

## **Summary of Research on Hydrogen Production From Fossil Fuels Conducted at NETL**

Abolghasem Shamsi

In this presentation we will summarize the work performed at NETL on the production of hydrogen via partial oxidation/dry reforming of methane and catalytic decomposition of hydrogen sulfide. We have determined that high pressure resulted in greater carbon formation on the reforming catalysts, lower methane and CO<sub>2</sub> conversions, as well as a H<sub>2</sub>/CO ratio. The results also showed that Rh/alumina catalyst is the most resistant toward carbon deposition both at lower and at higher pressures. We studied the catalytic partial oxidation of methane over Ni-MgO solid solutions supported on metal foams and the results showed that the foam-supported catalysts reach near-equilibrium conversions of methane and H<sub>2</sub>/CO selectivities. The rates of carbon deposition differ greatly among the catalysts, varying from 0.24 mg C/g cat h for the dipped foams to 7.0 mg C/g cat h for the powder-coated foams, suggesting that the exposed Cr on all of the foam samples may interact with the Ni-MgO catalyst to kinetically limit carbon formation. Effects of sulfur poisoning on reforming catalysts were studied and pulse sulfidation of catalyst appeared to be reversible for some of the catalysts but not for all. Under pulse sulfidation conditions, the 0.5%Rh/alumina and NiMg<sub>2</sub>Ox-1100°C (solid solution) catalysts were fully regenerated after reduction with hydrogen. Rh catalyst showed the best overall activity, less carbon deposition, both fresh and when it was exposed to pulses of H<sub>2</sub>S. Sulfidation under steady state conditions significantly reduced catalyst activity. Decomposition of hydrogen sulfide into hydrogen and sulfur was studied over several supported metal oxides and metal oxide catalysts at a temperature range of 650-850°C. H<sub>2</sub>S conversions and effective activation energies were estimated using Arrhenius plots. The results of these studies will further our understanding of catalytic reactions and may help in developing better and robust catalysts for the production of hydrogen from fossil fuels.

# Summary of Research on Hydrogen Production From Fossil Fuels Conducted at NETL



U.S. Department of Energy, National Energy  
Technology Laboratory  
P.O. Box 880, 3610 Collins Ferry Road,  
Morgantown, WV 26505-0880  
[Abolghasem.Shamsi@NETL.doe.gov](mailto:Abolghasem.Shamsi@NETL.doe.gov)

# Hydrogen From Coal/Biomass

## ***Project Title:***

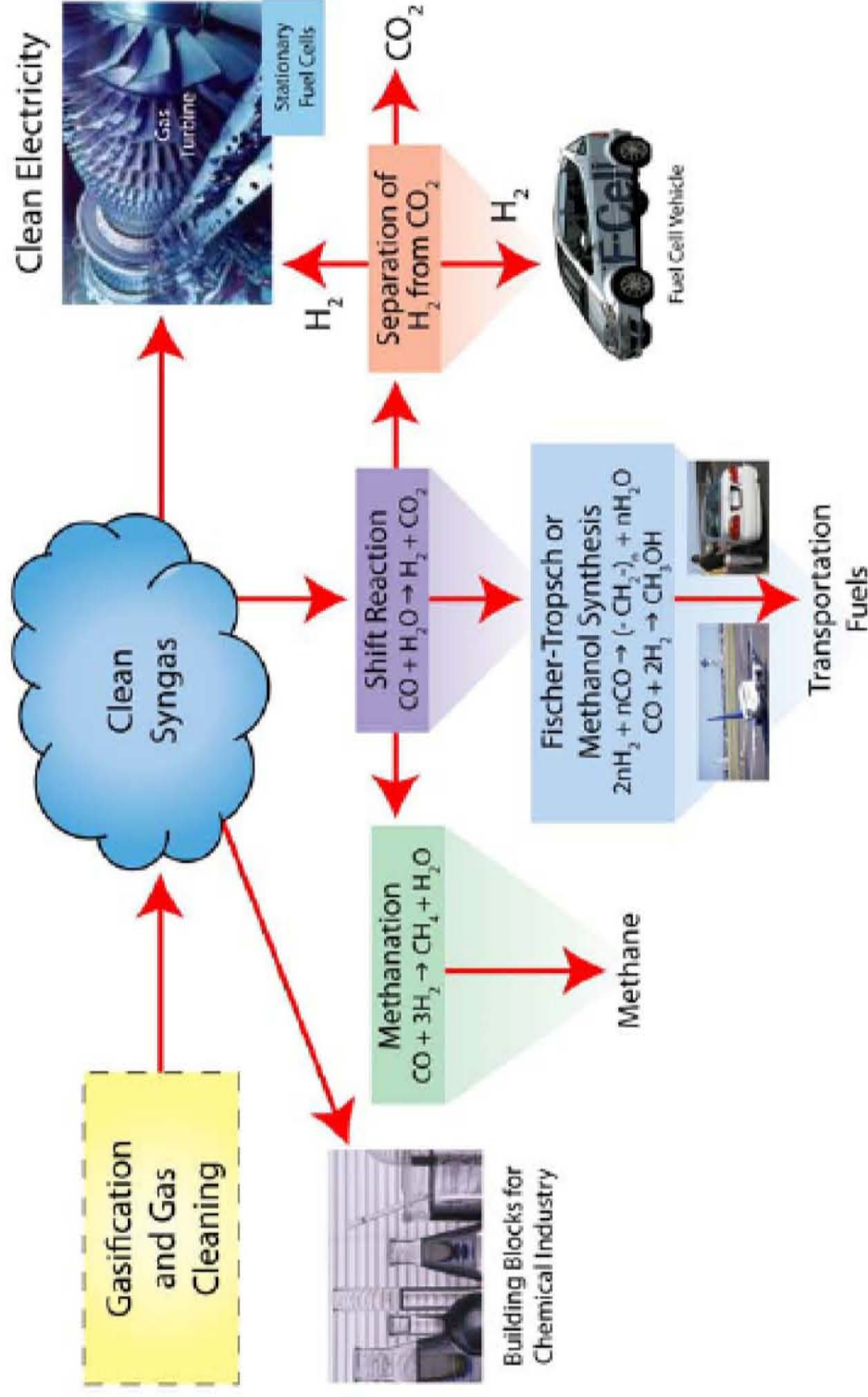
Evaluation of Sorbent Enhanced Water Gas Shift (WGS) Catalyst Systems for Production of Hydrogen

## ***Project Objective:***

The goal of this project is to evaluate novel processes for producing hydrogen from coal/biomass: Evaluating sorbent-enhanced WGS catalyst systems by combining carbon dioxide separation technologies with water gas shift catalyst using fewer steps "process intensification", producing pure hydrogen and separating carbon dioxide for sequestration



