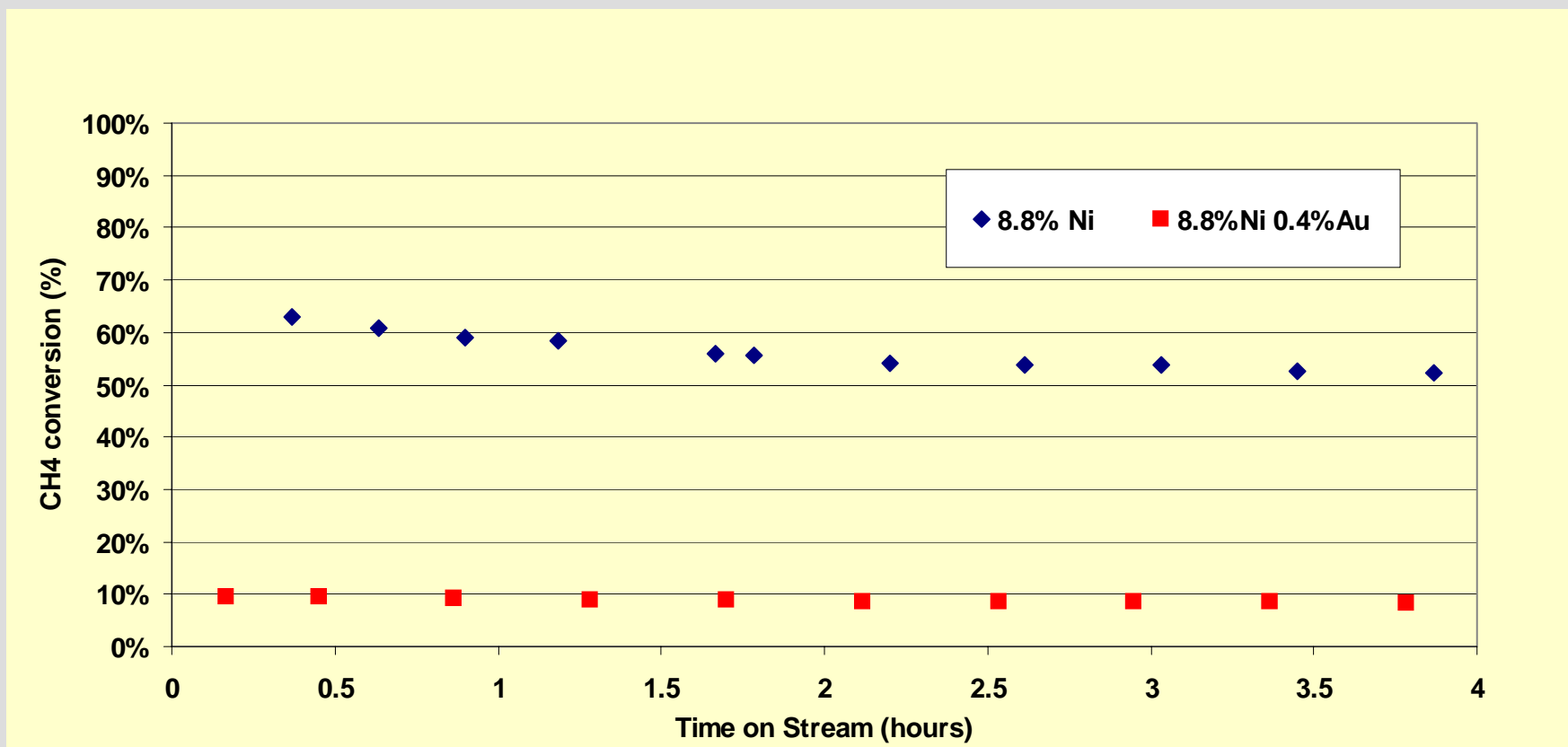
Ni_{0.8}Cu_{0.2}O
0.3 m²/g

NiO
1.15 m²/g

Ni_{0.8}Mg_{0.2}O
4.17 m²/g

