

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

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Presentation Outline

- Motivation for project
- Background on nickel catalysts
 - Carbon formation
 - Approaches to carbon reduction
 - Concepts in alloy and bimetallic catalysts
 - Role of nickel surface topology
- Ni-Au alloy catalysts
 - Previous literature
 - Initiated studies at PNNL
- Summary and conclusions
- Future work

Motivation For Project

- Cost effective nickel catalysts avoid precious metal costs

but

- Nickel catalysts form carbon
- Nickel catalysts require costly use of high steam/carbon ratios to maintain activity

and

- Literature indicates that nickel catalysts surface alloyed with gold have improved stability toward carbon formation, potentially reducing steam requirements for fuel reformation
- Understanding Ni-Au catalyst principles may lead to alternative catalyst formulations with less expensive promoters

Spot Market Prices for Various Catalytically Active Metals

- As of 9/16/03

Precious Metal

Price, \$/troy ounce

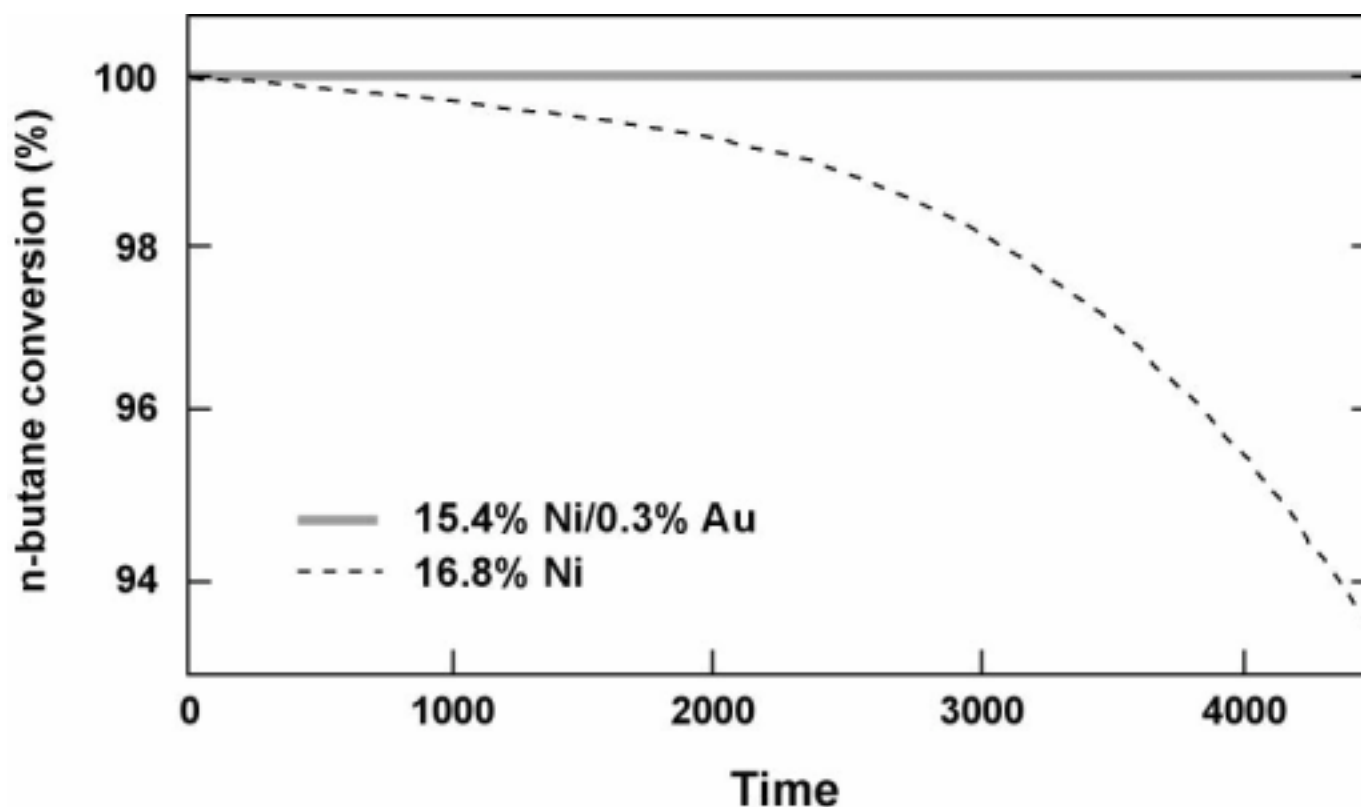
Platinum	697
Palladium	221
Rhodium	450
Gold	373

Non-Precious Metal Price, \$/lb

Price, \$/troy ounce

Nickel	4.50	0.31
Copper	0.81	0.07
Tin	2.21	0.15

Nickel-Gold Catalysts Show Resistance to Deactivation



Conditions: 3% n-butane--7% hydrogen--3% water-- 550°C—space velocity 1.2 hr⁻¹

F. Besenbacher, I Chorkendorff, B.S. Clausen, B. Hammer, A.M. Molenbroek, J.K. Norskov, I. Stensgaard; Science Vol. 279, 1913, 20 March 1998, reproduced with permission from AAAS

Carbon Formation With Nickel-Based Catalysts

- Theoretical and experimental studies indicate that surface carbon atoms bound to certain nickel sites are stable intermediates
- Such a site may react with “O” (from H₂O) to form CO or may nucleate to produce graphite or whisker carbon
- Catalyst stability is determined by relative rates of carbon growth vs. gasification
- Carbon formation leads to
 - Loss of activity by site blockage
 - Potentially catastrophic reactor plugging
 - Support degradation

Approaches to Reduce Carbon Formation

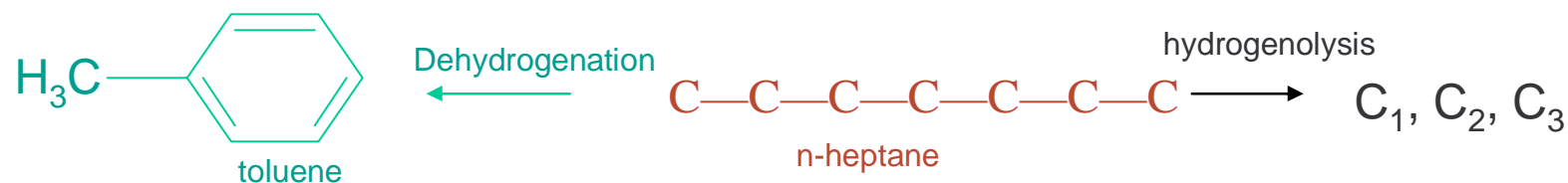
- Use of high steam/carbon ratios (higher O/C)—oxidize (gasify) carbon
- Use of basic supports (alkalized- Al_2O_3 ; MgO ; $\text{Mg-Al}_2\text{O}_4$) to avoid hydrocarbon cracking
- Alkali addition (primarily K_2O) to nickel surface to increase water adsorption
- Continuous feeding low concentration of H_2S to catalyst
- Add other metals to form alloys or bimetallics, modifying the catalyst surface

Alloys and Bimetallic Catalysts

- Some catalytically useful alloys combine Group VIII and IB metals
 - Ni-Cu
 - Pd-Ag
 - Pd-Au
- Other bimetallic combinations exist as surface alloys or simple mixtures of components
 - Ru-Cu
 - Ni-Au
- Most catalytically active alloys show surface enrichment of one component
 - Element having lower surface energy migrates to surface of catalyst particle
 - May be driven by interaction with surrounding gases