# Current Hydrogen from Coal Production\*



\*DOE Hydrogen from Coal Program RD&D Plan 2007

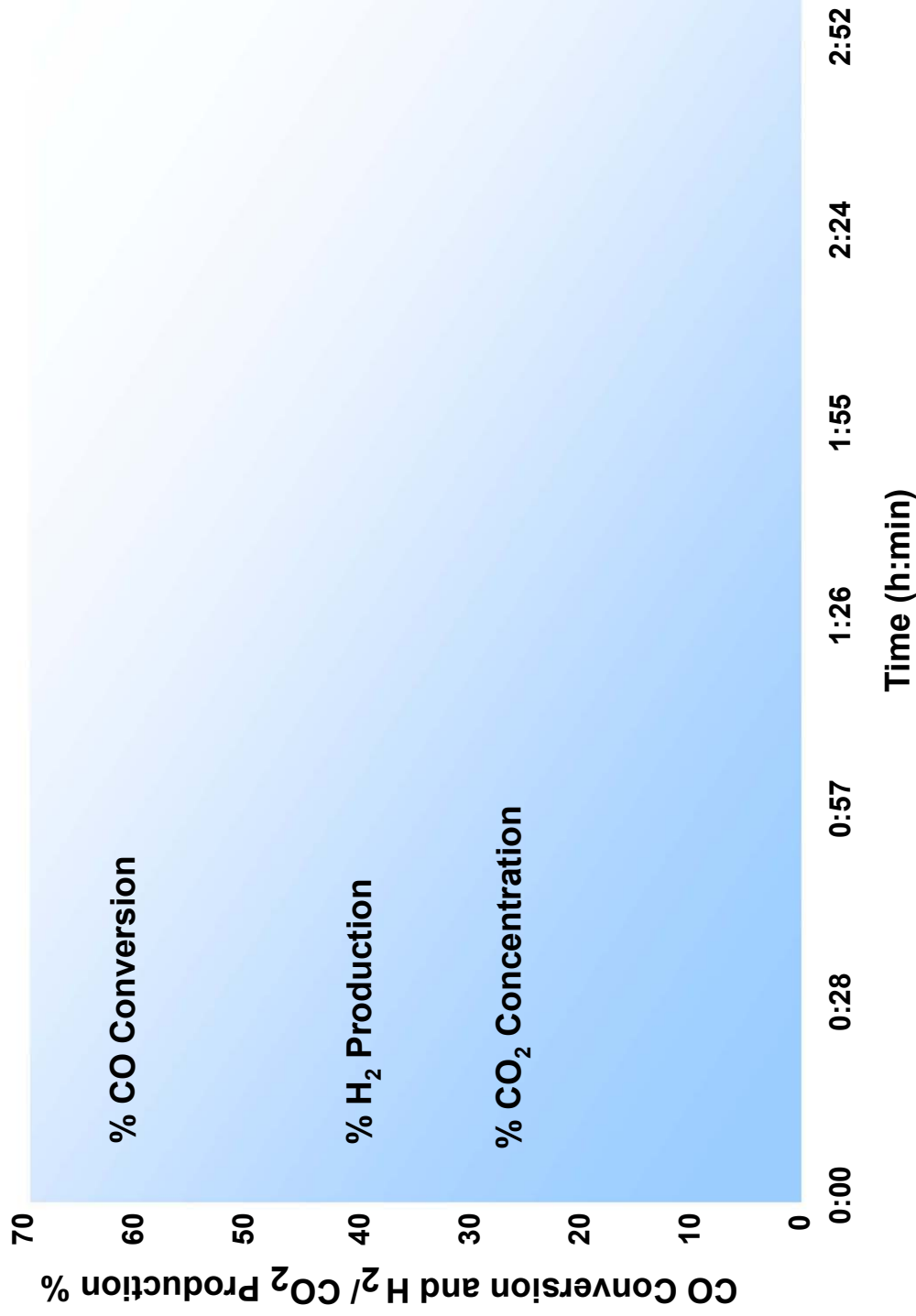
# Current Technologies

- Industrially, water gas shift reactions are carried out in two steps in several reactors
- High-temperature shift reactor (Fe, Cr)
- Low-temperature shift reactor (Cu, Zn)
- Copper/zinc oxide is not suitable for coal gas
  - Copper/zinc oxide requires pre-reduction and operation at controlled conditions
  - Deactivation via oxidation, temperature fluctuation, or sintering is a problem with Cu/Zn catalyst

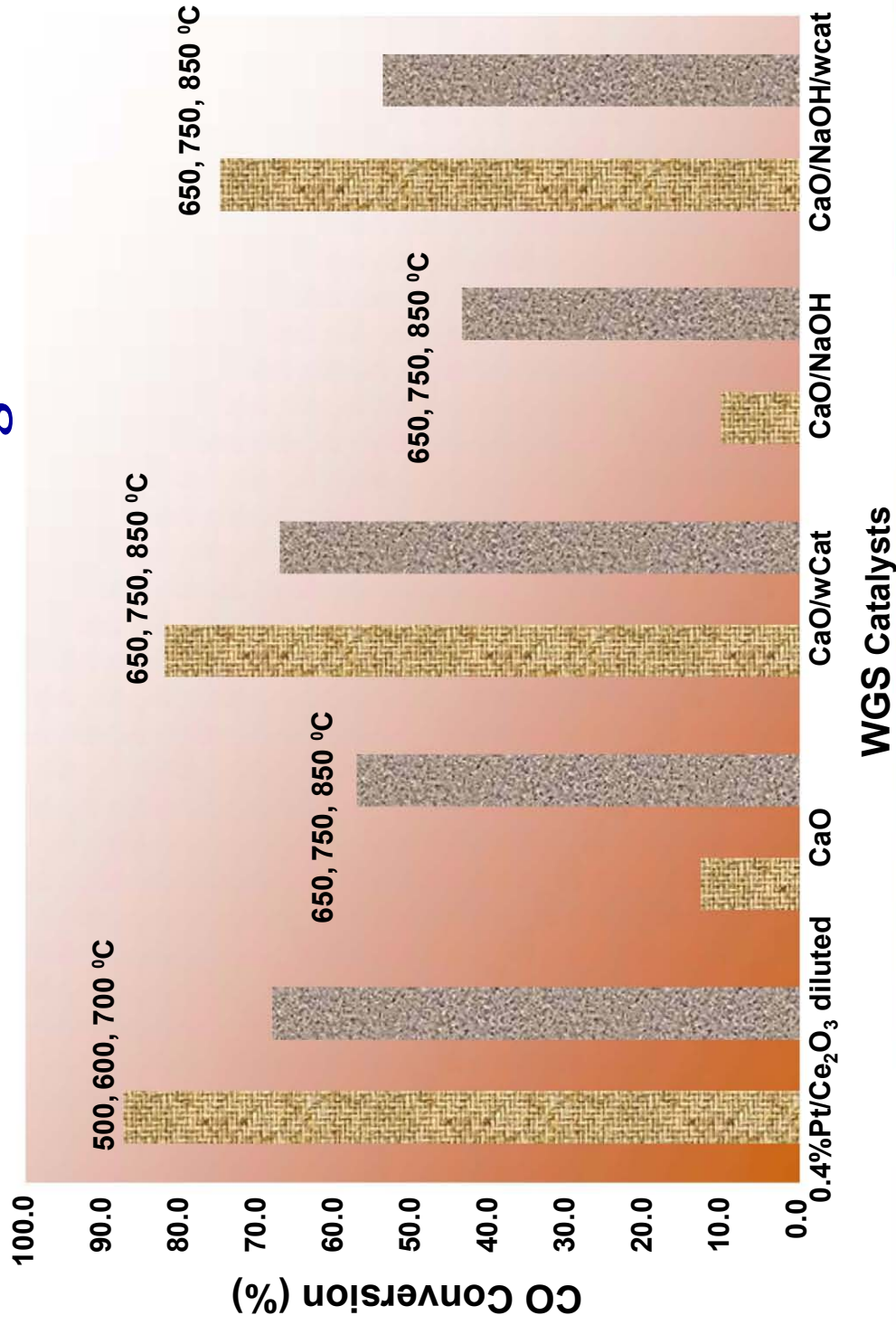
# Benefits of Removing CO<sub>2</sub> during WGS Reaction

