Reduction of Carbon Formation From Nickel Catalysts Using Nickel-Gold Surface Alloys

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Project Objectives

- Evaluate ability of gold modification of nickel catalysts to minimize carbon formation during hydrocarbon reformation
- Quantify effect of gold addition to nickel catalyst surface on catalyst activity
- Develop characterization techniques to clarify the effect of gold on nickel surface properties
- Extend catalyst modification concepts to Ni anodes, enabling partial on-anode reforming of natural gas

What is Known

- Carbon can form during reforming with nickel catalysts even under conditions not predicted by thermodynamics
- Small crystallite nickel particles (<10nm) have been shown to be more resistant to carbon formation
  - Maintenance of small crystallites under reforming conditions is challenging due to sintering and compound formation
  - Plausible approach for pre-reforming
- Addition of gold to nickel catalysts retards deposition of carbon and consequent deactivation

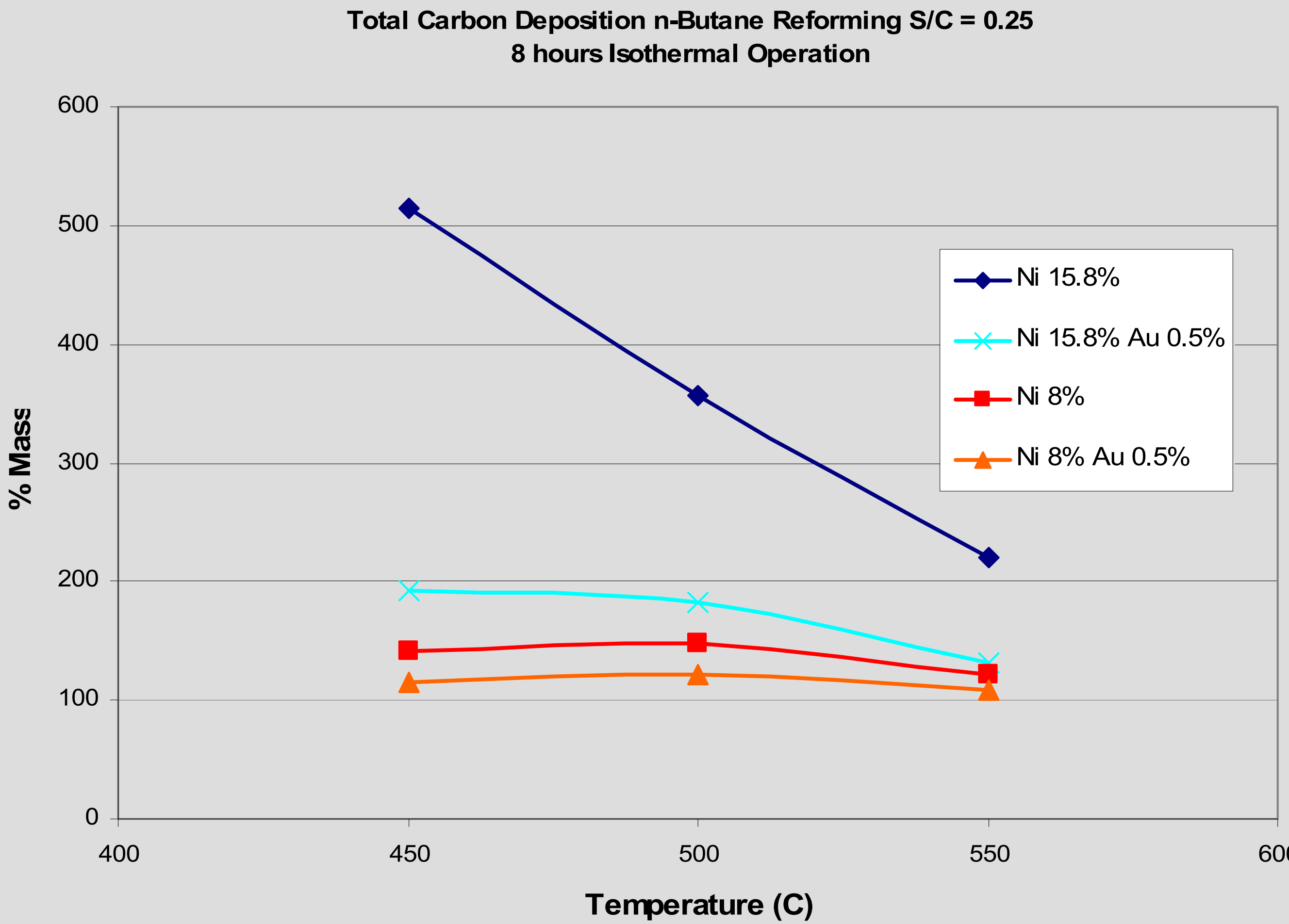
Relevant Theories

- Step site model
  - The most active catalytic sites on nickel (step and edge sites) are also nucleation points for carbon formation
  - Deactivation of these most active sites (by sulfur, gold, other) results in reducing carbon formation at some loss of catalytic activity
- Ensemble model
  - Groups of contiguous nickel atoms (ensembles) have high tendency to deposit carbon during reforming
  - An impurity atom that breaks up ensemble size may retard carbon formation more than reforming activity
  - Electronic properties of nickel atoms can also be altered by an ad-atom (ligand effect)

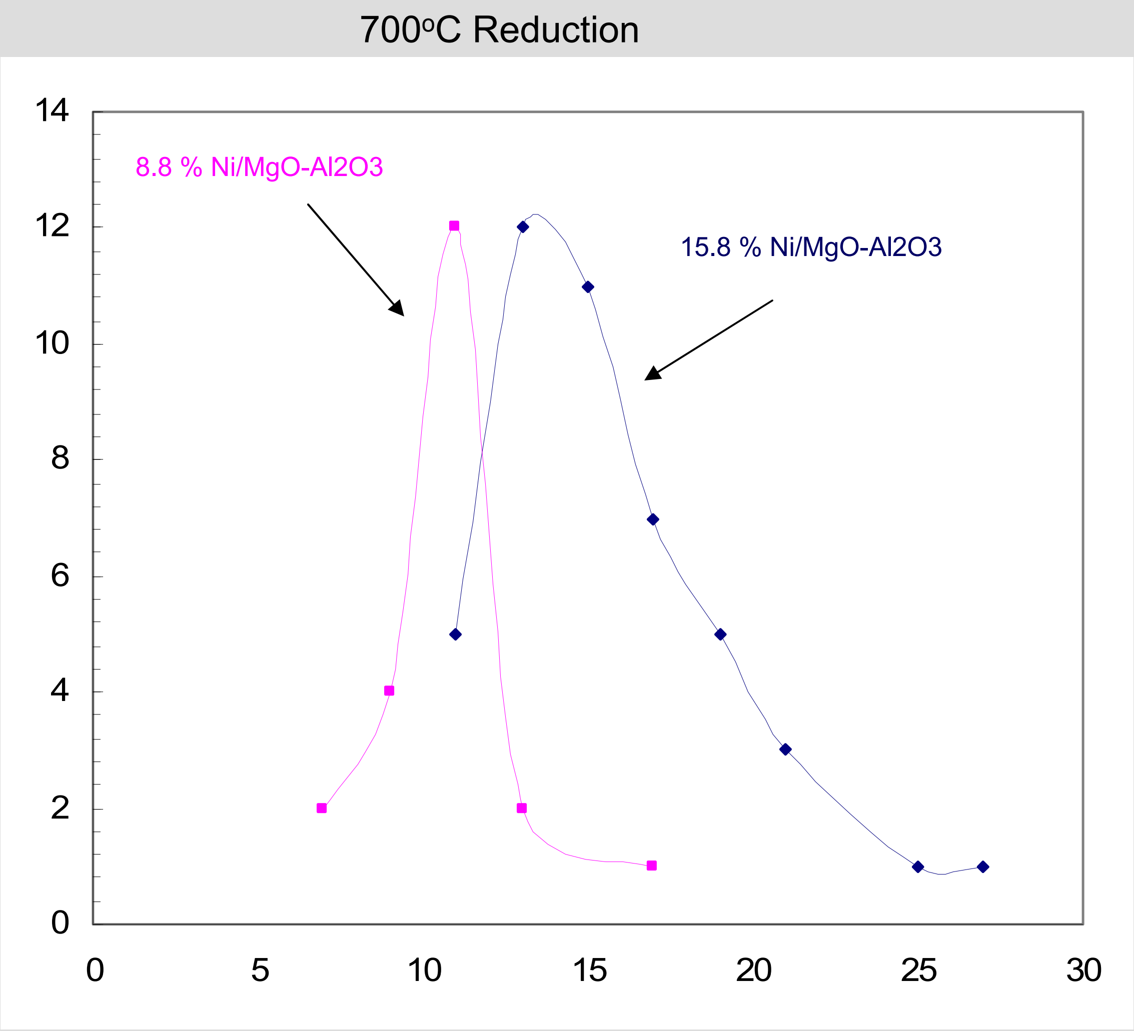
Project Tasks

- Baseline supported nickel catalyst ($Ni/MgAl_2O_4$) performance in reforming methane and butane
- Quantify effect of gold addition on carbon formation and reforming activity with supported Ni catalyst
- Develop analytical methodology to characterize nickel surface
- Verify methane reforming kinetics with Ni/YSZ anode
  - Provide to modeling effort
- Quantify effect of gold addition on carbon formation and reforming activity with nickel anode catalyst