Metal Alloy Catalysts May Show Unusual Catalytic Selectivities

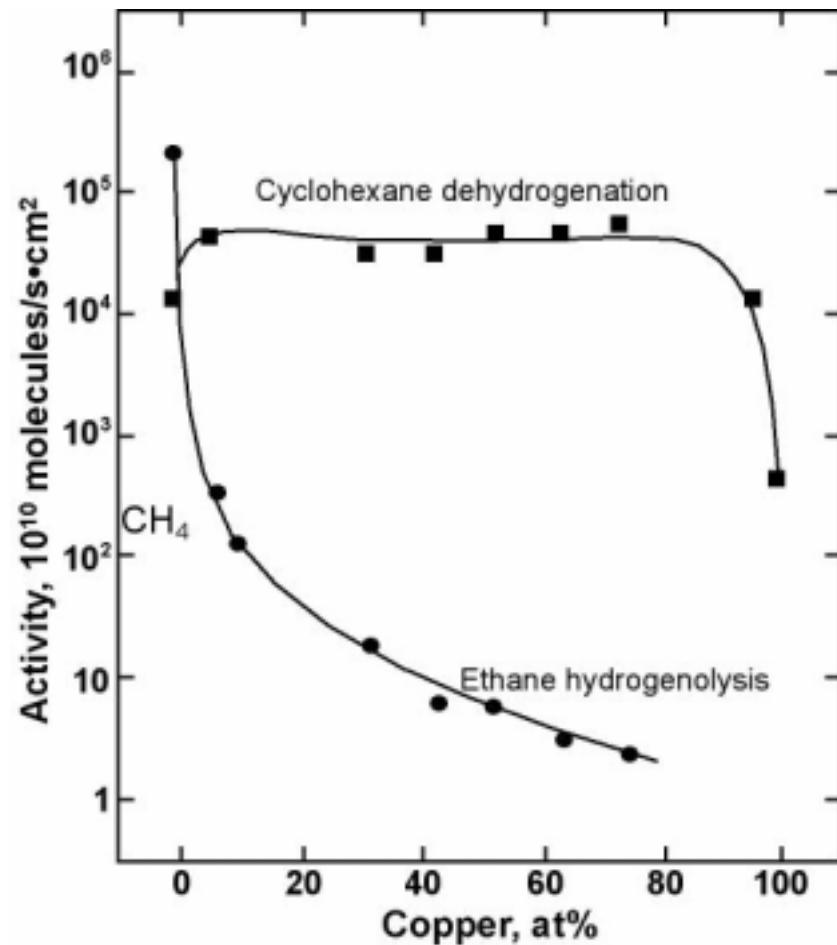
- Pathfinding work with alloys focused on improvement of gasoline reforming catalysts
 - De-hydrogenation of alkanes to form high octane value aromatics
 - High yield requires minimization of light hydrocarbons



- Well-studied example: Ni-Cu alloy catalyst
 - Non-catalytic copper concentrates at surface under reaction conditions
 - Relative to pure Ni
 - Copper addition significantly retards ethane hydrogenolysis
 - Copper addition modestly retards cyclohexane dehydrogenation

Metal Alloy Catalysts May Show Unusual Product Selectivities

Rates of hydrogenolysis of ethane to methane and cyclohexane to benzene at 589K for a series of Ni-Cu catalysts



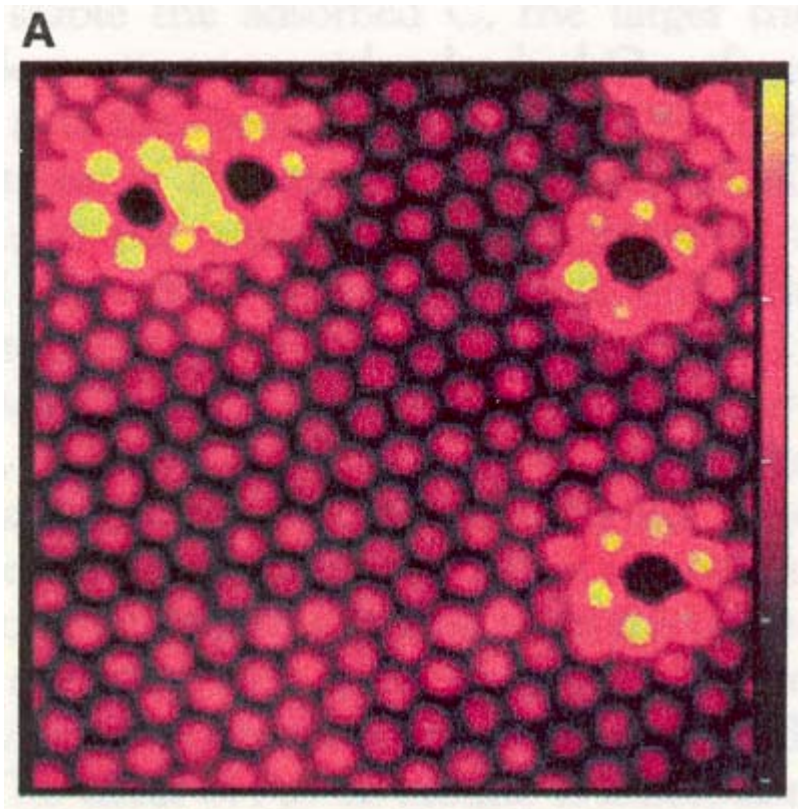
Sinfelt, J.H., Carter, J.L. and Yates, D.J.C.; Journal of Catalysis, **24**, 283-296, (1972)
Reproduced with permission from Elsevier

The Alloy Effect—Theories

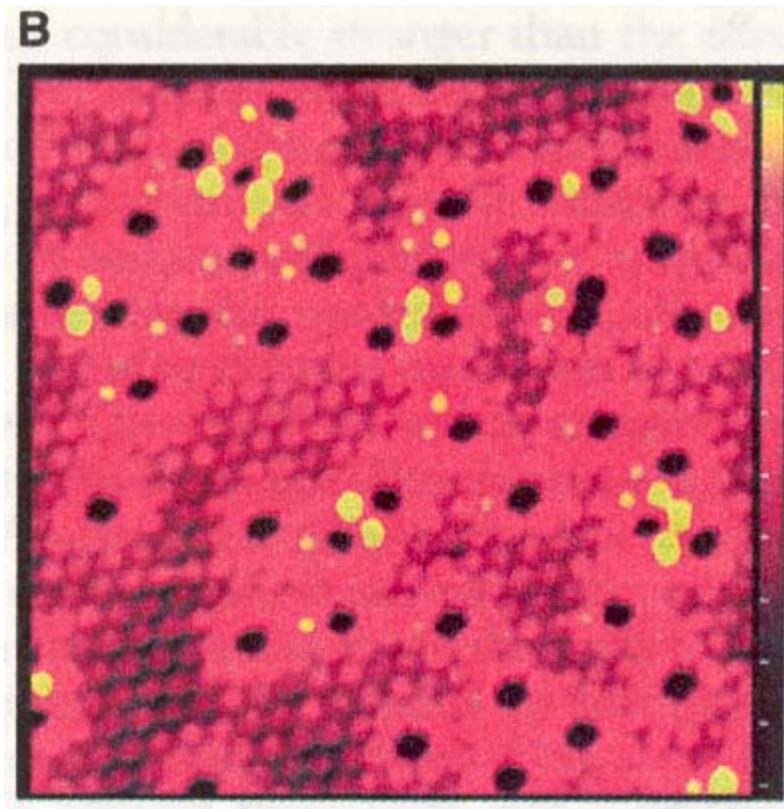
- Ensemble size reduction—surface component breaks up large regions of primary metal component
 - Hydrogenolysis may require larger ensemble sizes than does dehydrogenation
- Chemical interactions (ligand effects)
 - Electronic properties of the active metal component are altered by alloying with second metal
 - Affects bonding of adsorption energies, stability of intermediates