- Increases CO conversion
- Increases hydrogen selectivity
- Produces high pressure hydrogen
- Facilitates CO<sub>2</sub> sequestration
- Reduces the cost for CO<sub>2</sub> separation
- Reduces required H<sub>2</sub>O/CO ratio
- Increases the range of operating conditions for achieving equilibrium conversion of CO

# Water Gas Shift Reaction Conducted at NETL Over CaO at 850°C, 150 Psig, GHSV = 10051 cm<sup>3</sup>g<sup>-1</sup>h<sup>-1</sup>



# CO Conversion Over CaO and CaO/NaOH With and Without WGS Catalyst (0.4%Pt/Ce<sub>2</sub>O<sub>3</sub>) at 150 psig, GHSV= 10051 cm<sup>3</sup>g<sup>-1</sup>h<sup>-1</sup>



# Hydrogen From Hydrogen Sulfide

## *Goal*

- To Conduct Basic and Applied Catalysis Research for Production of Hydrogen from Natural Gas and H<sub>2</sub>S-Containing Natural Gas

## *Challenge*

- Development of robust catalysts with much higher activities, selectivities, impurity tolerances, and capabilities for operating under extreme environments\*
  - Sulfur
  - Carbon deposition

\* <http://www.science.doe.gov/bes/hydrogen.pdf>

# Why H<sub>2</sub>S?

- The mission of The Strategic Center for Natural Gas and Oil (SCNGO) is “to **increase domestic oil and natural gas production**, assure the reliability of the natural gas delivery system, and produce a cleaner environment ”
- H<sub>2</sub>S is associated with drilling and production of natural gas and crude oil, under pressure H<sub>2</sub>S remains in oil and as the pressure released the gas bubbles out of oil with other gases such as methane, ethane, propane, butane, CO<sub>2</sub> and water vapor
- More than 12 million tons of H<sub>2</sub>S/year produced from refining fossil fuels in the US
- A well known technology that utilizes H<sub>2</sub>S is Claus process (producing sulfur and low -valued steam) which doesn't produce any hydrogen

# Conversion of Hydrogen Sulfide to Hydrogen

## Thermodynamics of H<sub>2</sub>S Dissociation

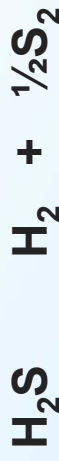


$$\Delta H_f^\circ = 20.4 \quad \text{kJ/mole}$$

$$\Delta G_f^\circ = 33.3 \quad \text{kJ/mole}$$

- The free energy  $\Delta G_f^\circ$  is low, suggesting that a good conversion is possible at equilibrium
- Low energy costs would only be achieved in a processes that have negligible heat loss

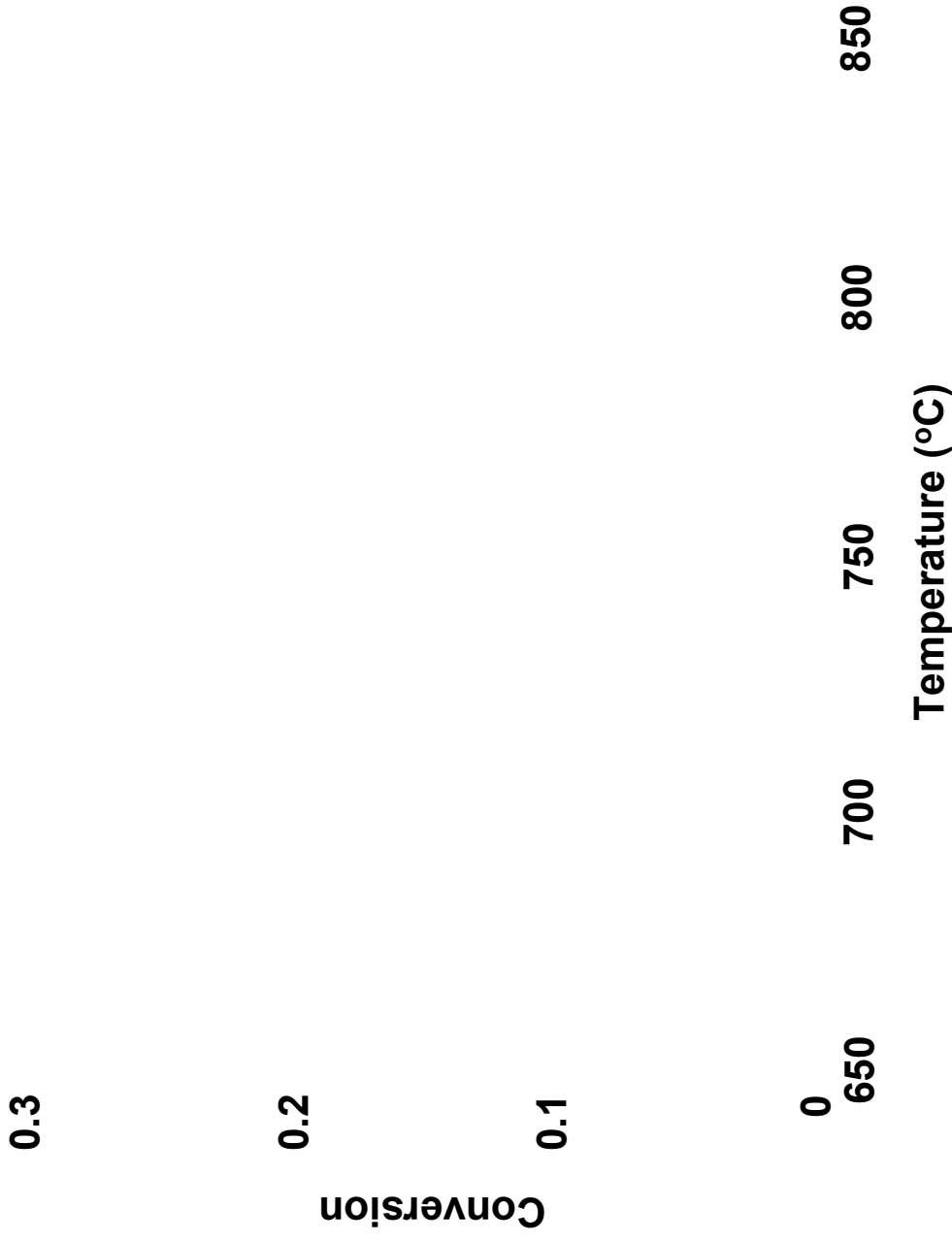
# Thermal Decomposition of H<sub>2</sub>S