TGA Studies Show Gold Addition Reduces Carbon Deposition From Supported Ni Catalysts



Particle Counting by TEM Shows Difference in Crystallite Size

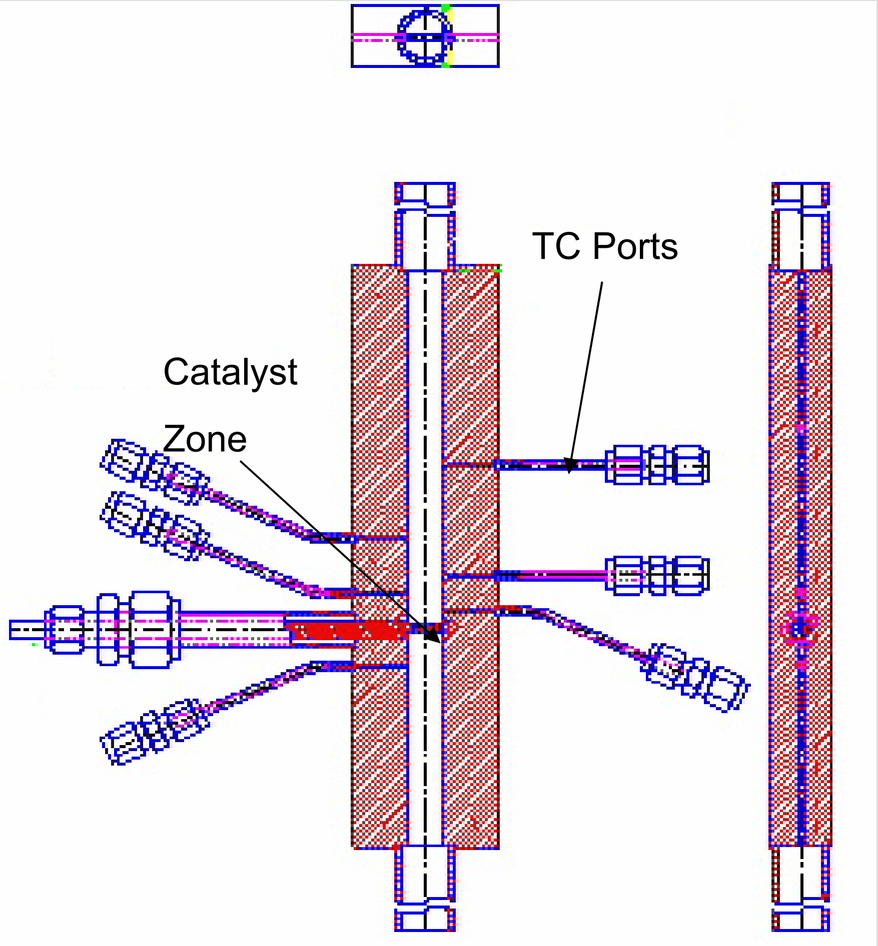


Catalyst Preparation and Pretreatment

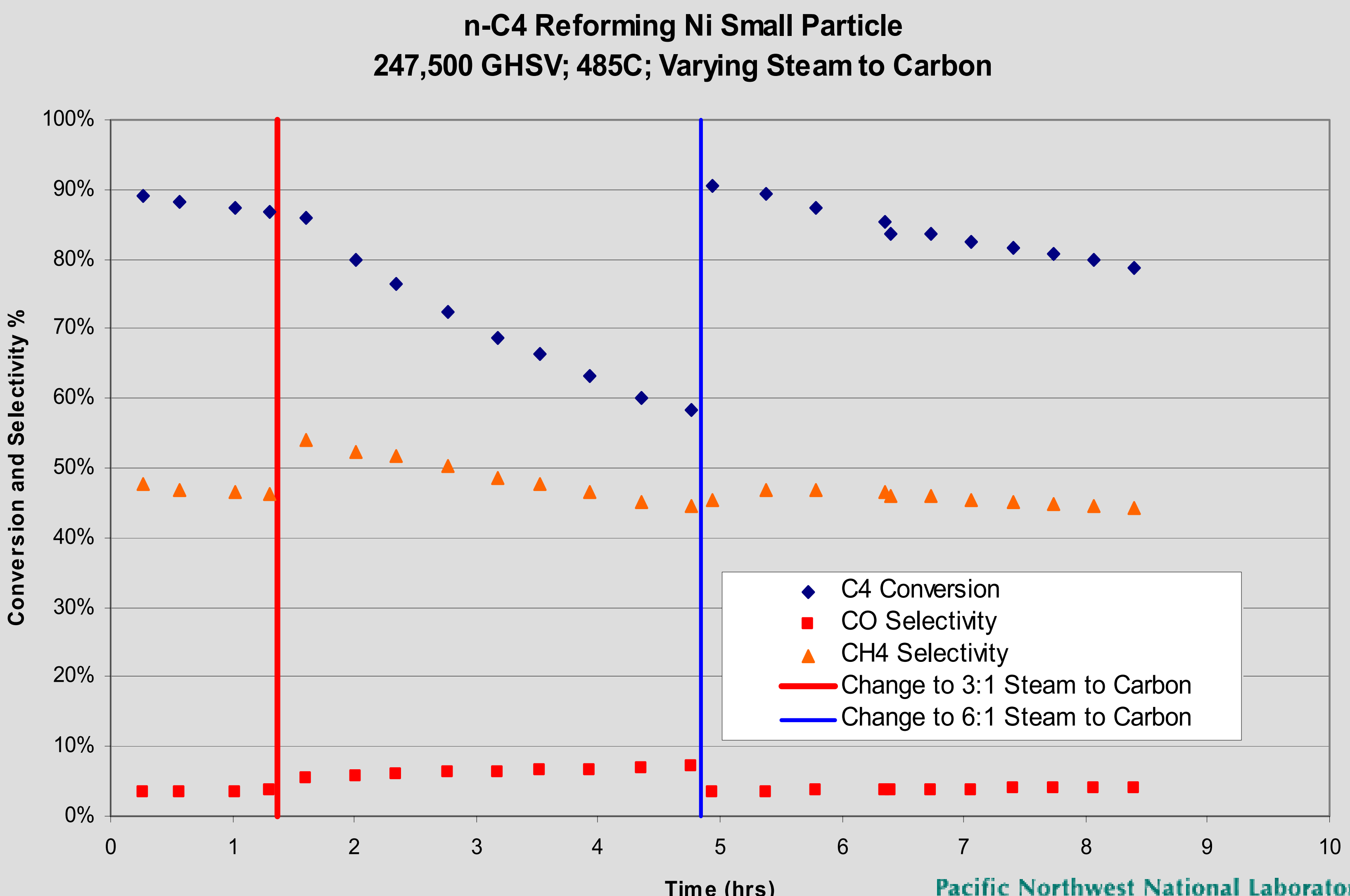
- $Ni/MgAl_2O_4$
  - Preparation
    - $MgAl_2O_4$ acquired from supplier, surface area 271 m^2/g
    - Incipient wetness impregnation using $Ni(NO_3)_2$
    - Calcination: 500^{o}C
  - Testing
    - Reduction: 700^{o}C in H_2 (2h)
    - Begin flow H_2 and steam, then butane or methane

- $Ni\text{-}Au/MgAl_2O_4$
  - Preparation
    - Reduce (700^{o}C) and passivate (1%O_2/He, ambient, 12h) $Ni/MgAl_2O_4$ catalyst
    - Add Au by incipient wetness impregnation of $HAuCl_4$
    - Dry at 200^{o}C under inert atmosphere
  - Testing
    - Same as above