Gold Addition to Single Crystal Nickel Surface Affects Properties of Nickel Site

Scanning tunneling microscopy images of Ni (111) modified by gold atoms



2% gold monolayer

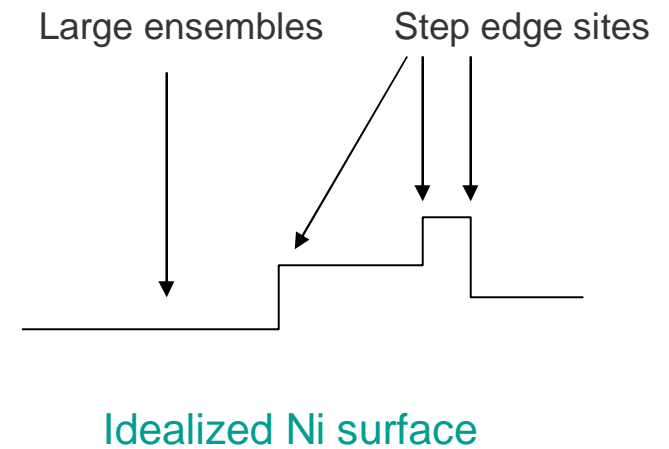
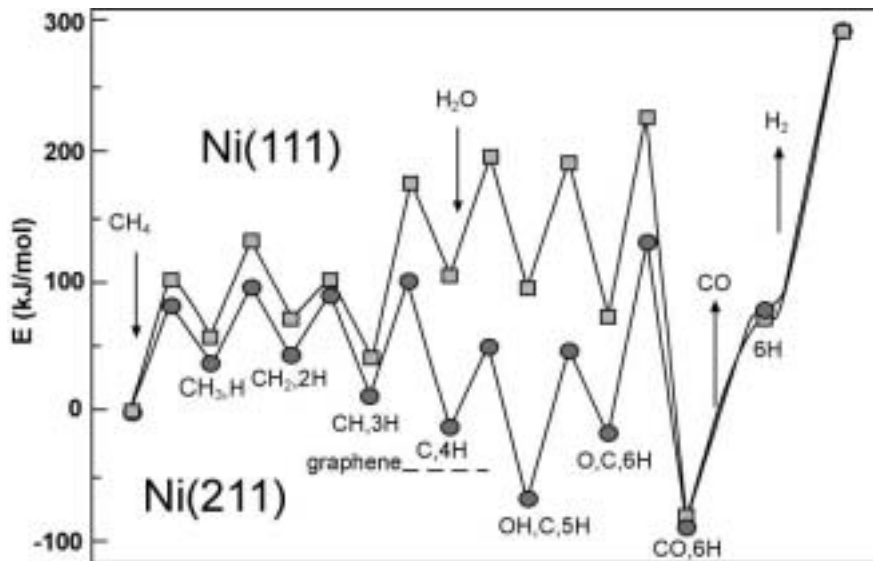


7% gold monolayer

Science Vol. 279, 1913, 20 March 1998

Nickel Catalyst Surface Comprises Different Site Types

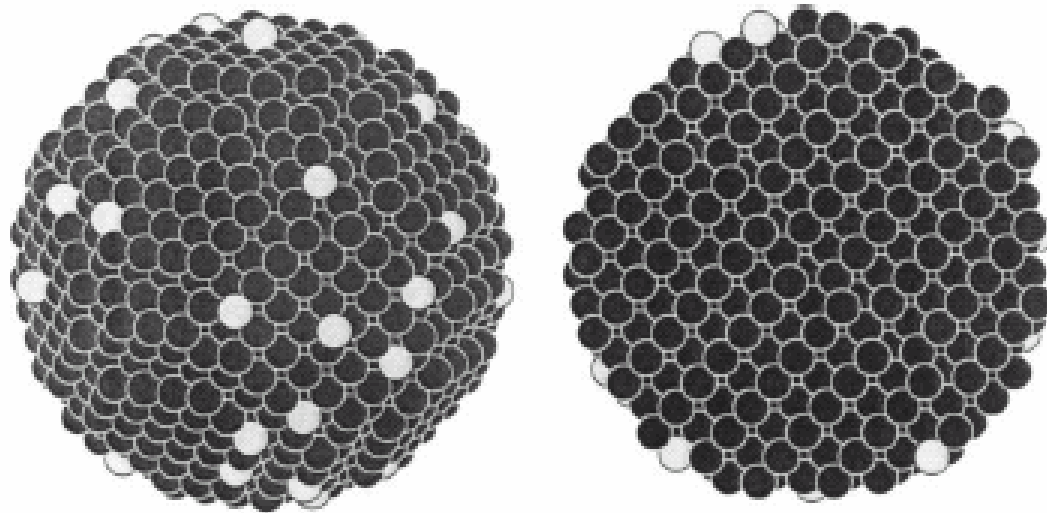
- Large ensembles — planes or facets
 - Favored by larger Ni crystallites
 - Sites tend toward lower activity
- Steps, edges, defect sites
 - Favored by smaller Ni crystallites



Benggaard et. al., "Steam Reforming and Graphite Formation on Ni Catalysts"
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Nickel-Gold Catalyst Surface

- In inert or reducing atmospheres, gold migrates to external surface of particle
- Studies with prepared nickel-gold catalysts indicate
 - Gold preferentially positions on Ni step sites
 - Lowers catalyst surface energy

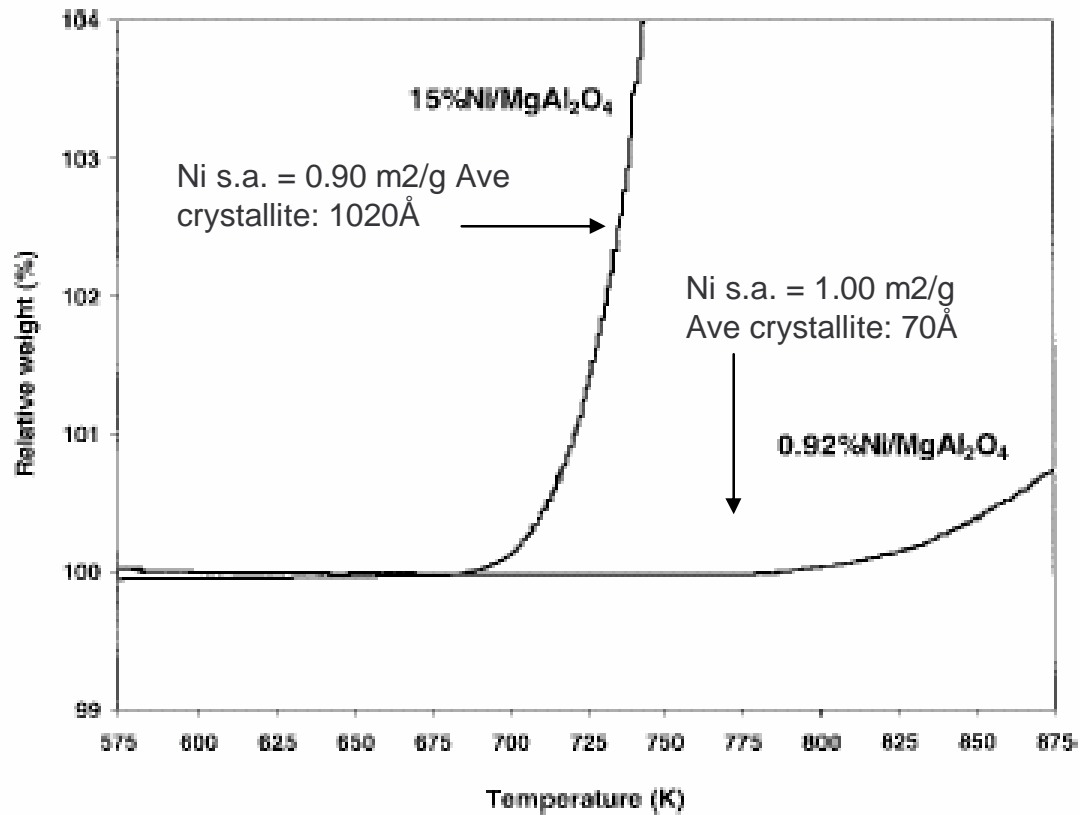


Bengard et. al., *Journal of Catalysis*, **209**, 365-384 (2002)