- Calculated equilibrium conversion at 1 atm of pure H<sub>2</sub>S at different temperatures
- This process appears to be simple. But yields are very low even at high temperatures due to equilibrium limitation

| Temperature, °C | Percent Conversion |
|-----------------|--------------------|
| 700             | 3.8                |
| 900             | 12.8               |
| 1100            | 28                 |
| 1200            | 38                 |

# Conversion of $\text{H}_2\text{S}$ to $\text{H}_2$ and Sulfur



# H<sub>2</sub>S Conversion and Estimated Activation Energy Over Supported Metal Catalysts at 850°C

| Catalysts                                           | Composition                                                                         | H <sub>2</sub> S Conversion (%) | E <sub>a</sub> (kJ/mol) |
|-----------------------------------------------------|-------------------------------------------------------------------------------------|---------------------------------|-------------------------|
| Cu-PdO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub> | 5% (Cu <sub>4</sub> Pd <sub>6</sub> O <sub>x</sub> )/Al <sub>2</sub> O <sub>3</sub> | 1990                            | 32.32.0                 |
| Pd-Ru/ Al <sub>2</sub> O <sub>3</sub>               | Pd (0.12%)Ru(0.12%)/Al <sub>2</sub> O <sub>3</sub>                                  | 1889                            | 29.329.3                |
| Rh/Al <sub>2</sub> O <sub>3</sub>                   | Rh (0.5%)/Al <sub>2</sub> O <sub>3</sub>                                            | 1883                            | 27.827.8                |
| Ru/Al <sub>2</sub> O <sub>3</sub>                   | Ru (0.5%)/Al <sub>2</sub> O <sub>3</sub>                                            | 1882                            | 44.244.2                |
| Cu-PdO <sub>x</sub> /GDC                            | 5% (Cu <sub>4</sub> Pd <sub>6</sub> O <sub>x</sub> )/GDC                            | 1655                            | 29.229.0                |

# Hydrogen From Natural Gas

- Hydrogen and hydrogen-rich fuels will play an important role in reducing emissions, increasing fuel efficiencies, and in minimizing environmental concerns associated with fossil fuels
- Hydrogen-rich fuels such as Synthesis gas is a valuable feedstock for producing transportation fuels (high quality FT Diesel), *Hydrogen*, fuel additives and chemicals
- Estimated cost reduction around 25% can be achieved by reducing steam/carbon and/or oxygen/carbon ratios