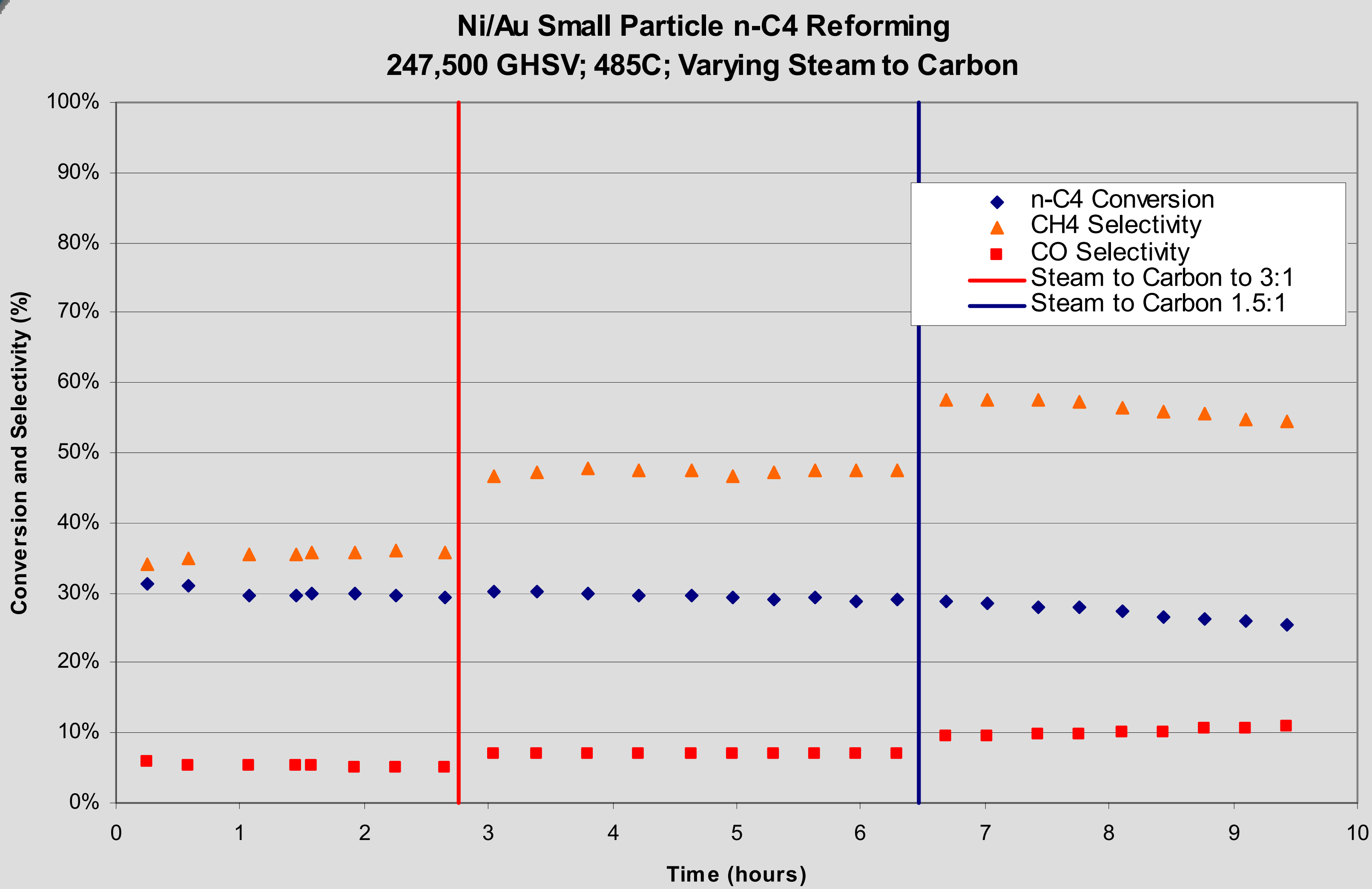
Test Reactor



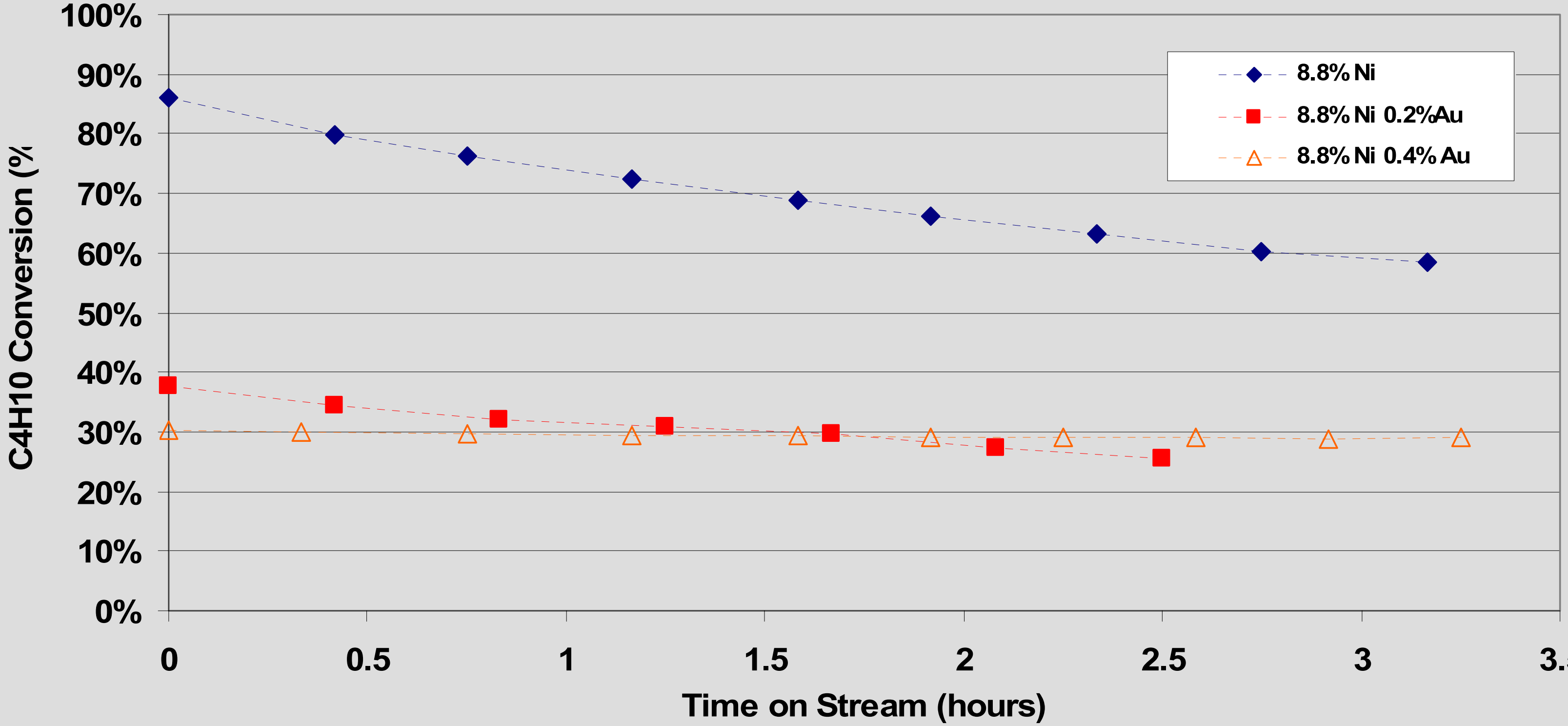
Supported Nickel Catalyst Shows Rapid Deactivation in Butane Reforming



0.4% Gold Addition Eliminates Nickel Catalyst Deactivation



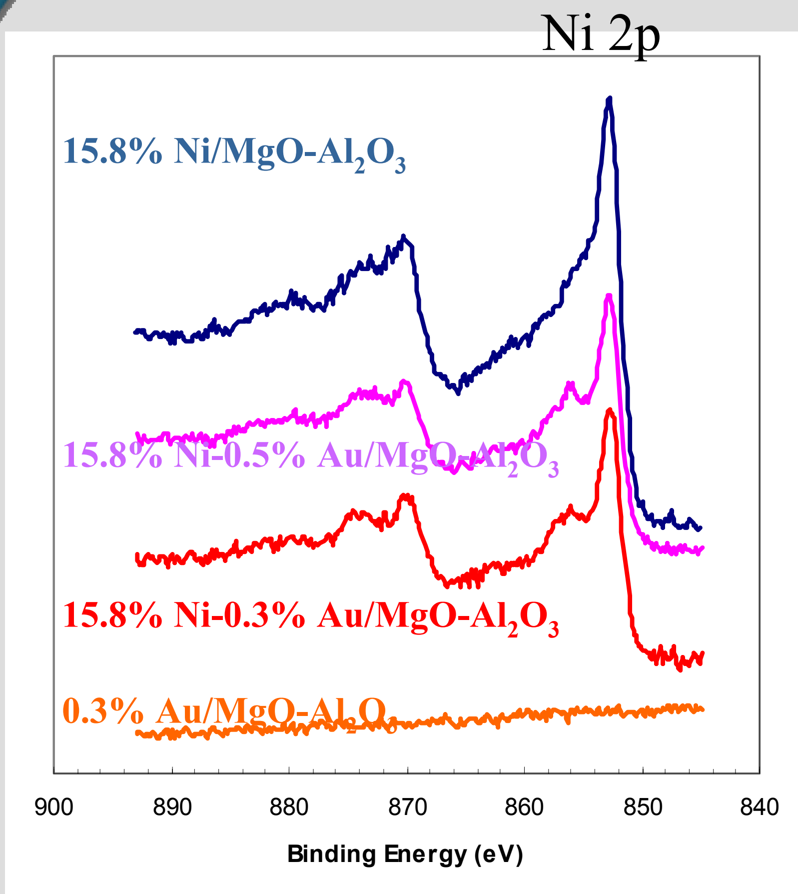
Effect of Gold Addition on n-Butane Reforming with Supported Nickel Catalyst