Deactivation Of Step Sites Reduces Carbon Deposition

- Single carbon atom is most stable at step edge site
 - Site for nucleation
 - Both nucleation and subsequent growth enhanced by higher hydrocarbons compared to methane
- Carbon layer grows from nucleation site, facilitated by Ni planar surfaces
 - Size of carbon layer determines its stability (~80 atoms)
 - Smaller nickel planes less likely to facilitate carbon layer growth
- High activity step edge sites removed by coordination with gold atoms
 - Retards carbon nucleation
 - Retards reformation activity, but to lesser extent
- Sulfur atom poisoning of nickel step edge sites has similar effect

Nickel Catalyst Particle Size Affects Carbon Production



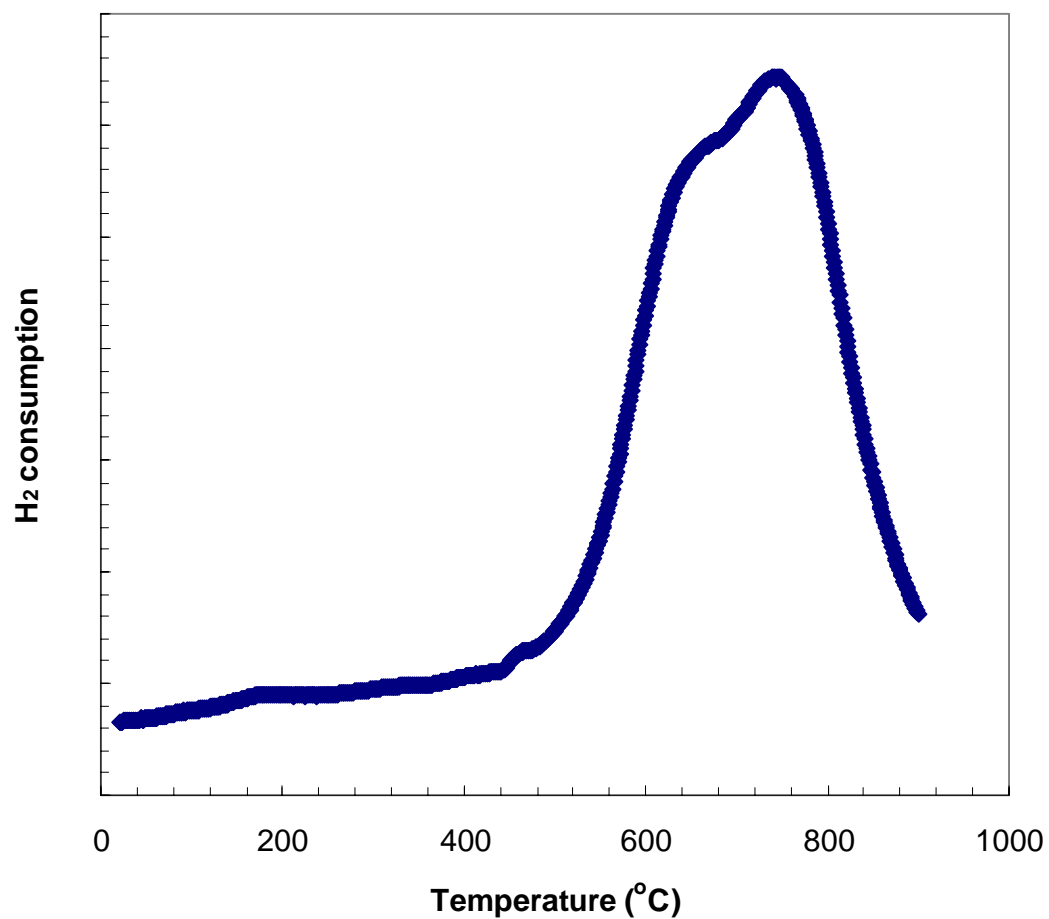
Feed: 7%H₂, 3%n-butane, 2.1%H₂O, balance He; O/C=0.7
Bengaard et. al., Journal of Catalysis, **209**, 365-384 (2002)

Evaluation of Ni and Ni-Au Catalysts at PNNL

Catalyst preparation

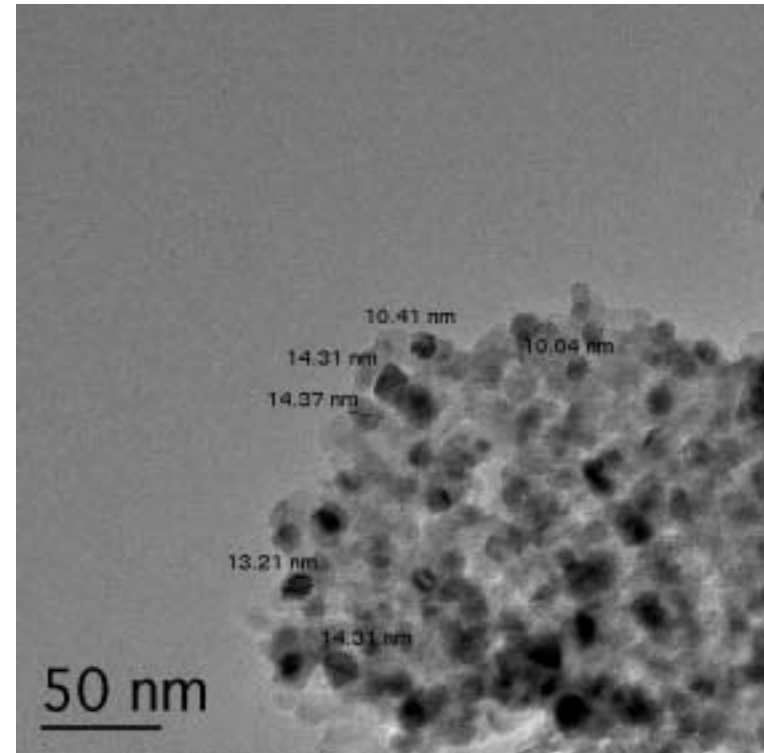
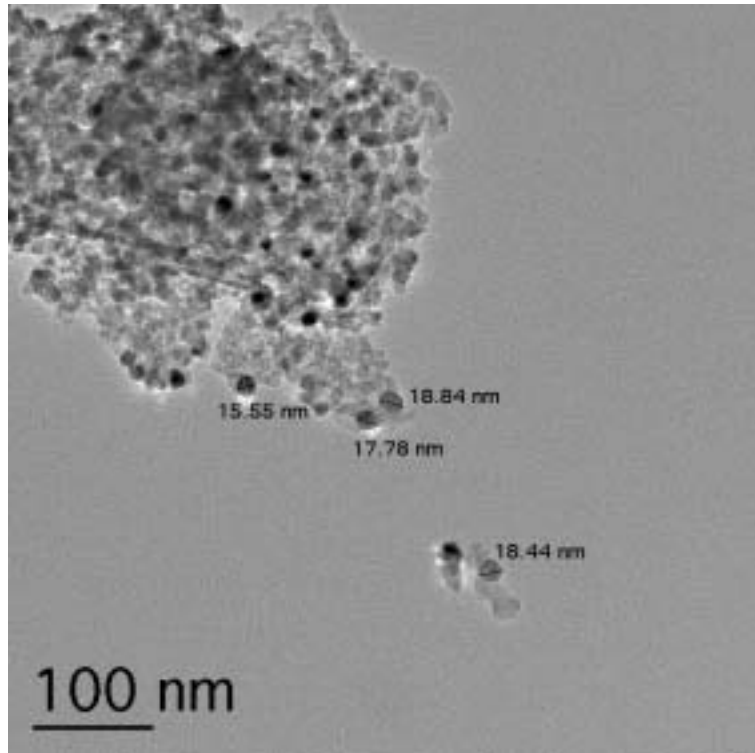
- Nickel catalysts
 - Use commercially available MgO-Al₂O₃ support; calcine 700°C
 - Incipient wetness impregnation Ni(NO₃)₂, 15.8 wt.% Ni
 - Calcine 500°C, 4h
 - Reduce 900°C, 2h
- Nickel-gold catalysts
 - Passivate reduced Ni catalyst with 2% O₂/He
 - Incipient wetness impregnation HAuCl₄, 0.3 or 0.5 wt.% Au
 - Dry 200°C in He
 - Reduce 500-600°C, 2h