# Conversion of Natural Gas to Syngas

## 1. Steam Reforming



## 2. Partial Oxidation



## 3. Dry Reforming

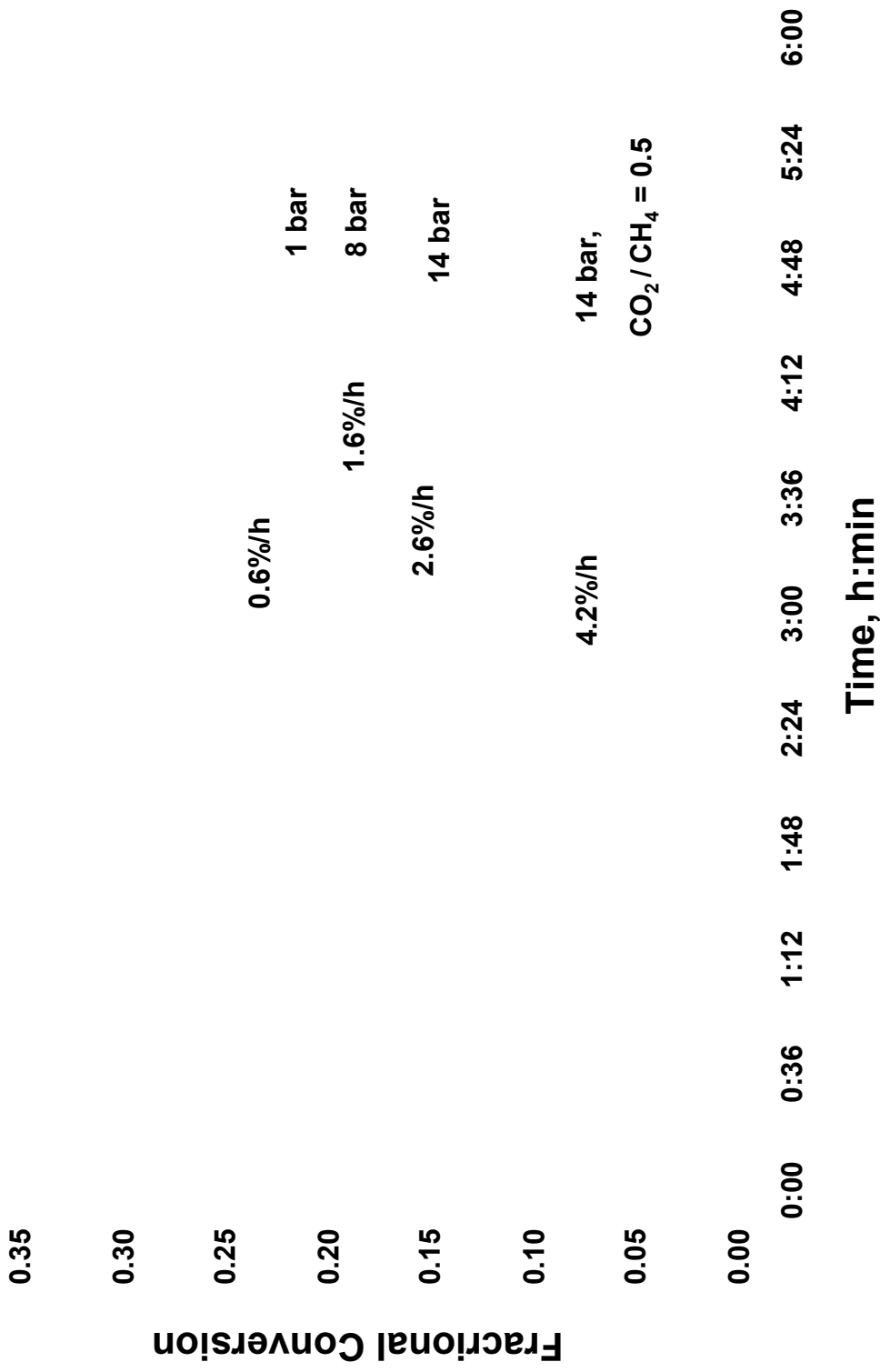


## Challenges:

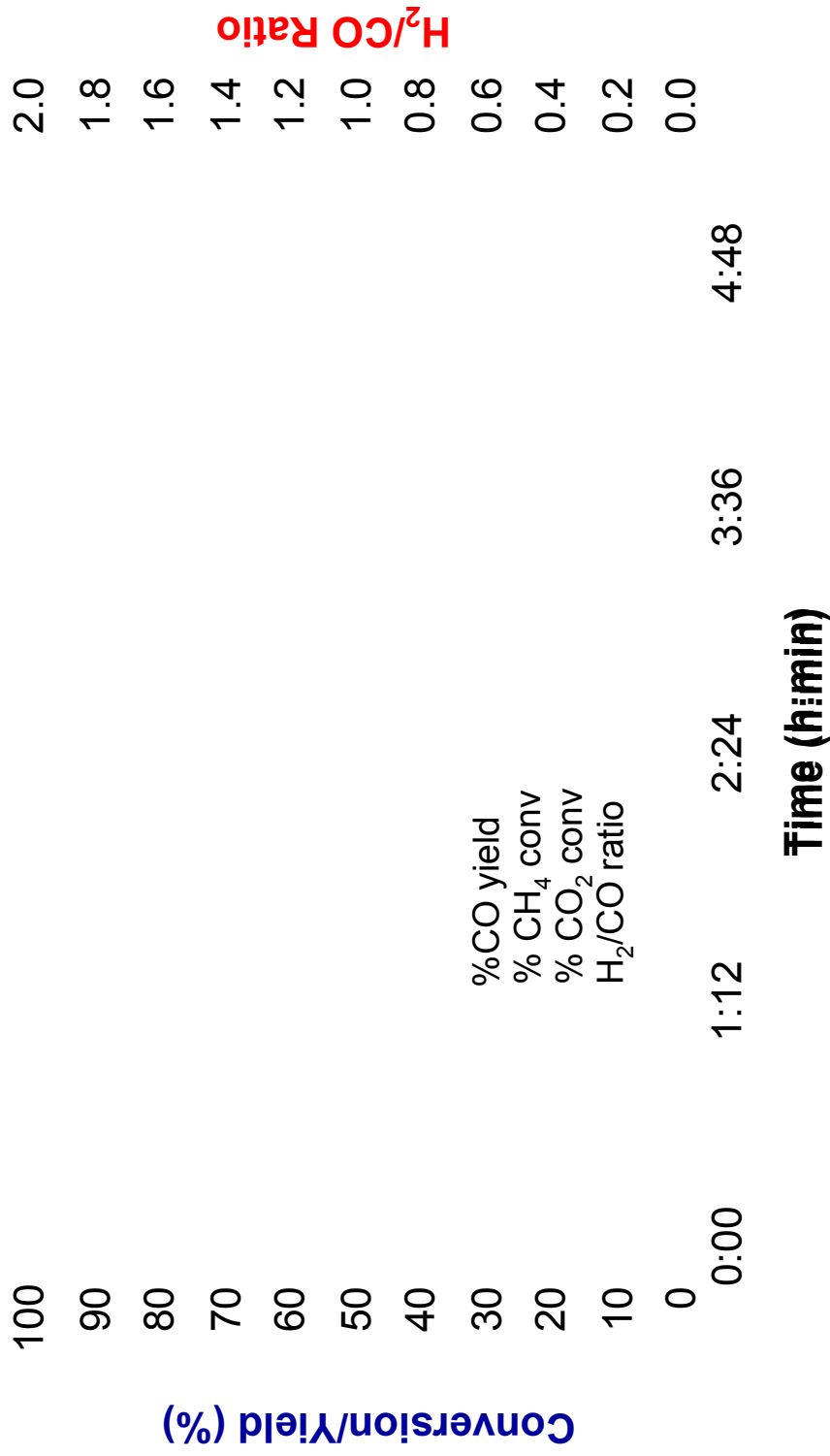
- Minimizing carbon formation on the catalyst
- Improve catalyst tolerance to impurities



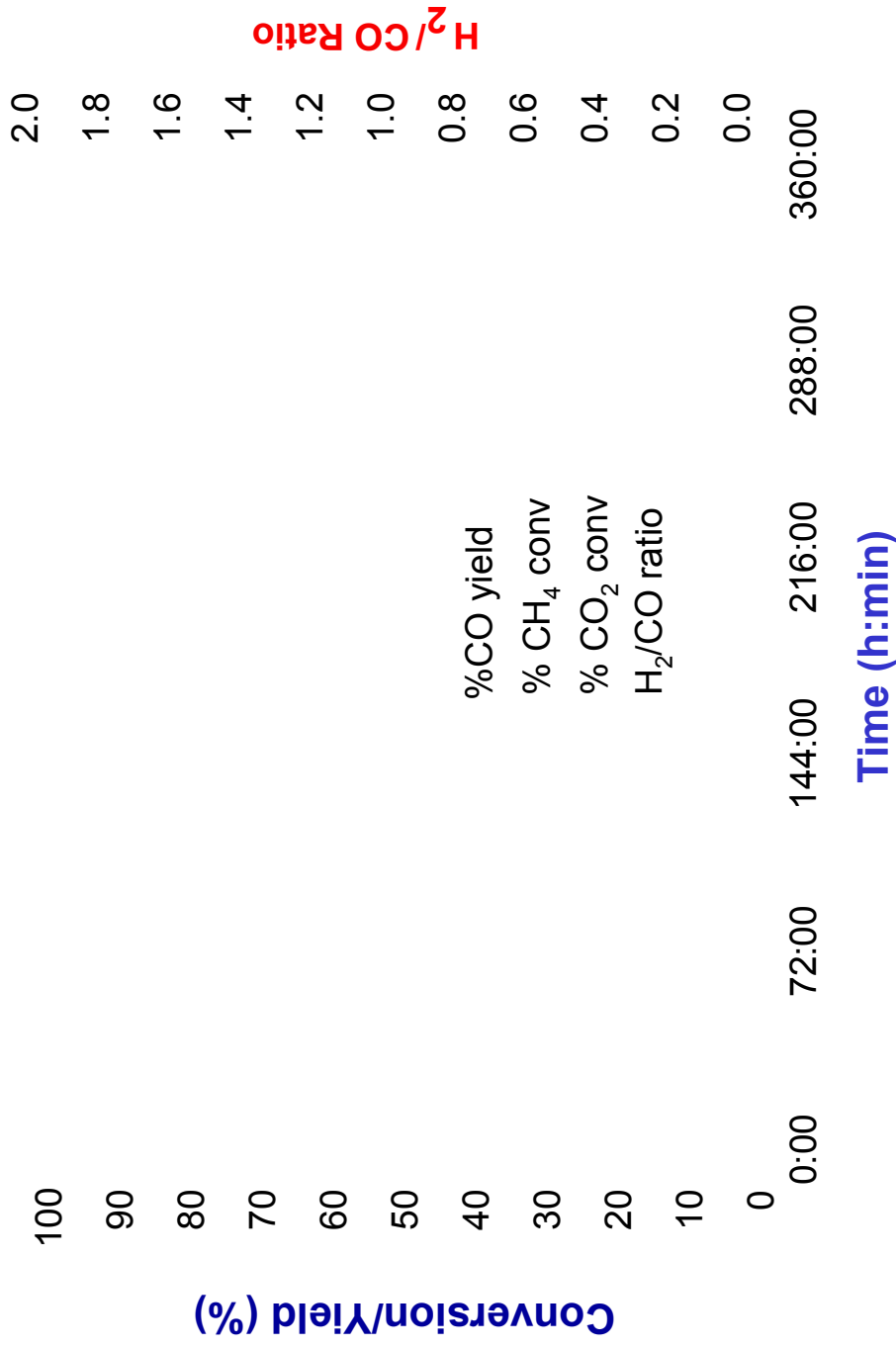
# Effect of Pressure on Methane Conversion Over Pt/ZrO<sub>2</sub> Catalyst, CO<sub>2</sub>/CH<sub>4</sub> = 1.14