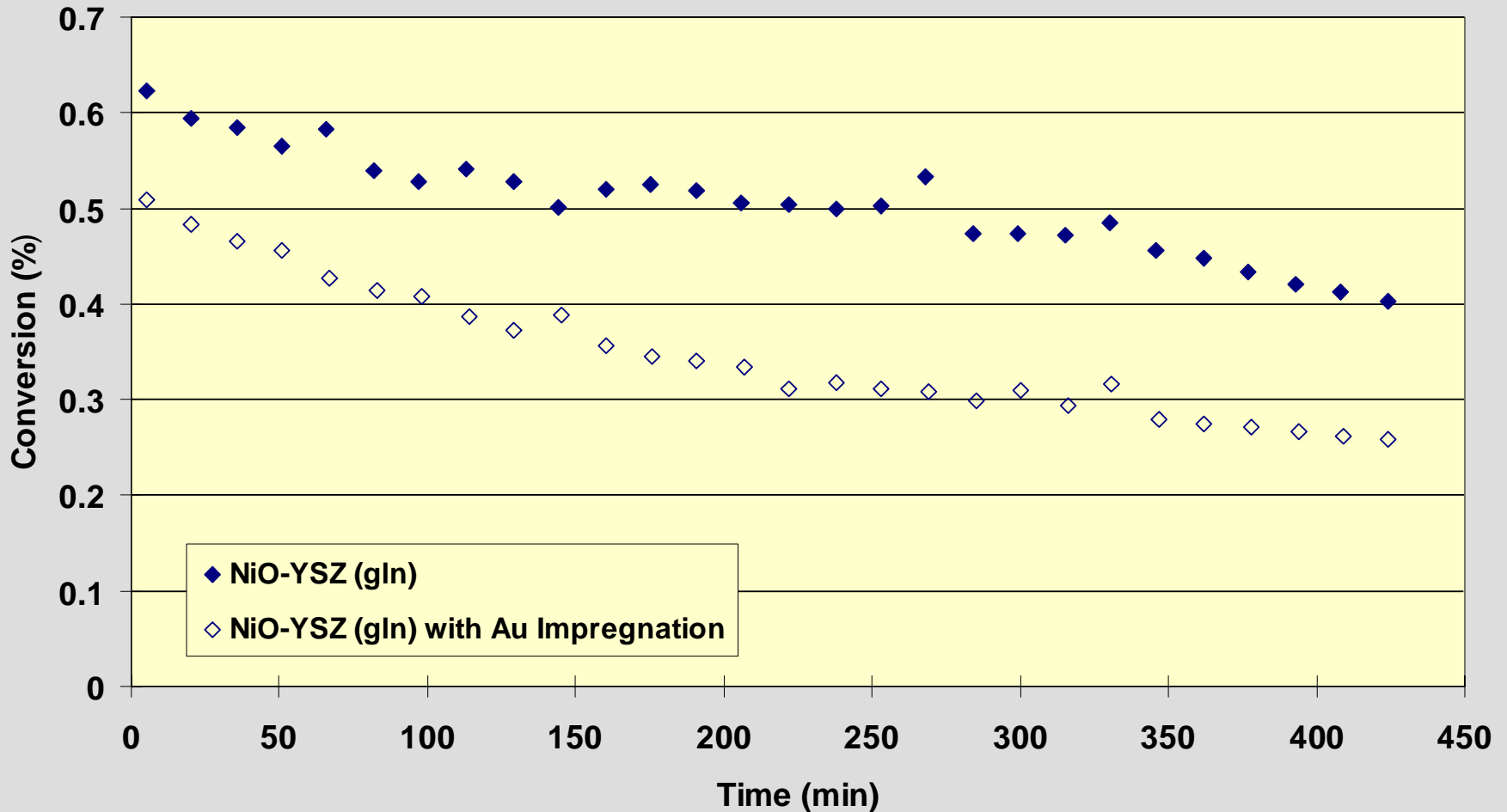
Gold Addition to Supported Nickel Catalyst Significantly Reduces Methane Steam Reforming Activity