TPR of Ni/MgO-Al₂O₃ Shows Full Reduction at 900°C



Reduction temperature of 900°C employed is higher than typical but may be representative of severe conditions used to reform heavy fuels

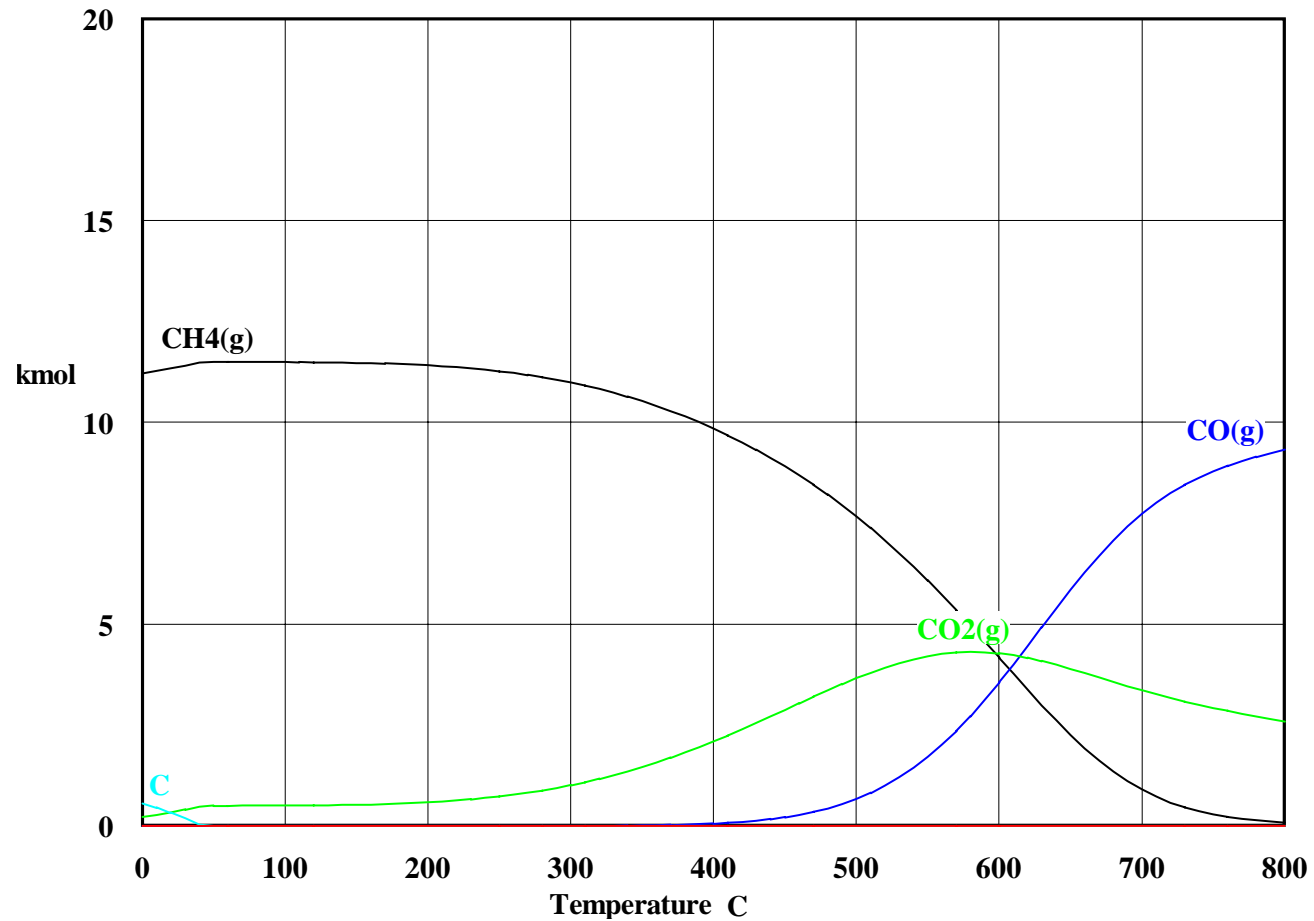
TEM of Ni/MgO-Al₂O₃ Reduced at 900°C



Metal dispersion: 6.7%
Nickel metal surface area 3.2 m²/g

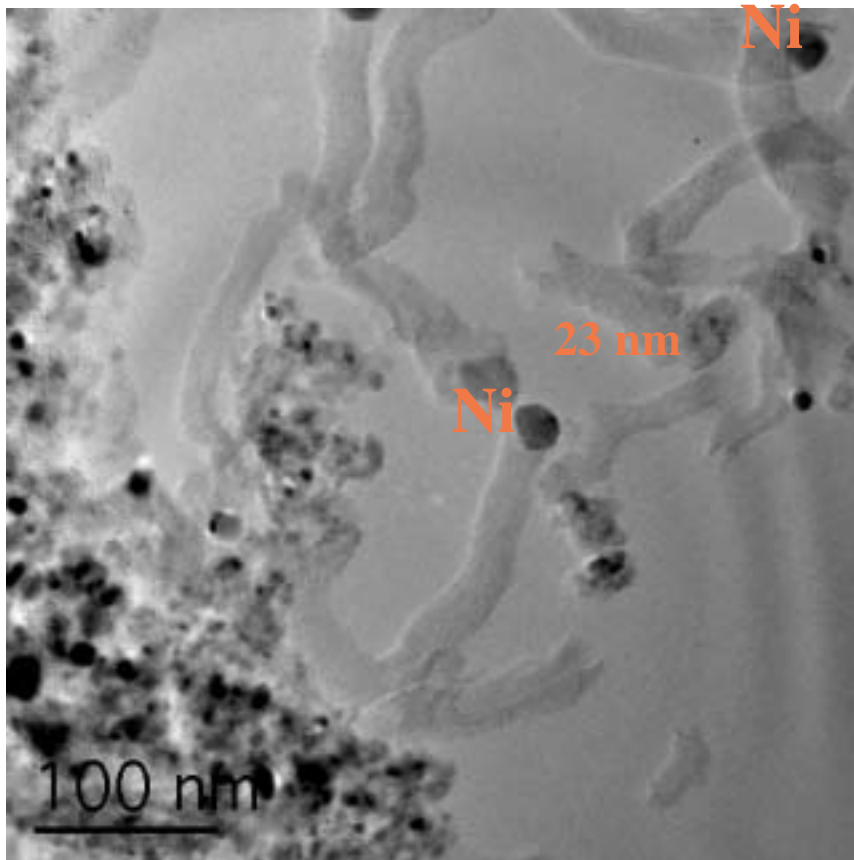
Thermodynamic Equilibrium Predicts No Carbon Formation Under Conditions Utilized

