NETL-TPR-2123 DOE/NETL-IR-2008-125

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

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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_2 conversions, as well as a H_2/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_2/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 studies 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 NiMg2Ox-1100ºC (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_2S. 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_2S 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.

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Hydrogen From Coal/Biomass

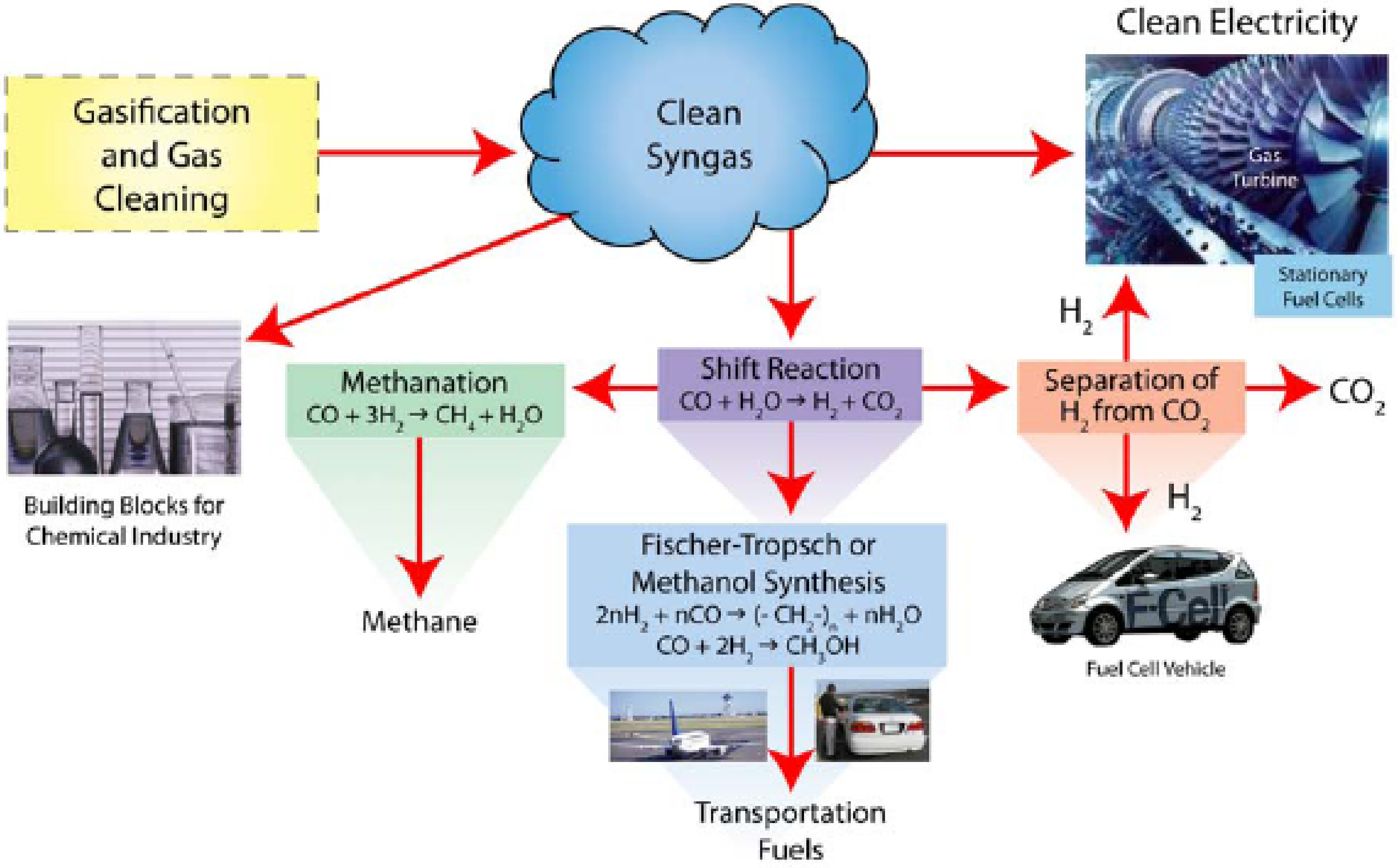
***Project Title*:**

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

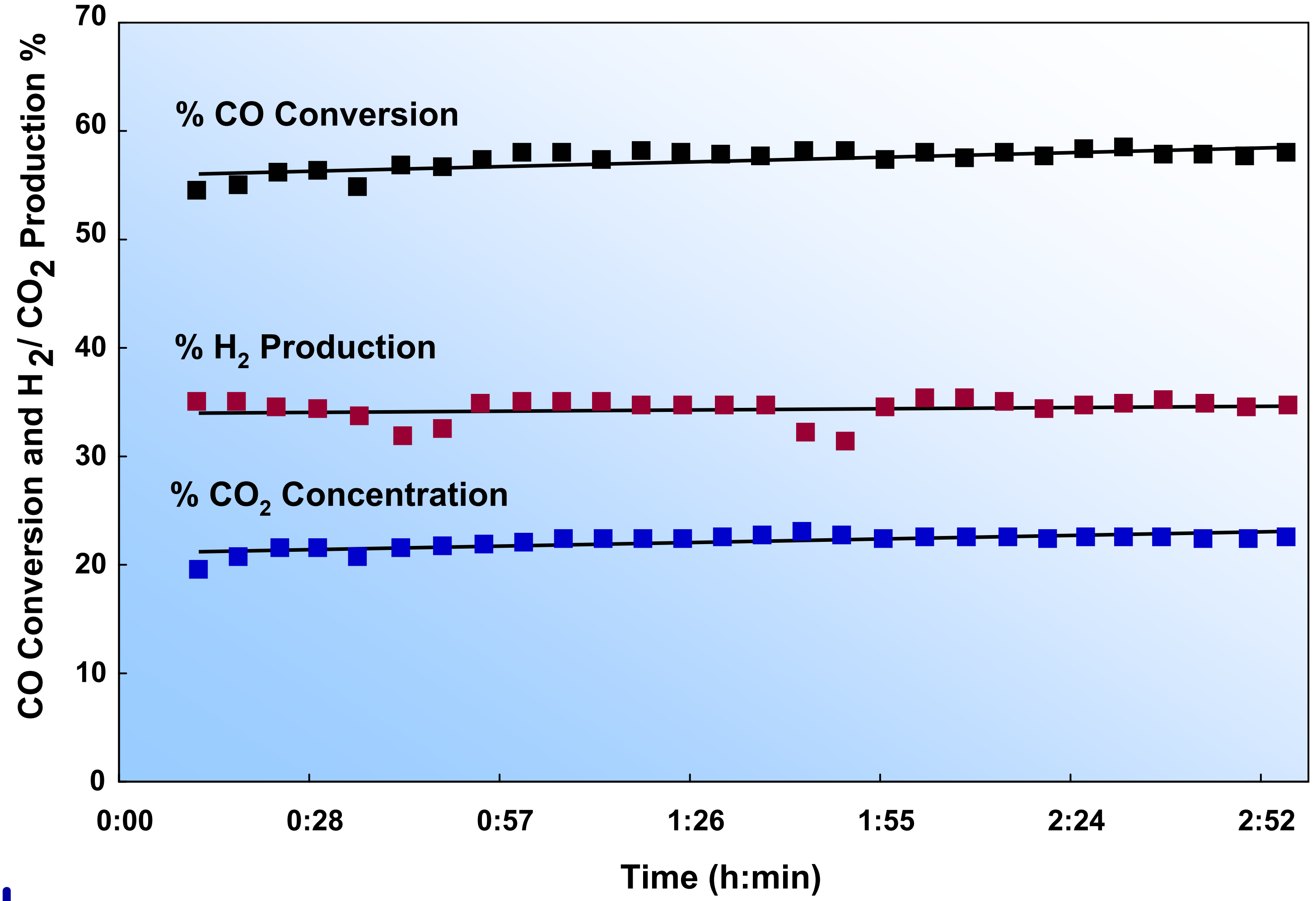
Current Technologies