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

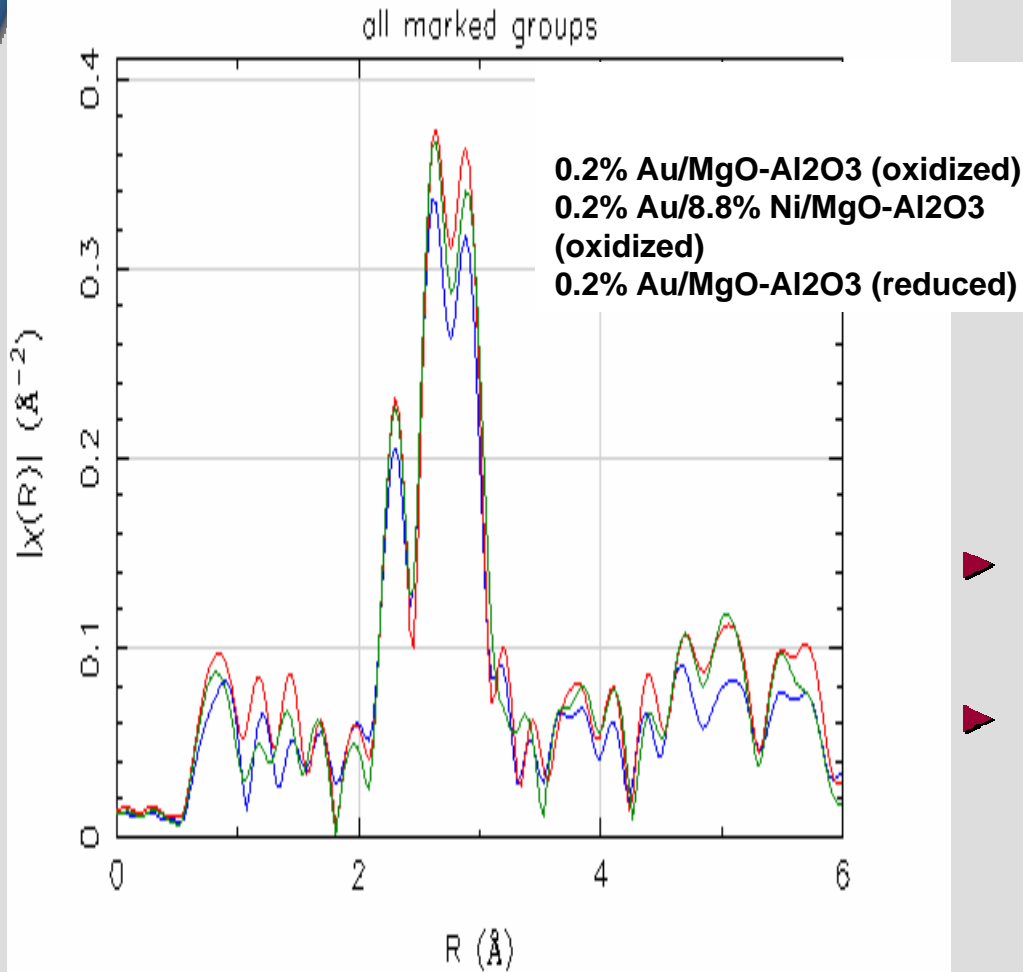


0.5% Gold Addition to Ni-YSZ (GN) Reduces Activity But Not Deactivation

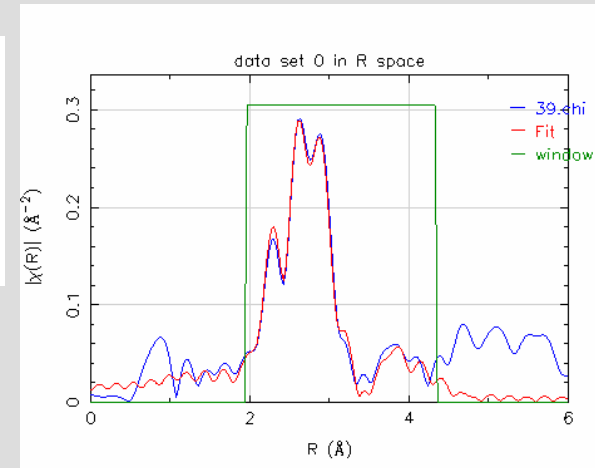
Gold Addition by Impregnation
Conditions: 700°C, S/C/H = 3/1/0.1, 628K ml/g-h