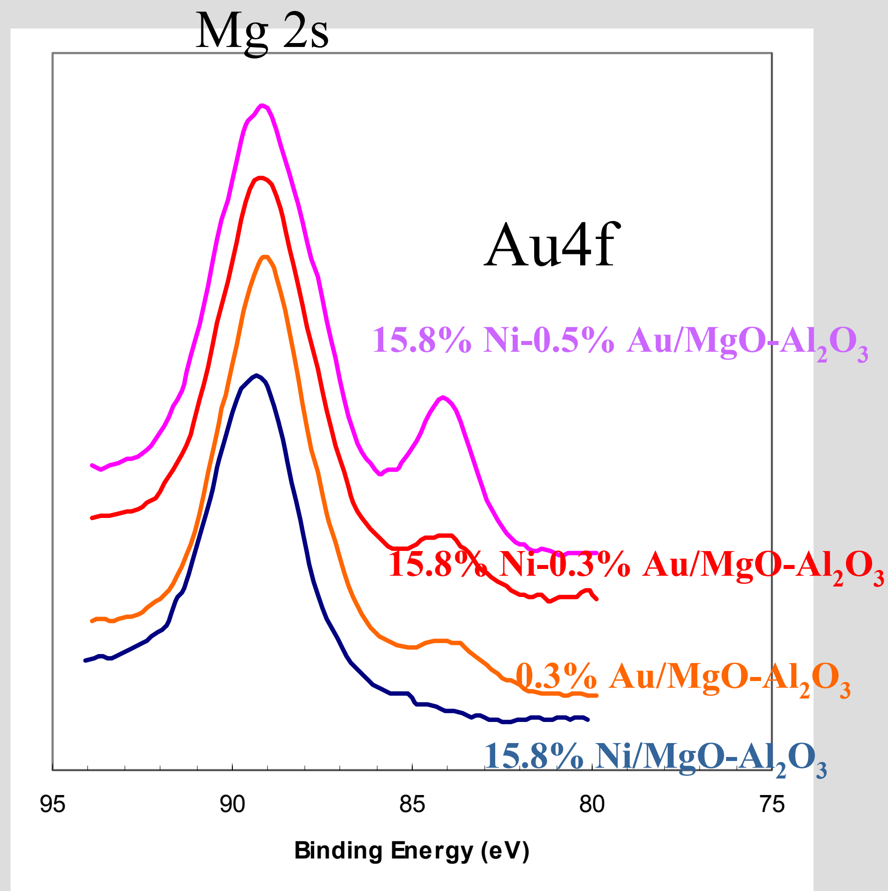


Gold Addition to Achieve Theoretical Monolayer Coverage

Catalyst	% Ni dispersion	Wt.% Au for monolayer coverage (1Au/3Ni)
15.8% Ni/MgAl2O4	4	0.61
8.8% Ni/MgAl2O4	4	0.36
50%Ni-50%YSZ anode	0.02	0.011

XPS Spectra of Nickel and Nickel-Gold Catalysts Supported on $Mg\text{-}Al_2O_4$

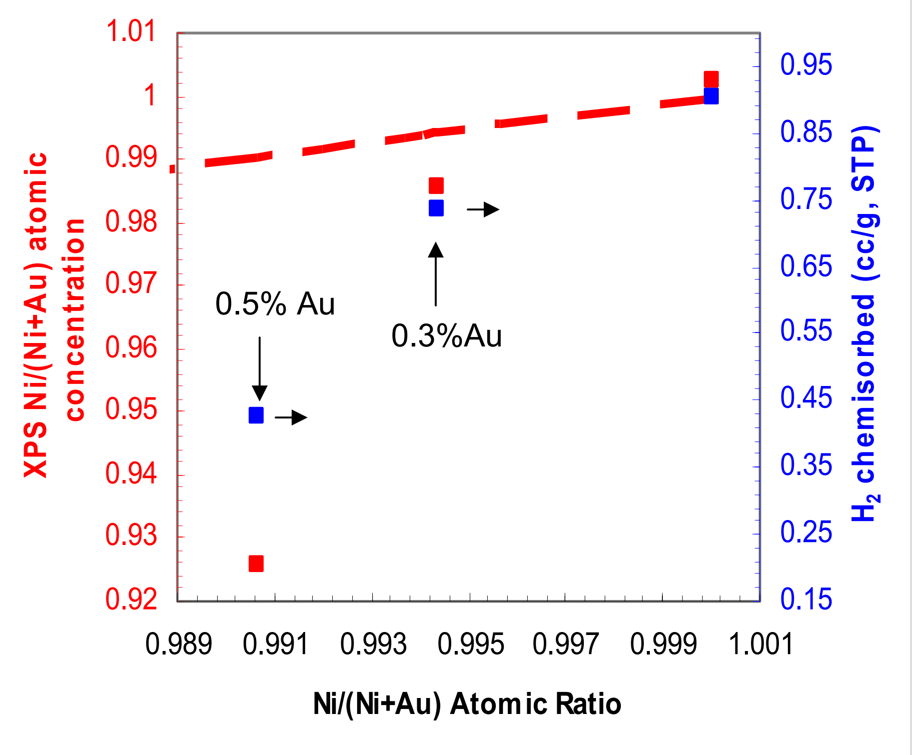




Suppression of Ni 2p peak observed with increasing Au loadings.

Comparison of XPS and Hydrogen Chemisorption on Au Promoted 15.8%Ni/MgAl2O4 Catalyst

- XPS represents possible method to determine the fraction of Ni covered by Au
  - Attenuation of Ni signal consistent with Au adsorbed on Ni surface
  - Addition of 0.5% Au estimated to provide approximately 8-9% of a monolayer
  - Not all Au is associated with Ni
- Decrease in H_2 chemisorption upon Au addition is far greater than estimated monolayer coverage by XPS
  - Consistent with effect of Au addition extending beyond simple site blocking