- **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

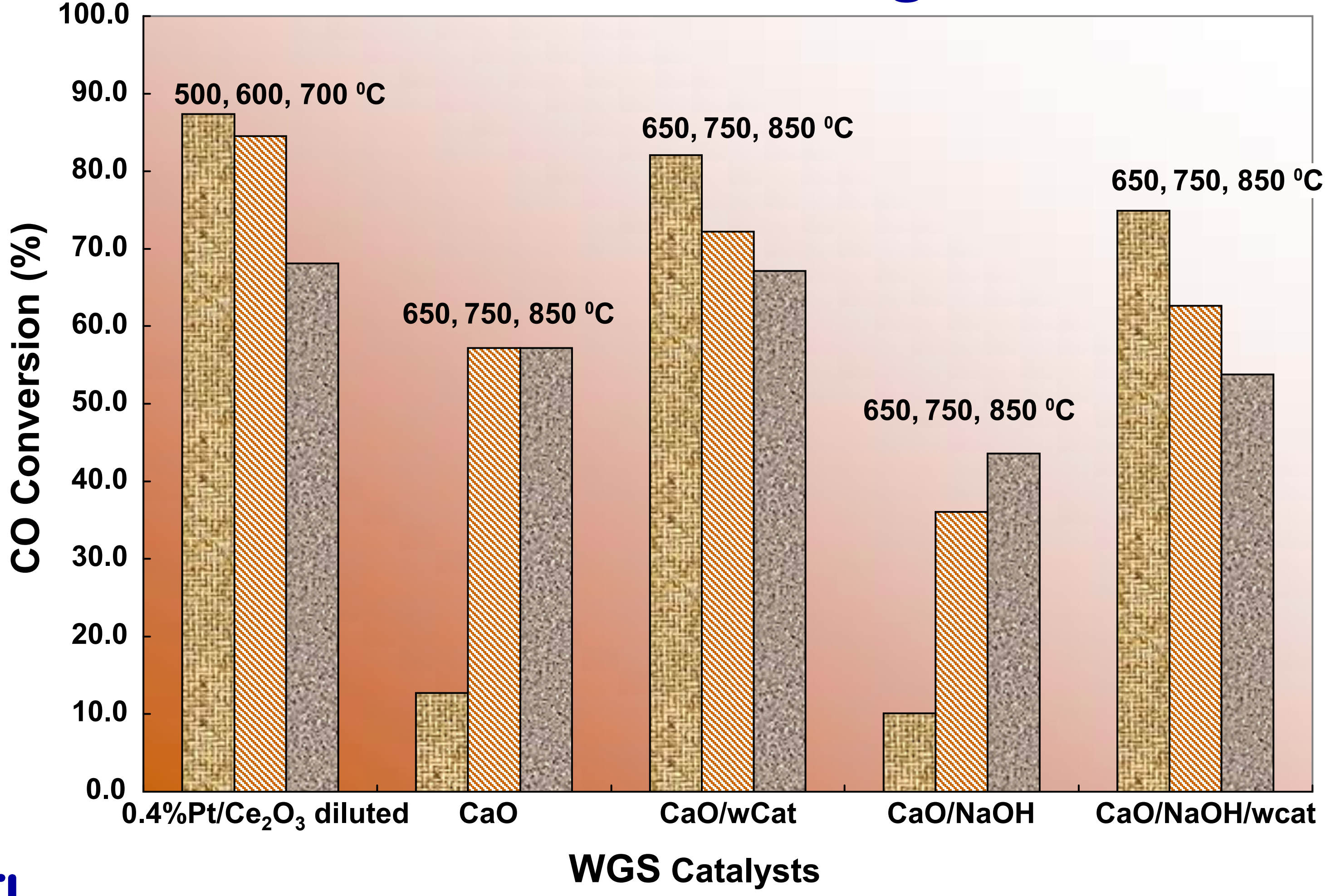
Benefits of Removing CO_2 during WGS Reaction

- Increases CO conversion
- Increases hydrogen selectivity
- Produces high pressure hydrogen
- Facilitates CO_2 sequestration
- Reduces the cost for CO_2 separation
- Reduces required H_2O/CO ratio
- Increases the range of operating conditions for achieving equilibrium conversion of CO

Water Gas Shift Reaction Conducted at NETL Over CaO ate 850^{o}C, 150 Psig, GHSV = 10051 cm^{3}g^{-1}h^{-1}



CO Conversion Over CaO and CaO/NaOH With and Without WGS Catalyst (0.4%Pt/Ce_2O_3) at 150 psig, GHSV= 10051 $cm^3g^{-1}h^{-1}$



Hydrogen From Hydrogen Sulfide

Goal

- **To Conduct Basic and Applied Catalysis Research for Production of Hydrogen from Natural Gas and H_2S-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_2S?

- 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_2S is associated with drilling and production of natural gas and crude oil, under pressure H_2S remains in oil and as the pressure released the gas bubbles out of oil with other gases such as methane, ethane, propane, butane, CO_2 and water vapor
- More than 12 million tons of H_2S/year produced from refining fossil fuels in the US
- A well known technology that utilizes H_2S is Claus process (producing sulfur and low-valued steam) which doesn’t produce any hydrogen

Conversion of Hydrogen Sulfide to Hydrogen

Thermodynamics of H_2S Dissociation

$$H_2S\ (g) \rightleftarrows H_2\ (g) + \tfrac{1}{8}S_8\ (c)$$

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

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

- **The free energy ΔG_f° 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**