Au K Edge EXAFS

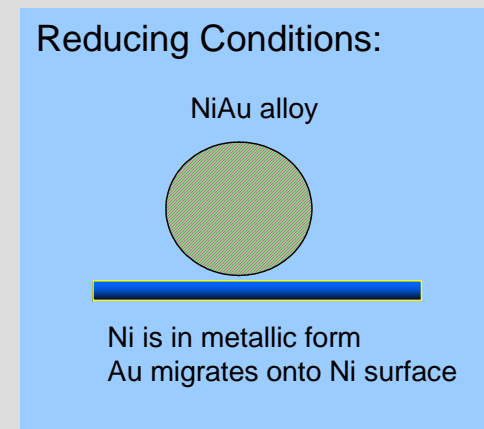
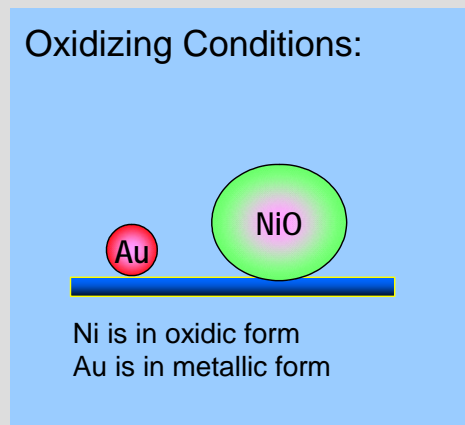
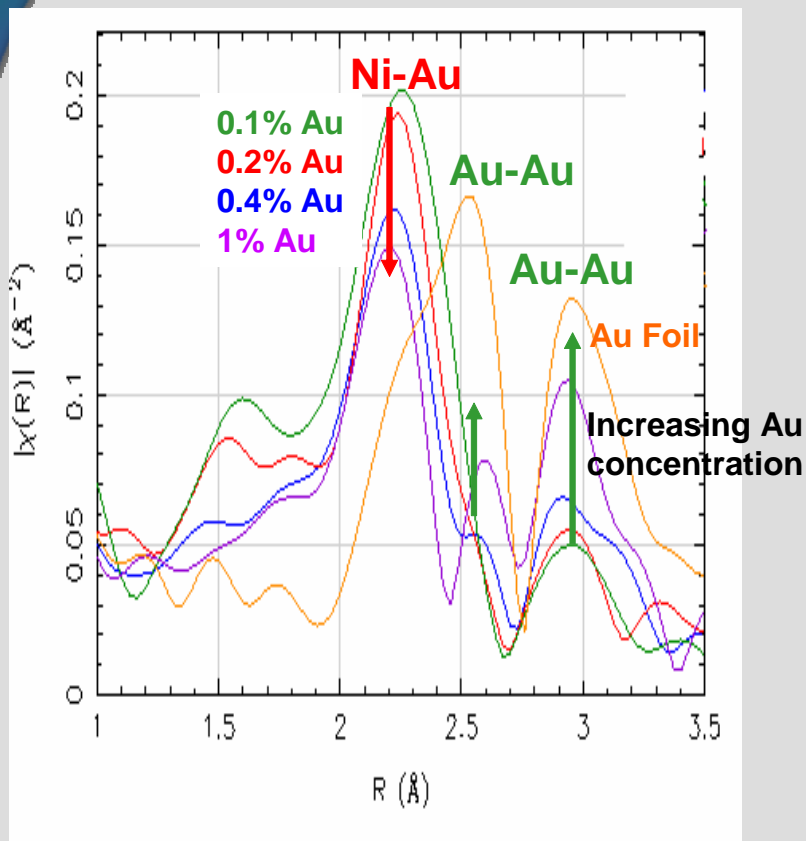


Fitted metallic Au EXAFS spectrum



- ▶ 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



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