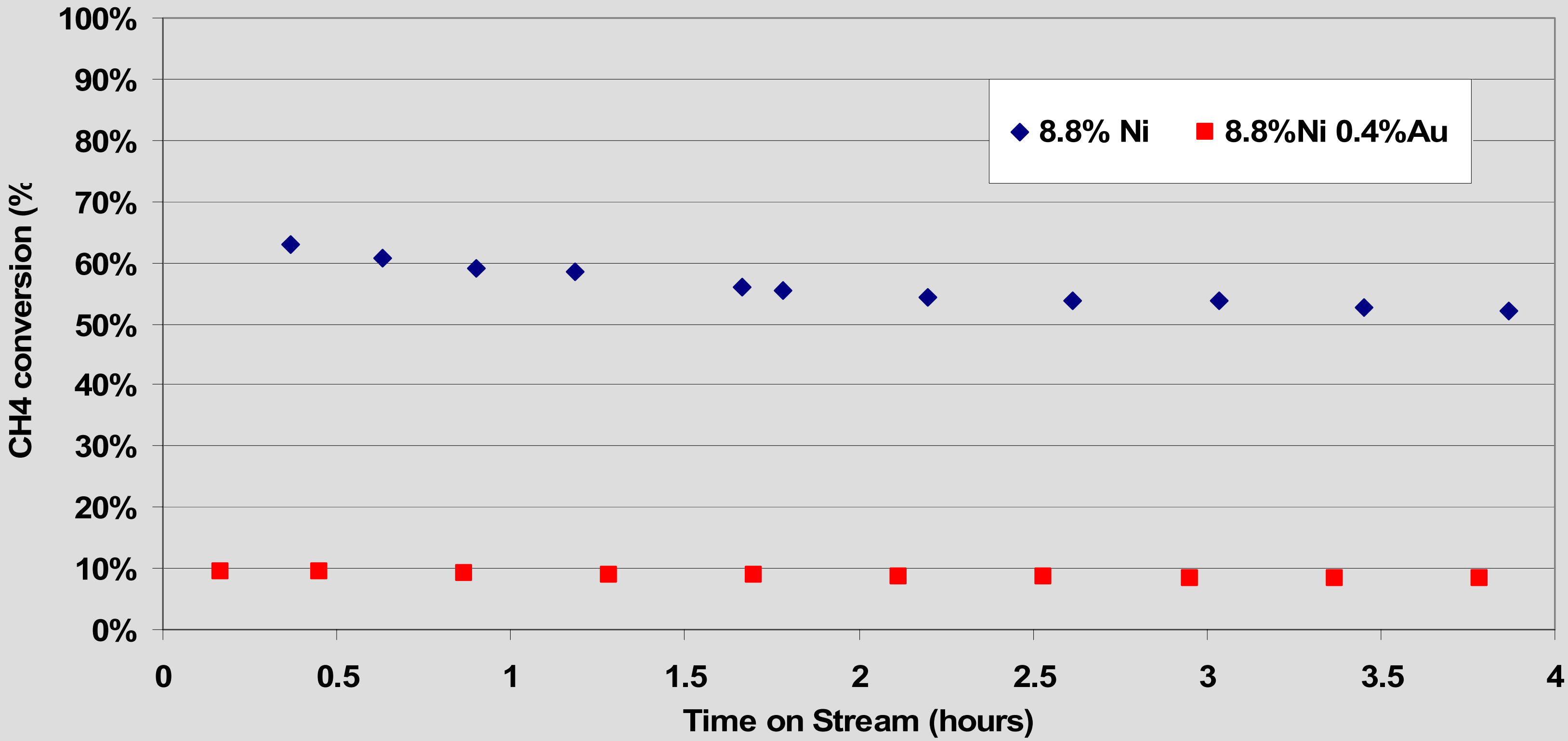


Summary of H_2 Chemisorption Data

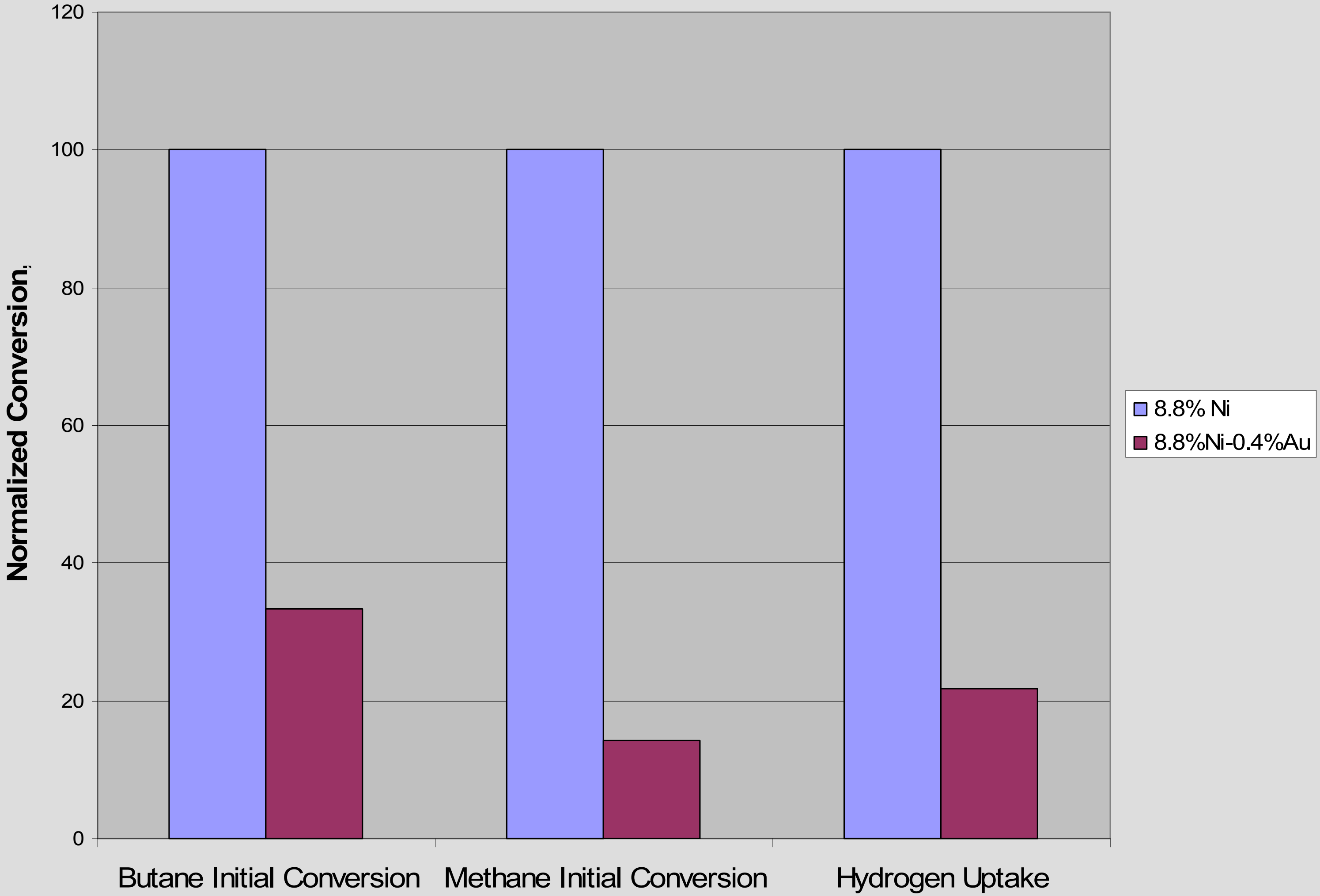
Catalyst	Pretreatment	H_2 Uptake, cc/g	Dispersion,%	Xtal size (H_2)	Xtal size (other)
15.8%Ni/$MgAl_2O_4$	H_2, 900C	0.967	3.1	40	14 (TEM)
15.8%Ni-0.3%Au/$MgAl_2O_4$	H_2, 900C	0.771			
15.8%Ni-0.5%Au/$MgAl_2O_4$	H_2, 900C	0.206			
8.8%Ni/$MgAl_2O_4$	H_2, 900C	0.642	4.5	25	6 (SEM); 10 (TEM)
8.8%Ni/$MgAl_2O_4$	H_2, 700C	0.856	6.0	20	
8.8%Ni-0.2%Au/$MgAl_2O_4$	H_2, 900C	0.196			
8.8%Ni-0.4%Au/$MgAl_2O_4$	H_2, 900C	0.10			