Feed:
3% n-butane,
7% H₂
S/C = 2.0

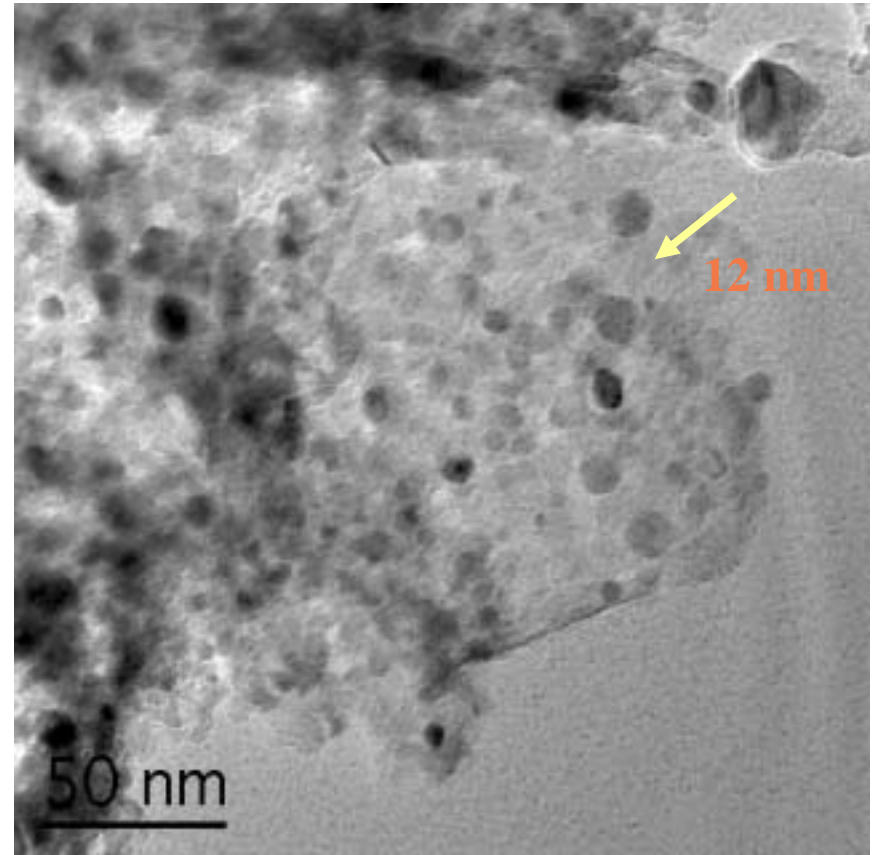


Spent Ni/MgO-Al₂O₃ Catalyst Shows Carbon Formation From Larger Particles

Feed: n-butane, H₂O; S/C = 2.0; Temperature: 600°C

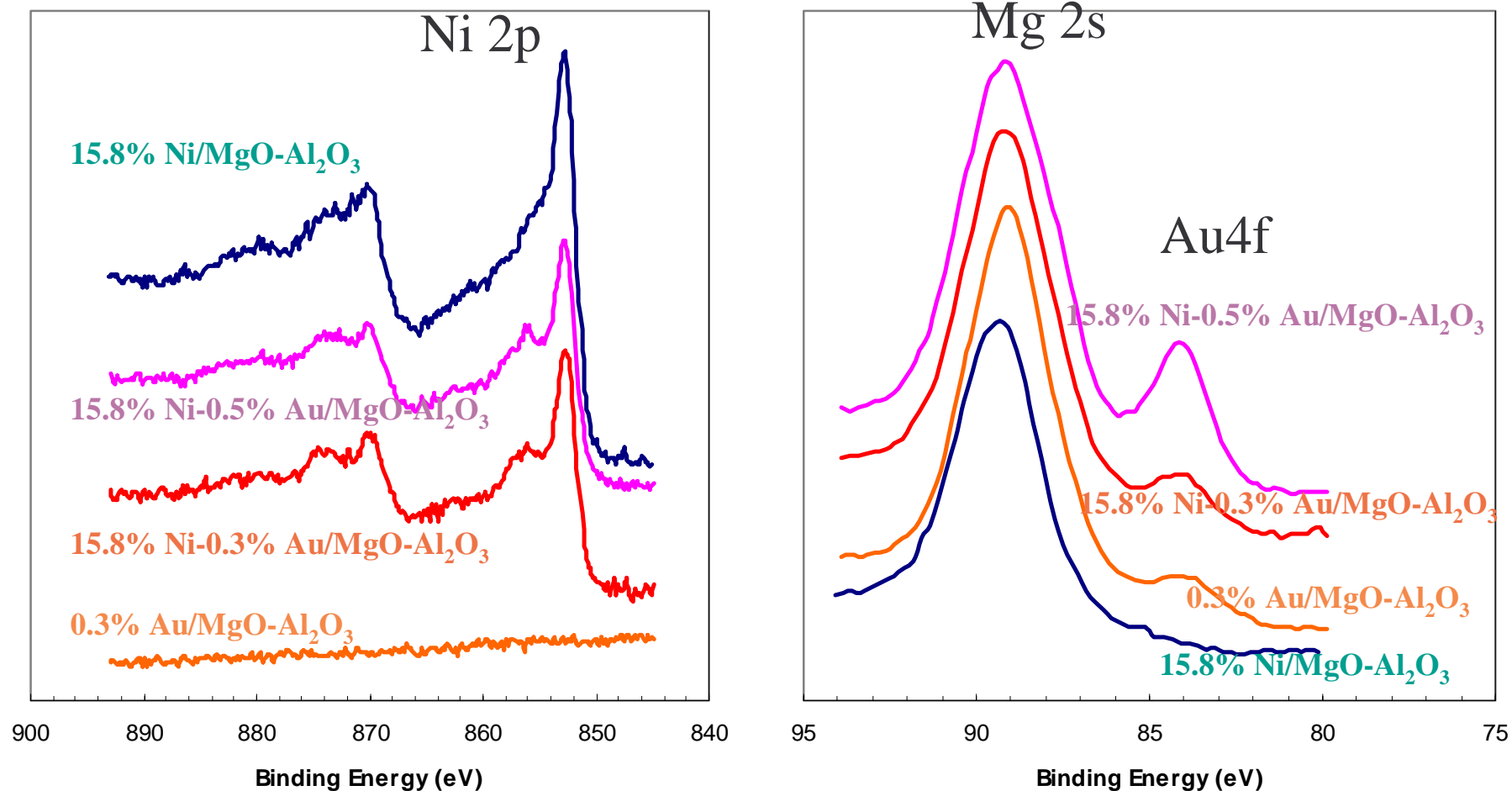


Region with Coke Formation
Ni Particles > 20 nm