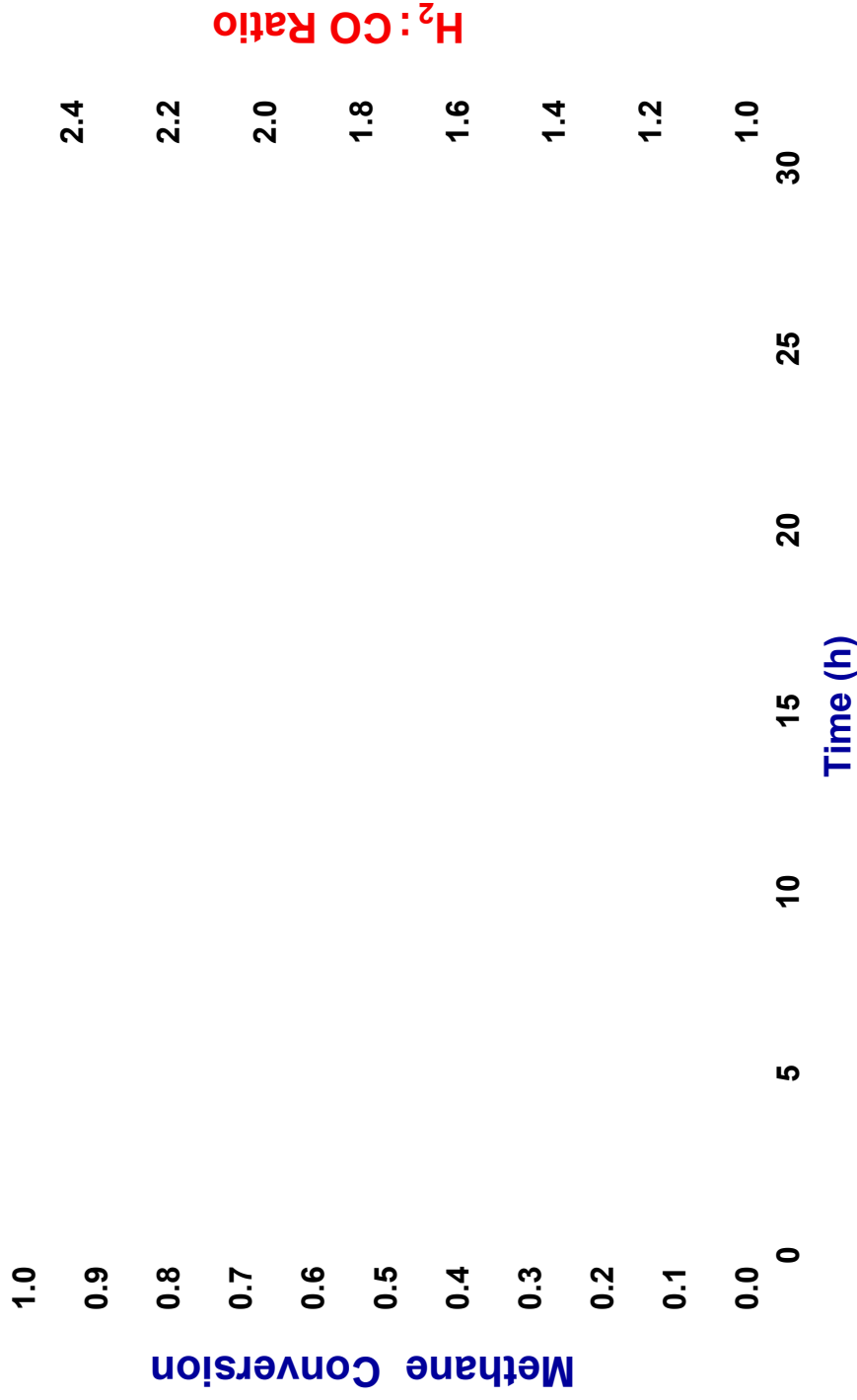
# Carbon Formed on Commercially Available Catalysts Plugged the Reactor in less than Five Hours During Reforming of Methane with CO<sub>2</sub> at 750°C



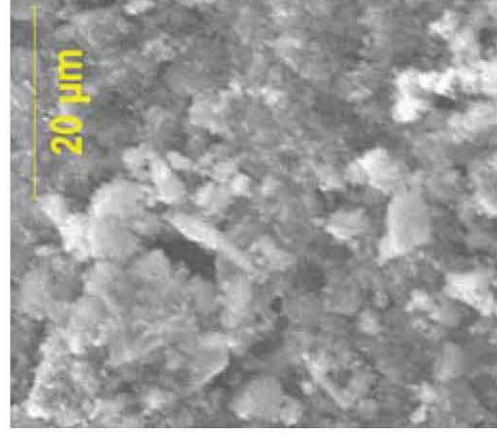
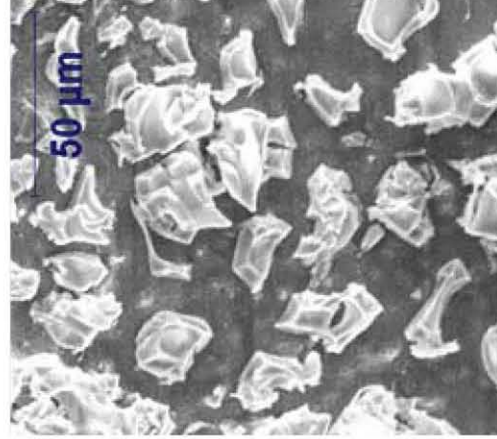
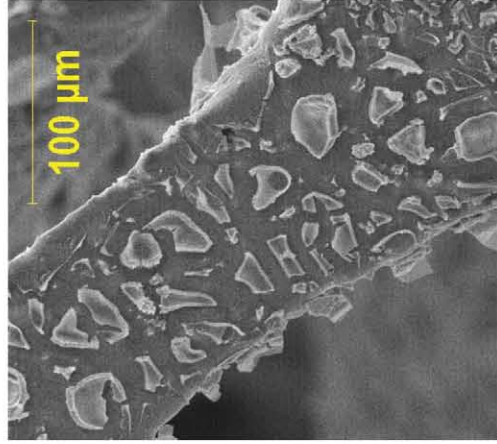
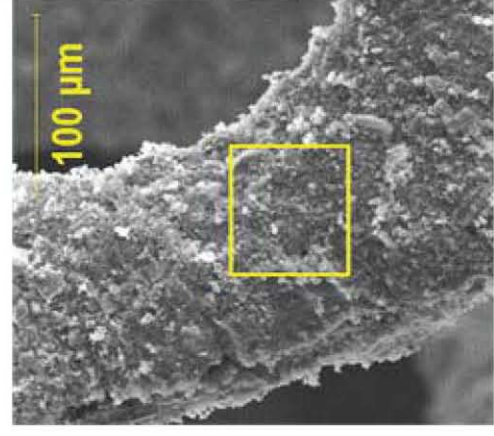
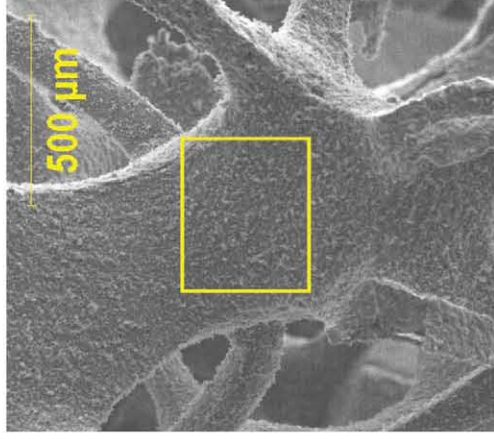
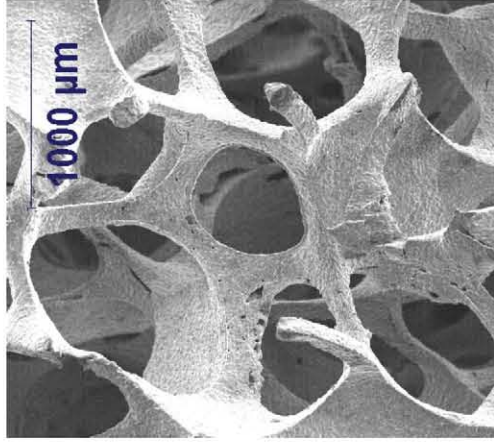
# K-Promoted Ni-Based Catalyst Developed at NETL for Dry Reforming of Natural Gas Into Syngas at 760 °C