Effect of Gold on Steam Reforming of Methane Over Supported Nickel Catalyst

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

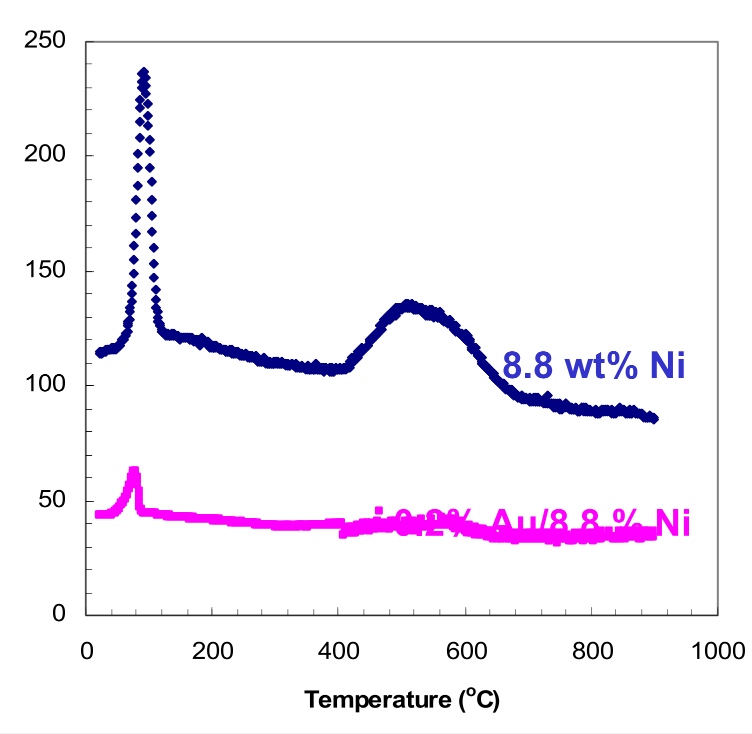


Effect of Gold Addition on Hydrocarbon Conversion

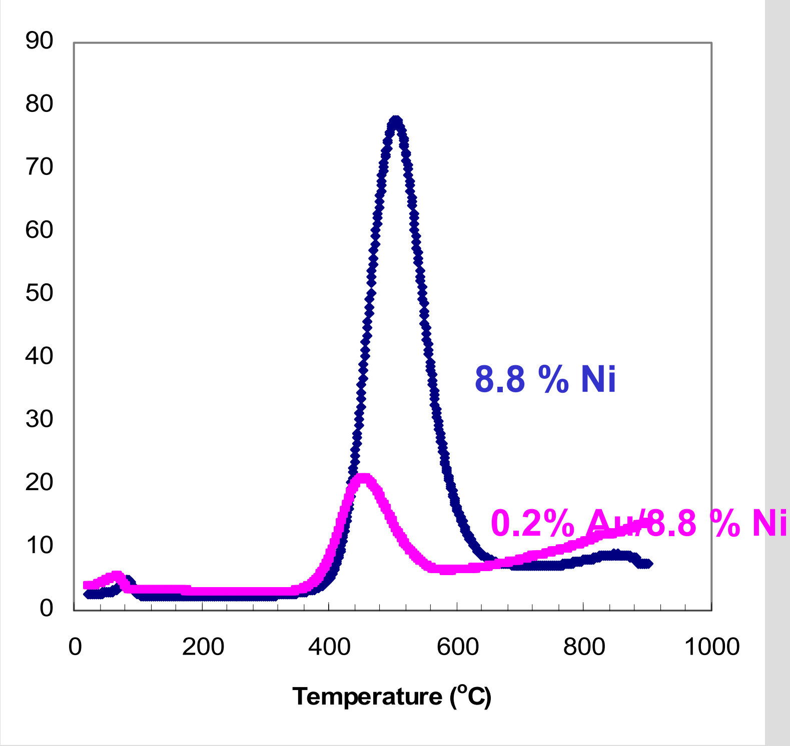


N_2O Temperature Programmed Desorption

Mass 28 N_2



Mass 46 N_2O



Area under the peak

	N_2O	N_2
Ni	9583	3500
Ni-Au	3430	366

Summary of Probe Molecule Results

- H_2 chemisorption
  - Best method to quantify available surface sites, dispersion
  - H_2 uptake less than expected from XRD line broadening or TEM
  - Uptake significantly decreased with Au addition
  - H_2 uptake correlates with observed activity
- N_2 chemisorption
  - Proposed (in literature) as method to titrate step sites ("B5" sites)
  - Does not correlate with catalyst activity, carbon formation, or gold effects
- H_2S titration of Ni surface sites
  - Ambient temperature H_2S adsorption is significantly greater than H_2 chemisorption—suggests formation of bulk plus surface sulfides
- N_2O TPD
  - Two types of sites observed:
    - "A" sites--desorb N_2 (form NiO) at low temperature
    - "B" sites--desorb N_2O at higher temperature
  - Addition of Au reduces "A" sites more than "B" sites
  - Evaluating approach as method to distinguish step from planar sites

Nickel Anode Steam Methane Reforming

- Potential benefits
  - Use endothermic reforming reaction to consume heat generated in fuel cell operation
  - Reduce cathode cooling by excess air
  - Reduce or eliminate external reformer
- Challenges
  - Carbon formation catalyzed by Ni
  - Temperature gradients near fuel inlet due to strong endotherm may lead to failure
  - Need to spread out conversion over broader area of anode to achieve thermal balance

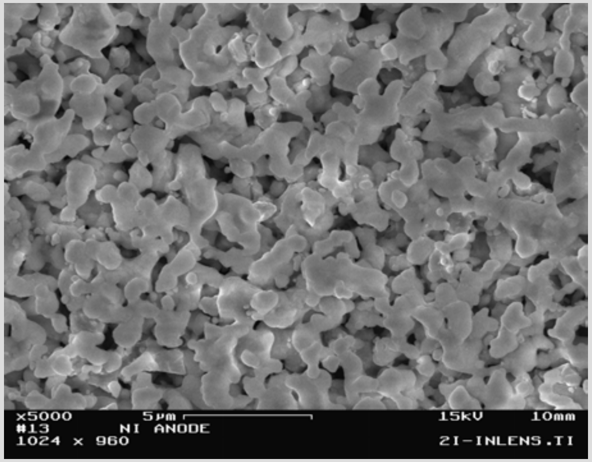
Nickel Anode Steam Methane Reforming

- Approach
  - Obtain kinetic data on methane reforming to support modeling effort
  - Identify operating parameters leading to deactivation by carbon formation
  - Quantify effect of Au addition on activity and activity maintenance under carbon forming conditions
  - Develop methods for reliable, reproducible introduction of Au to anode

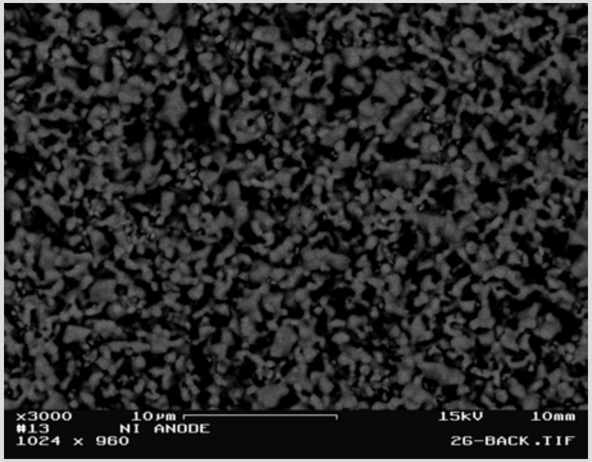
Ni YSZ Anode

- Composition: 60%ZrO_2-40% NiO_2 by volume; 50% NiO_2 by weight
- Particle size: 0.5-5 μm agglomerates
- BET: 0.43 m^2/g
- H_2 adsorption: 0.0221 cc/g; 0.023% Ni dispersion
- Testing method—anode substrate
  - Two test strips 0.5x1" against opposite walls of channel
  - Strips have YSZ on back side—only one active surface
- Gold doping procedure
  - Incipient wetness impregnation not viable method
  - Pore fill anode material with solution of appropriate concentration $HAuCl_4$
  - Procedure tends to give poorer dispersion of metals onto substrate

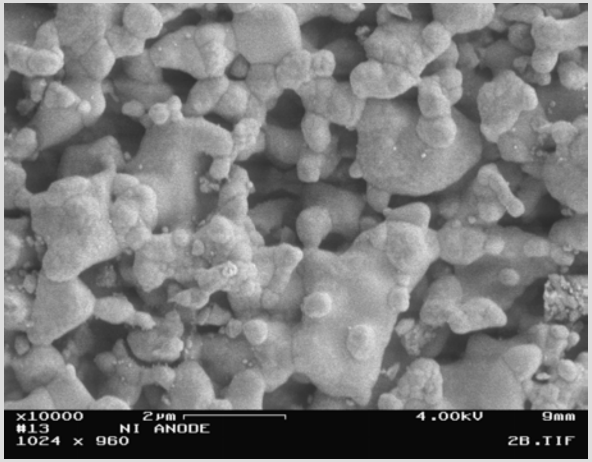
SEM of Ni/YSZ Anode (Reduced)