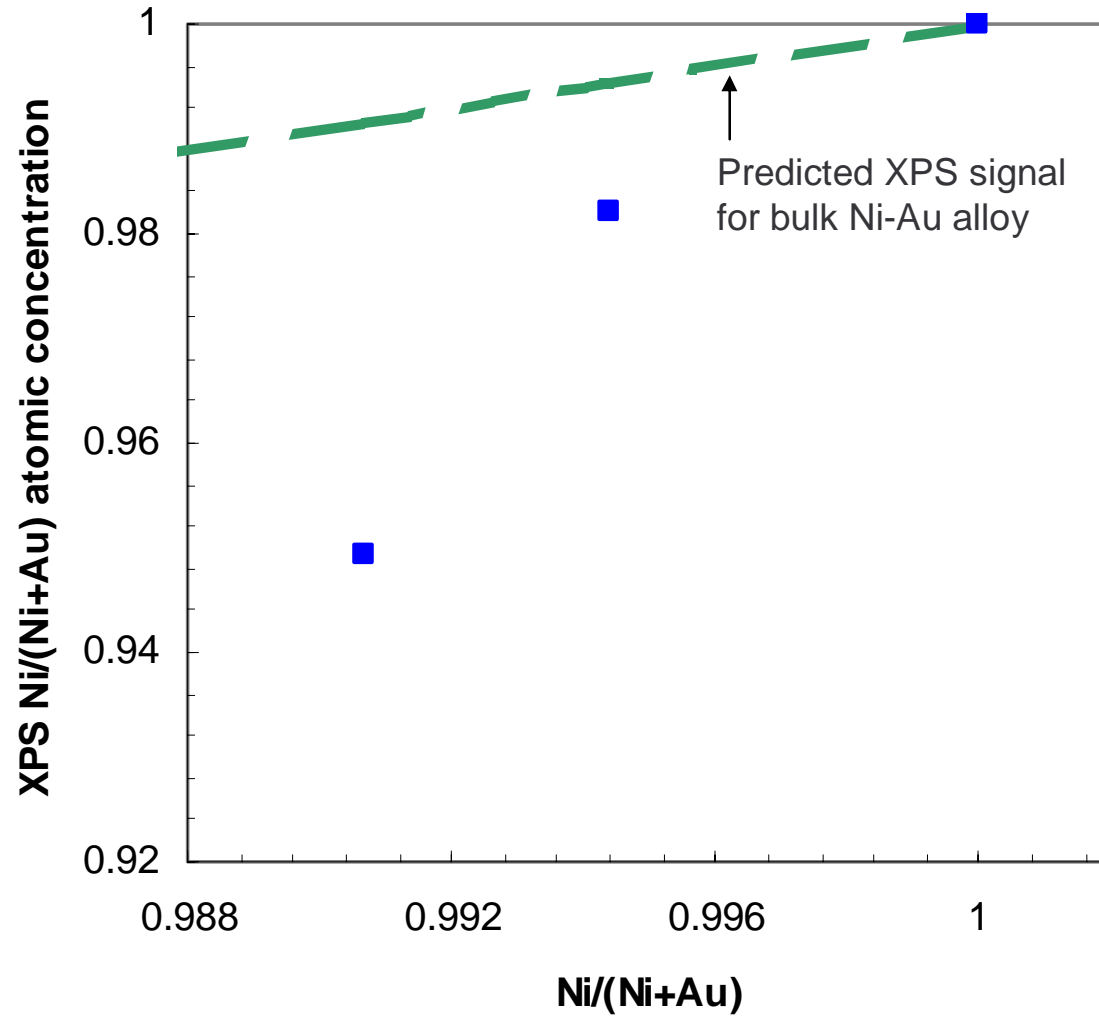
Region without significant coking
Ni Particles < 15 nm

XPS Spectra of Nickel and Nickel-Gold Catalysts Supported on Mg-Al₂O₄

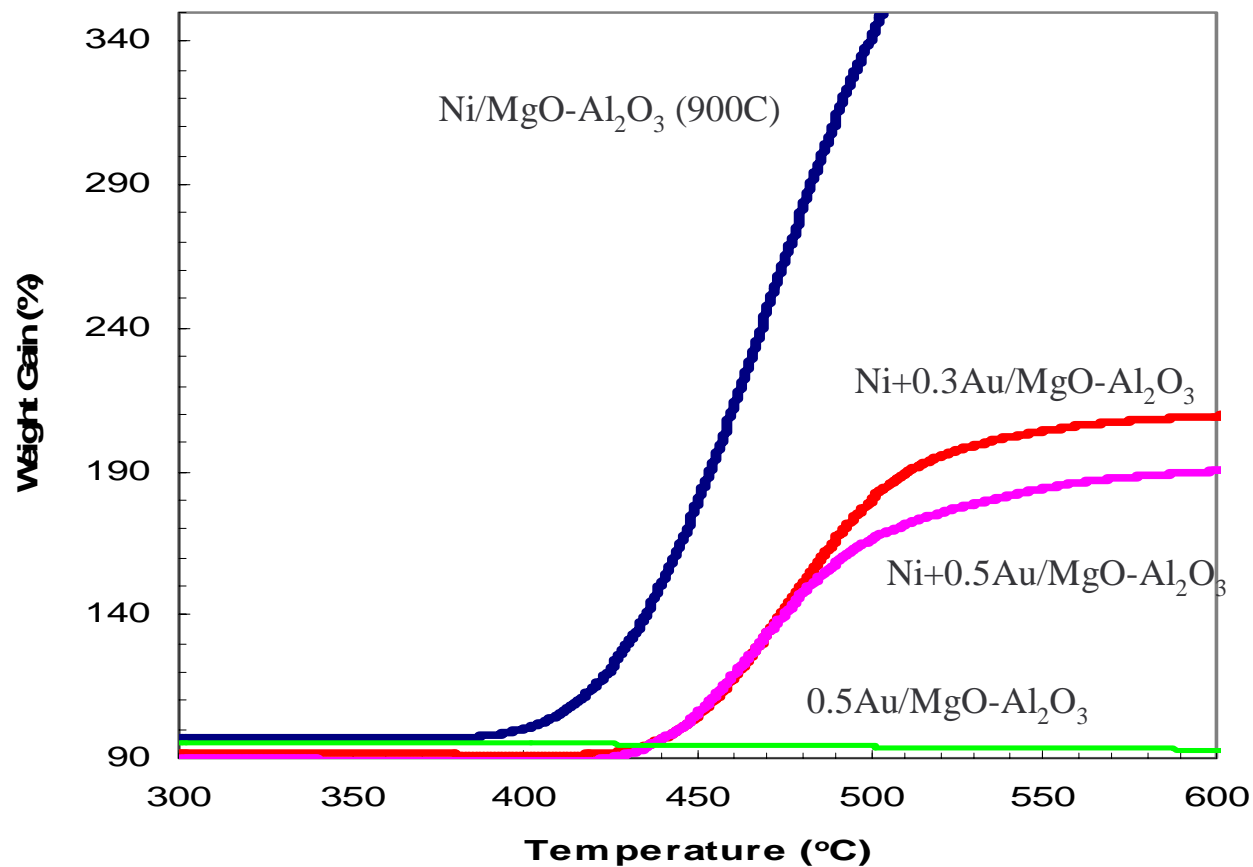


Suppression of Ni 2p peak observed with increasing Au loadings.