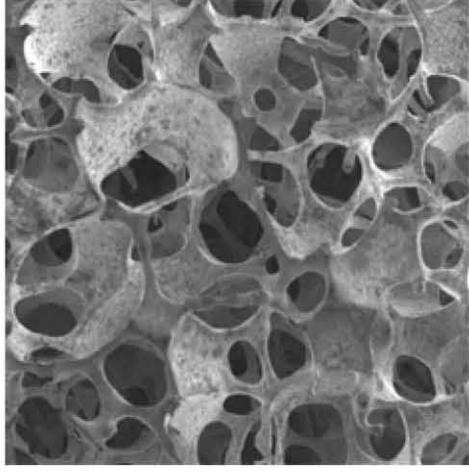
# Partial Oxidation of Methane Over Metal-Foam-Supported Ni-MgO (#11) at 800°C, GHSV = 3731 h<sup>-1</sup>, 29 Hours



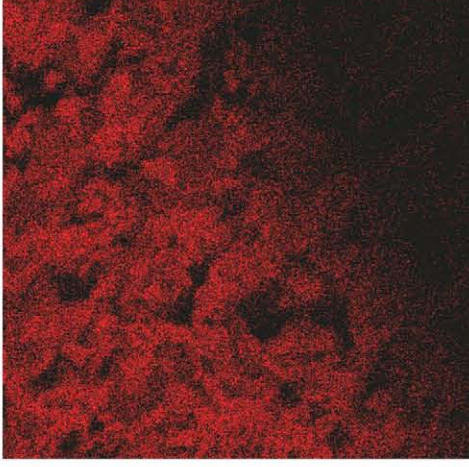
# Metal Foam Supported Reforming Catalyst Developed at NETL



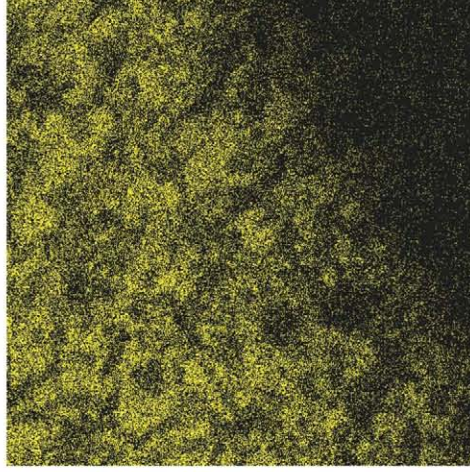
# Secondary Electron Image (X55) and Corresponding Elemental Distribution (after reaction)



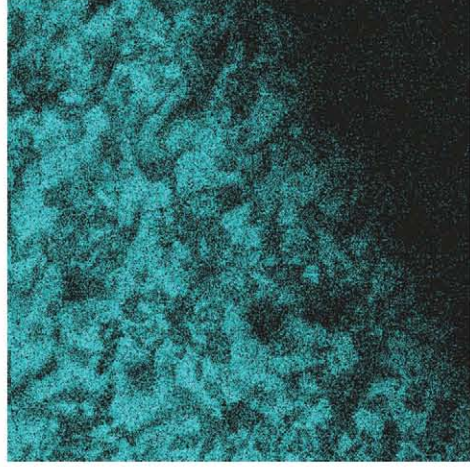
Al



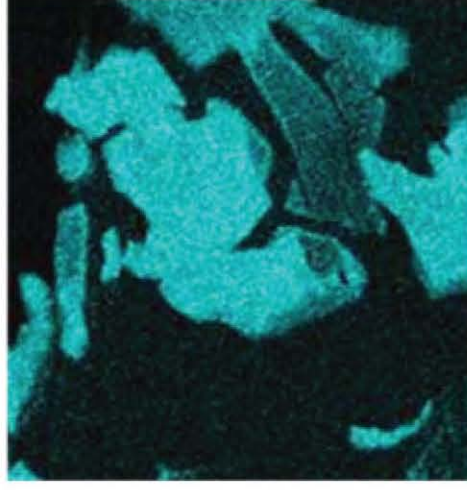
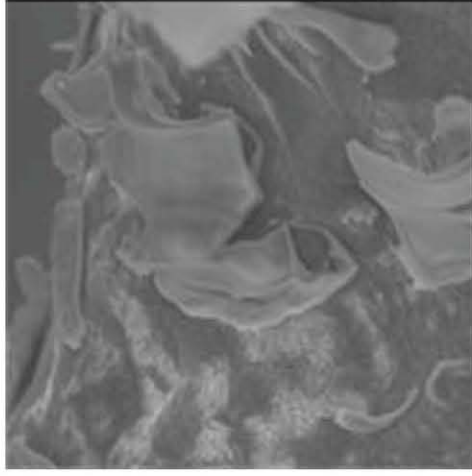
Cr



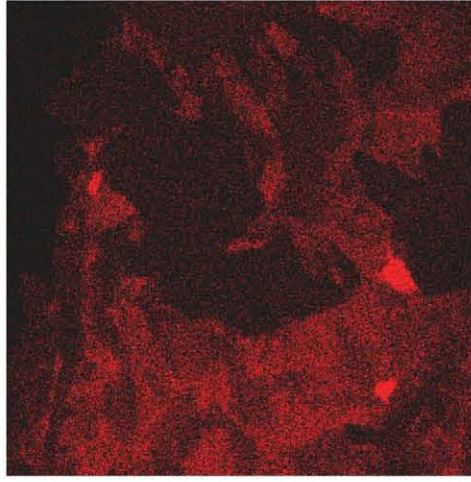
Fe



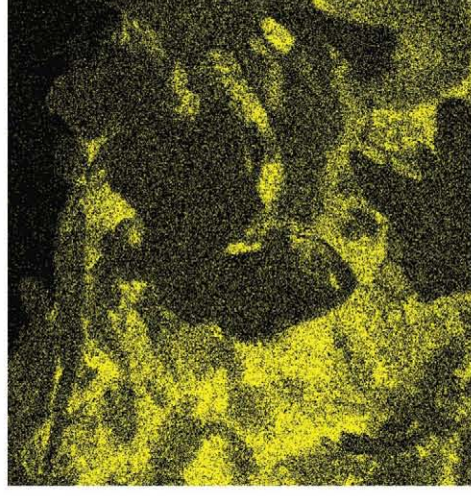
# Secondary Electron Image (X1200) and Corresponding Elemental Distribution (after reaction)