5000 X

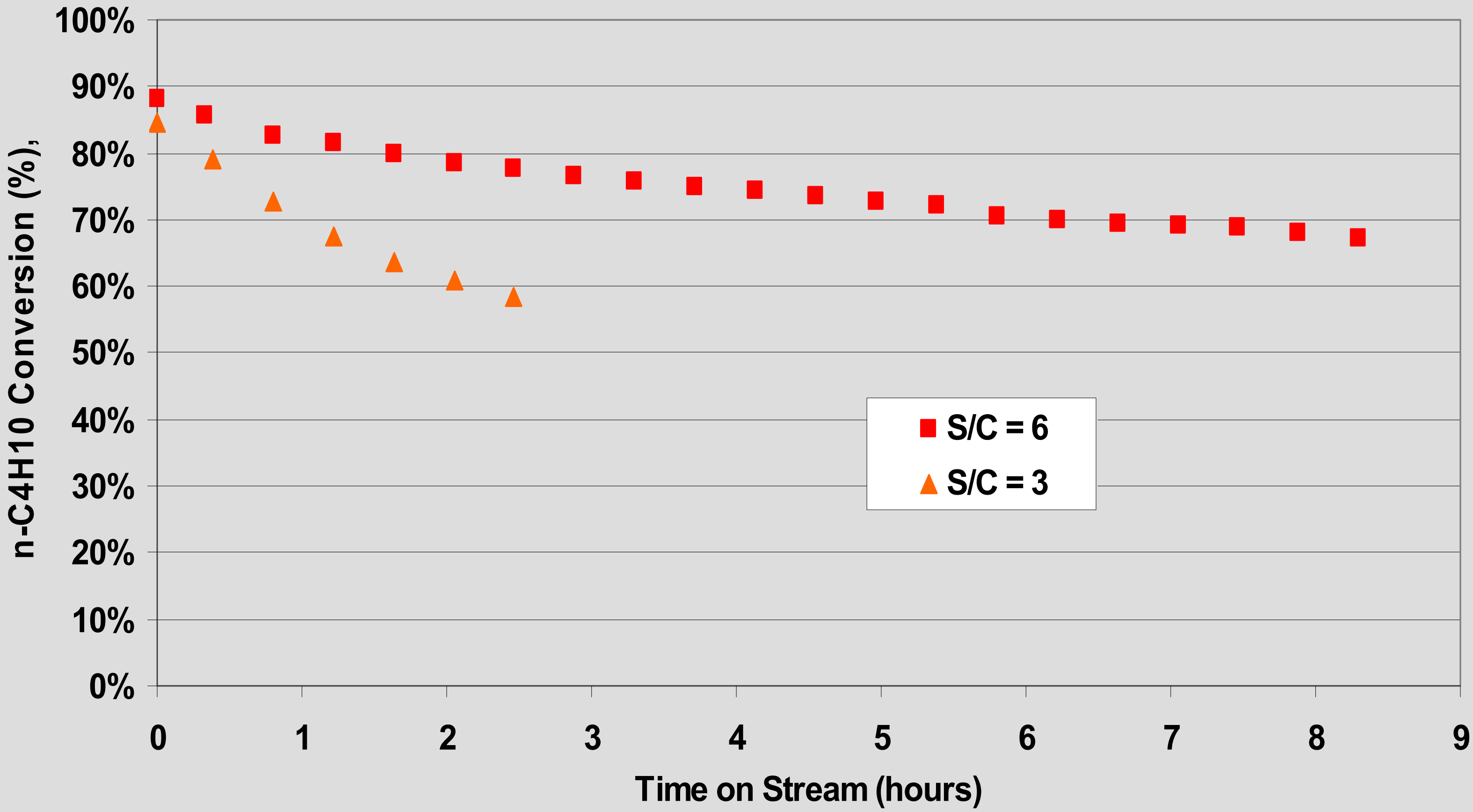


5000 X back-scattered image



10,000 X

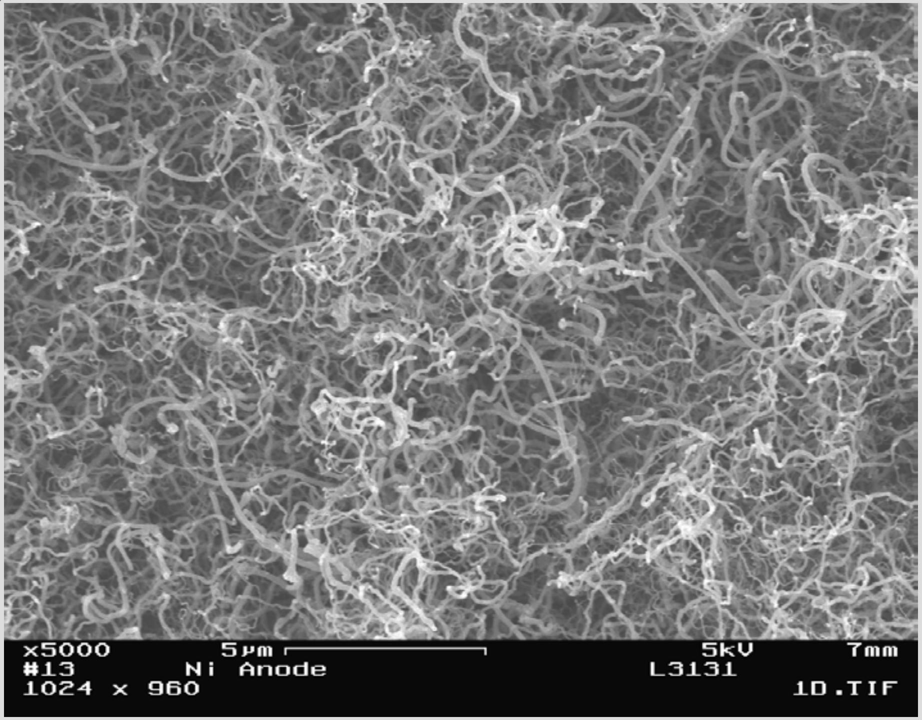
Ni/YSZ Anode Shows Significant Deactivation in Butane Reforming

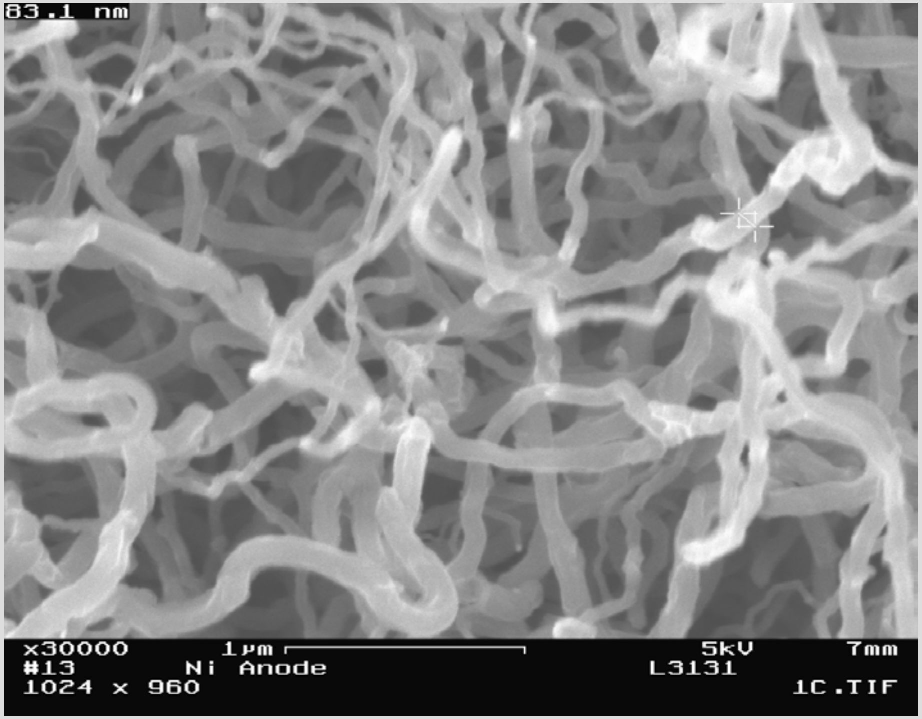


Anode Catalyst
Post Reaction with n-Butane

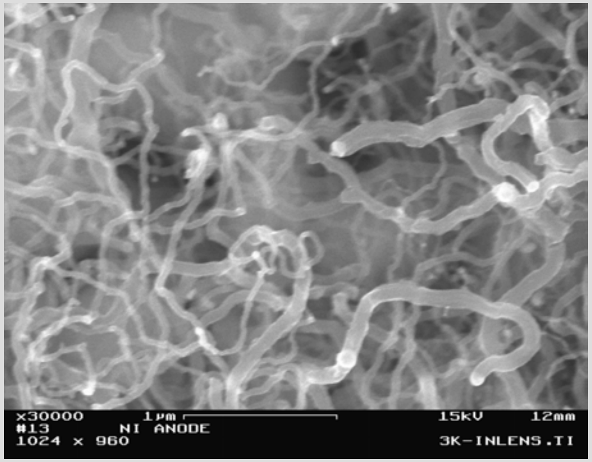
Carbon readily wipes off surface of anode

SEM of Deactivated Ni-Anode Following Butane Steam Reforming

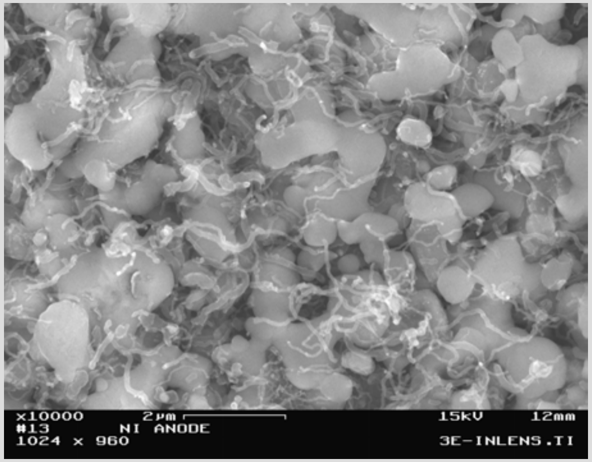




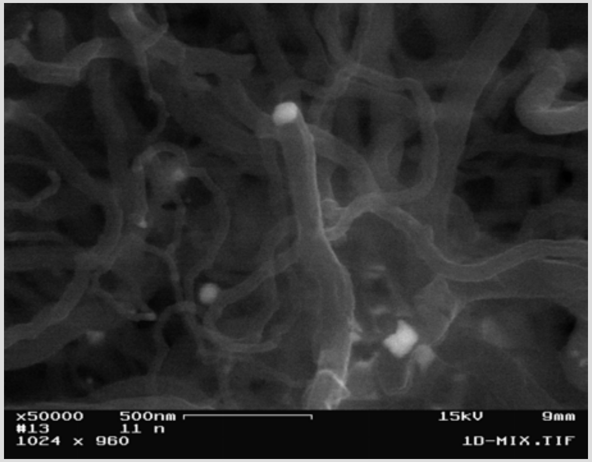
SEM of Ni/YSZ Anode (Spent)