XPS Spectra Show Surface Depletion of Nickel in Nickel-Gold Alloy Catalyst

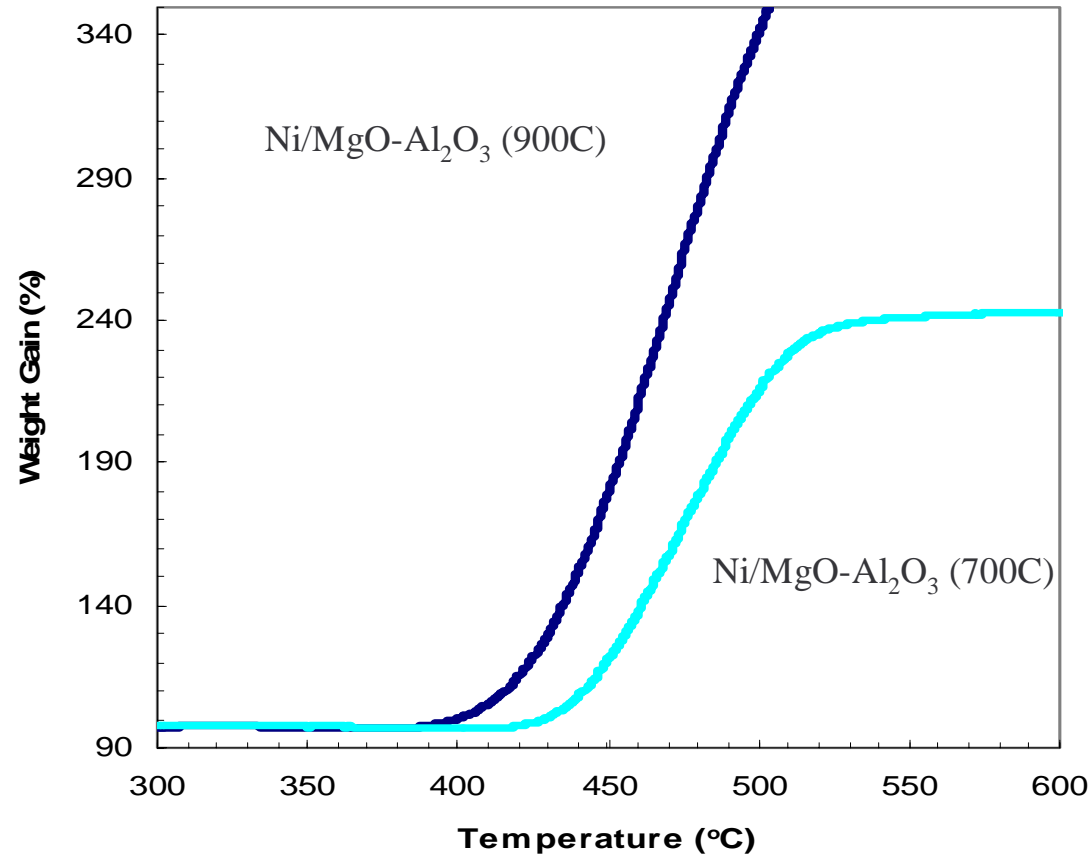


TGA Shows Reduction in Carbon Formation With Ni-Au Catalysts



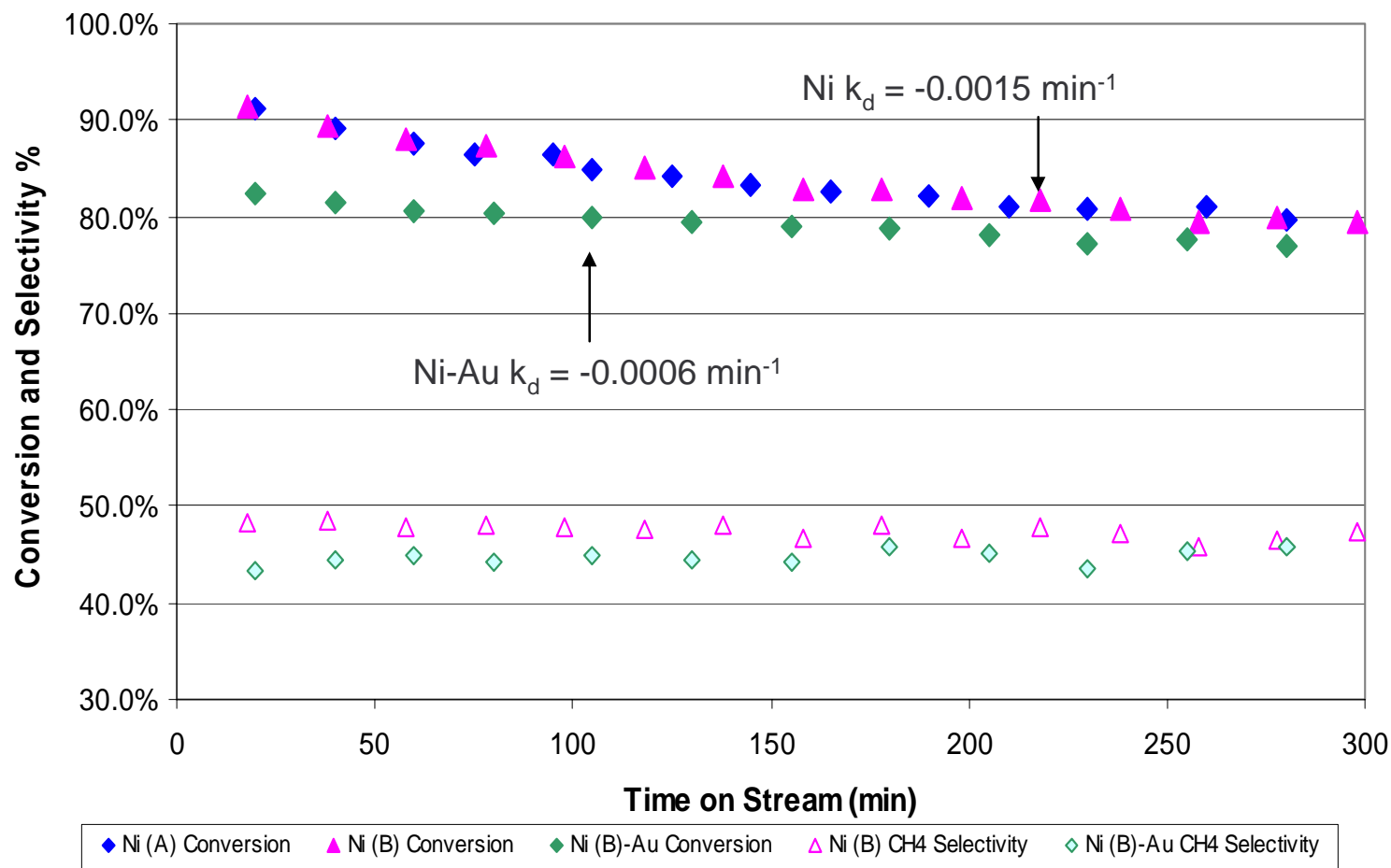
Feed: 0.84% n-butane; 0.84% H₂O; balance He
Ni-Au catalysts re-reduced at 600°C

Lower Catalyst Reduction Temperature Reduces Carbon Formation



Feed: 0.84% n-butane; 0.84% H₂O; balance He

Comparison of Nickel and Nickel-Gold Catalysts for n-Butane Steam Reforming



Feed: 3% n-butane, 7% H₂, balance N₂; S/C=4; T = 465°C
Ni/MgO-Al₂O₃ reduced at 900°C

Summary and Implications

- Nickel catalysts show substantial activity for carbon formation
 - Catalyst deactivation and weight gain observed
 - Carbon buildup even in region not predicted by thermodynamic calculations
- Nickel-gold catalysts show reduction in carbon formation
 - Gold concentrates at surface of Ni crystallite
 - Decrease in total carbon produced and rate of carbon formation
 - Increase in temperature onset for carbon formation
 - Lower catalytic deactivation rate
- Addition of gold to catalyst surface is not sufficient to eliminate carbon formation
 - Nature of nickel catalyst surface important: crystallite size also affects carbon formation
 - Other promoters may be needed to increase H₂O concentration at surface

Forward Work

- Determine effect of gold addition over range of operating conditions
 - Temperature, steam/carbon
 - Nickel particle size and concentration
 - Gold concentration and method of introduction
 - Hydrocarbon feedstock
- Evaluate N₂ titration method to quantify concentration of highly active nickel surface sites
- Investigate synergy of alkali or other promoters with Ni-Au catalysts