Ni

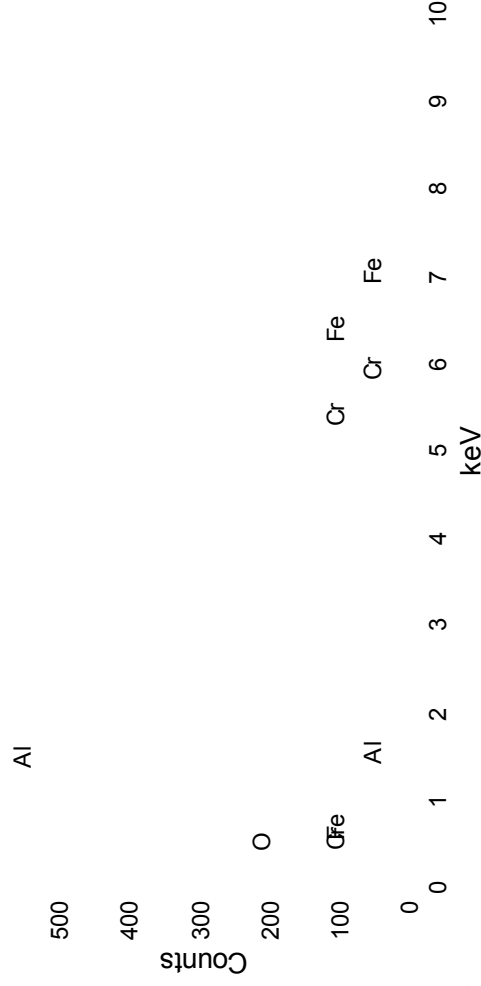
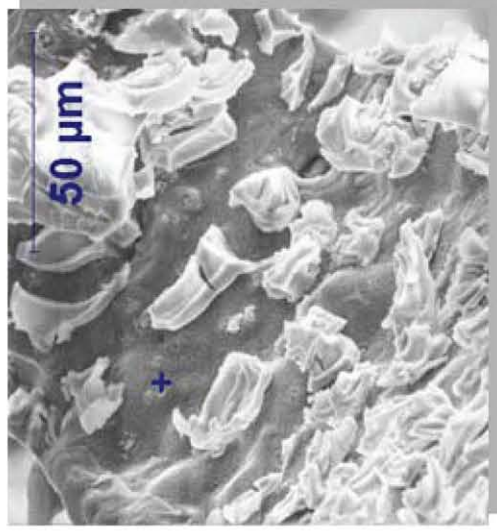
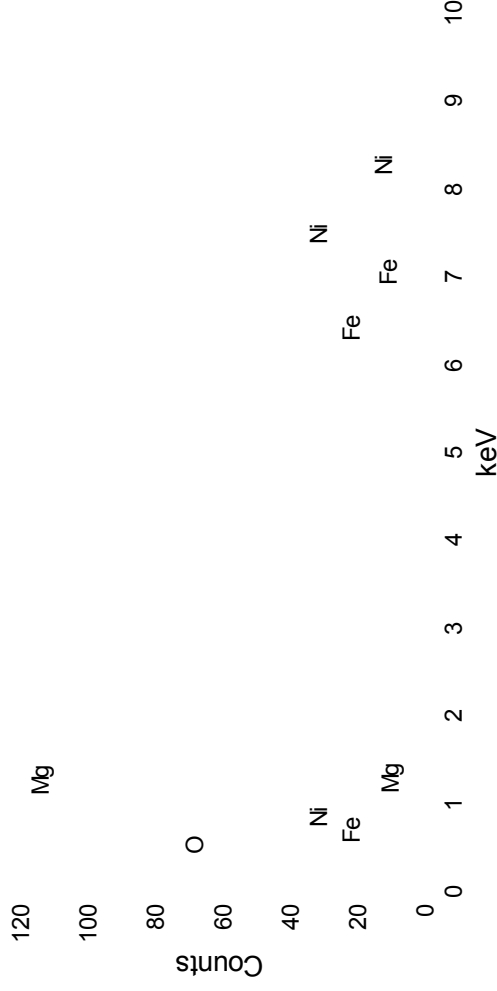
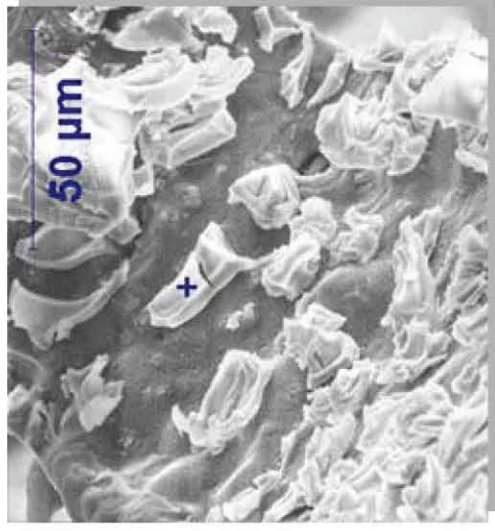


Cr



Fe

# SEM-EDX Analysis of Metal Foam Supported Reforming Catalyst Developed at NETL



# Summary

- We have successfully prepared Ni-MgO catalysts and supported on Fecralloy® metal foams
- The results show that the metal-foam supported catalysts reach near-equilibrium conversions of methane and H<sub>2</sub>/CO ratios of 2:1
- Rates of carbon deposition differ greatly among the catalysts, varying from 0.24 mg C/g cat h for the dipped foams to 7.0 mg C/g cat h for the powder-coated foams
- Rates of carbon deposition on metal-foam supported catalysts are much lower than for the calcined, unsupported powder (57 mg C/g cat h)
- The results suggest that exposed Fe and Cr on all of the foam samples may interact with the Ni-MgO catalyst to kinetically limit carbon formation

# Accomplishments

- Tested Molybdenum Tungsten Carbide catalyst for dry reforming of methane into Syngas
- Tested Commercially Available Catalyst for dry reforming methane into Syngas. Significant amount of carbon formed in the catalyst bed
- Studied effect of pressure on catalyst activity, selectivity, and carbon formation
- Developed new catalyst for reforming of natural gas into synthesis gas with forming little or no carbon on the catalyst
- Studied carbon decomposition route
- Completed high-pressure tests on reforming catalysts Pt / ZrO<sub>2</sub> and Pt / CeZrO<sub>x</sub>
- Investigated carbon deposition on noble-metal catalysts
- Developed a series of Ni-based Metal-foam catalysts for reforming of natural gas to hydrogen and synthesis gas