30,000 X



10,000 X



Back Scattered Image + SE image 50,000 X

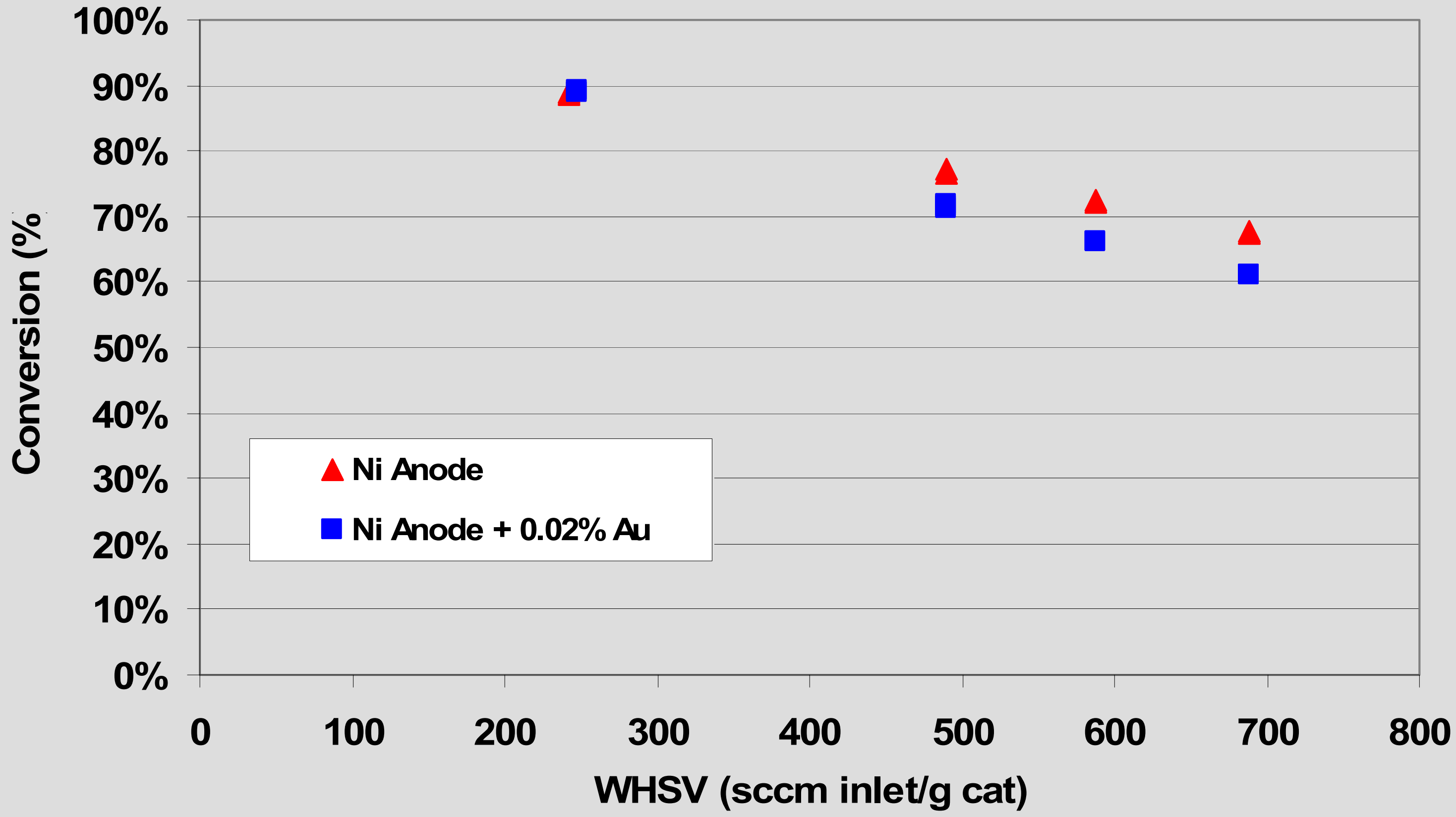
Ni Anode vs. Supported Nickel Catalyst Activity

	8.8%Ni/$MgAl_2O_4$	Ni/YSZ Anode	Ratio
Mols C_4 converted/g catalyst-min	0.00721	0.000232	31.1
Mols C_4 converted/g Ni-min	0.08190	0.000463	176.9
Mols C_4 converted/ (cc H_2 uptake-min)	0.015499	0.011349	1.4

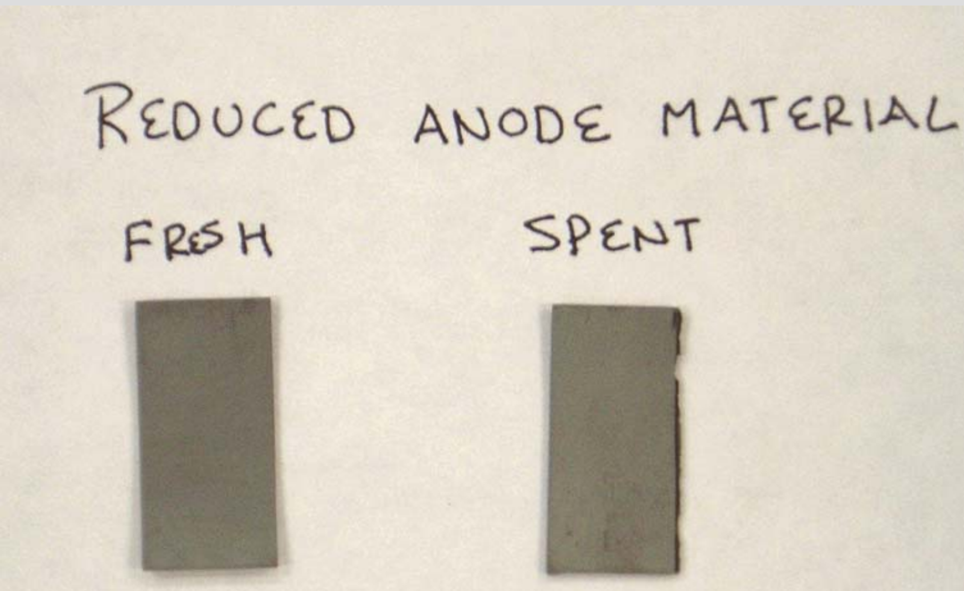
Ni/YSZ Shows Small Effect of Au Addition

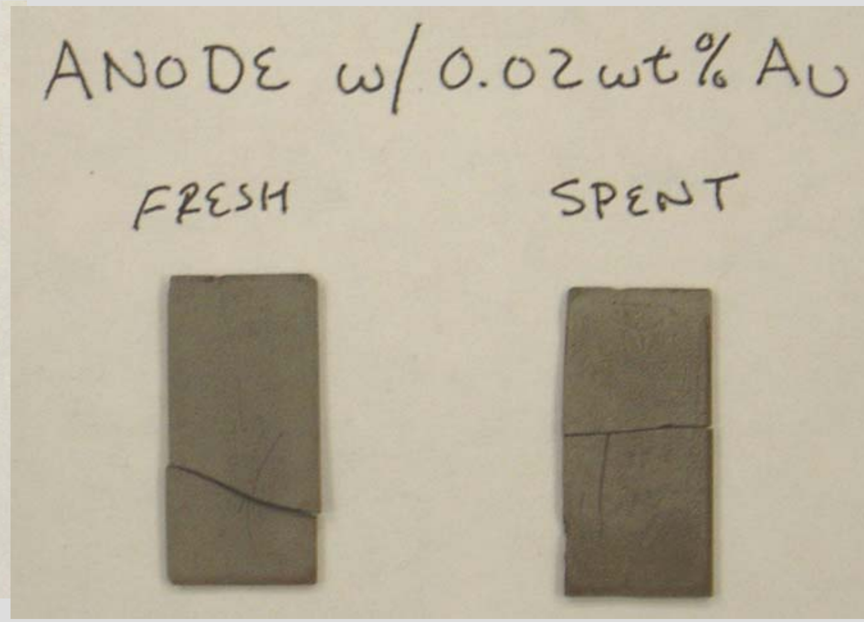
3:1 Steam to Carbon; 10:1 CH_4 to H_2, 700°C

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





Summary and Conclusions

- Addition of gold to supported nickel catalyst at sub-monolayer coverage significantly retards carbon formation
- Sufficient gold to retard carbon formation nickel results in decrease in catalyst activity by factor ~65-85%
  - Methane conversion more affected by Au addition than butane conversion
- H_2 chemisorption provides best method to correlate Ni availability with catalyst activity
- N_2O chemisorption may provide method to measure step sites

Summary and Conclusions

- Step site poisoning model does not fully explain results
  - Addition of gold affects many nearest neighbor Ni sites
  - Anode activity on surface Ni basis (H_2 chemisorption) comparable to supported Ni despite expected differences in step sites between two catalysts
- Reforming studies have been initiated over Ni/YSZ anode
  - Butane reforming at even 6:1 S:C observed
    - Filamentous carbon identified
    - Carbon filament diameter smaller than Ni/YSZ crystal size (by XRD)
  - Carbonizing effect not observed with CH_4 feed at 3:1 S:C and short reaction times
  - Addition of gold to Ni/YSZ shows small activity decrease compared to supported Ni case, based on current preparation method

Future Work

- Obtain kinetic data for on-anode reforming to support model development
- Evaluate effect of gold addition to Ni/YSZ for methane steam reforming
  - Carbon tolerance at reduced S/C ratios
  - Au concentration-reforming activity correlation
  - Identify best methods for Au introduction onto Ni/YSZ
- Evaluate effect of other additives to improve nickel anode performance (alkaline earth, Sn, Ce)
- Evaluate efficacy of natural gas pre-reforming with modified Ni catalysts
- Initiate studies of doped strontium titanate as sulfur-tolerant pre-reforming catalyst