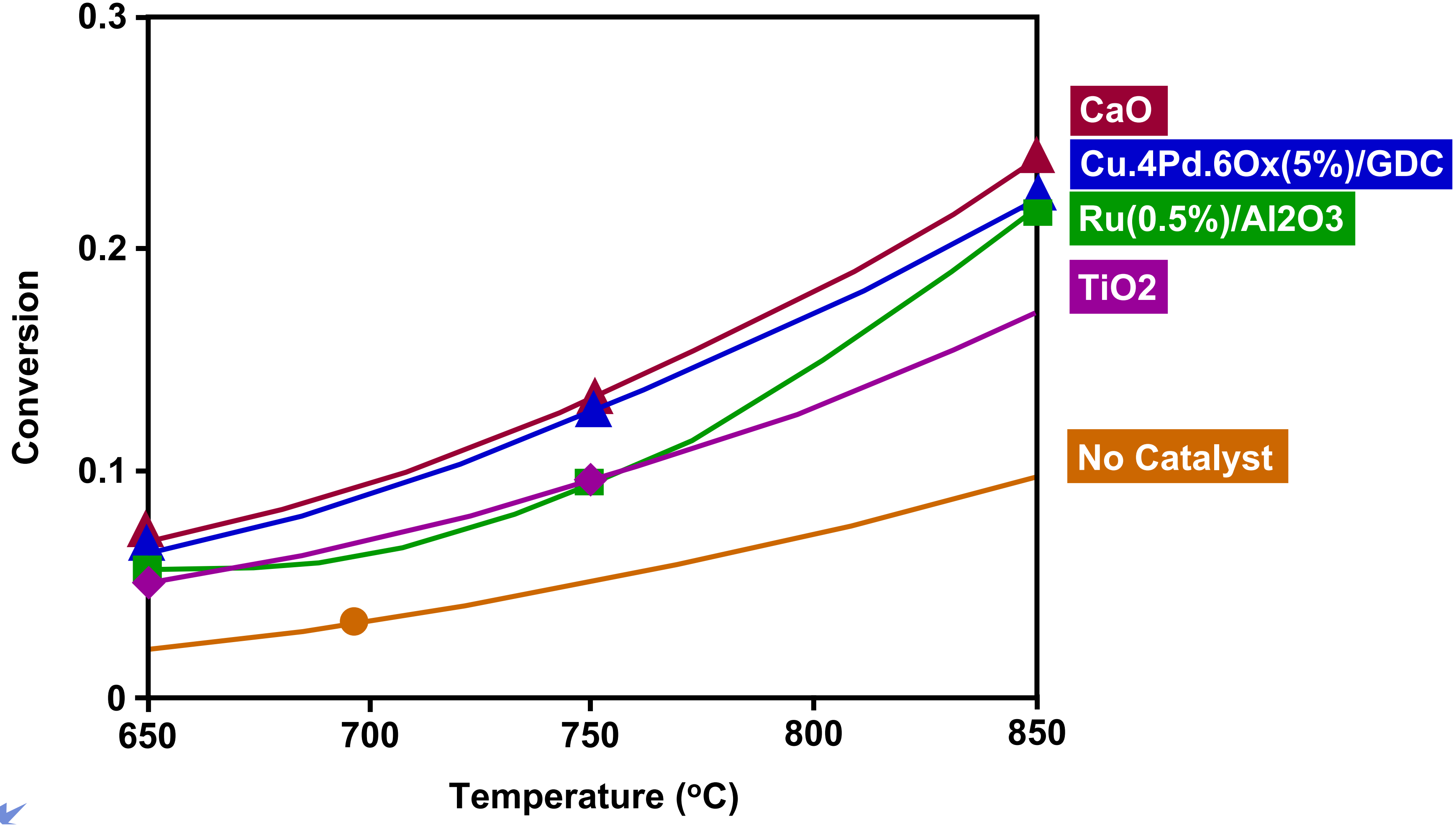
Thermal Decomposition of H_2S

$$H_2S \rightleftarrows H_2 + \tfrac{1}{2}S_2$$

- Calculated equilibrium conversion at 1 atm of pure H_2S at different temperatures
- This process appears to be simple. But yields are very low even at high temperatures due equilibrium limitation

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

Conversion of H_2S to H_2 and Sulfur



H_2S Conversion and Estimated Activation Energy Over Supported Metal Catalysts at 850 °C

Catalysts	Composition	H_2S Conversion (%)	Ea (kJ/mol)
Cu-PdO_x/Al_2O_3	5% $(Cu_{.4}Pd_{.6}O_x)/Al_2O_3$	19.0	32.0
Pd-Ru/ Al_2O_3	Pd (0.12%)Ru(0.12%)/A	18.9	29.3
Rh/Al_2O_3	Rh (0.5%)/Al_2O_3	18.3	27.8
Ru/Al_2O_3	Ru (0.5%)/Al_2O_3	18.2	44.2
Cu-PdO_x/GDC	5% $(Cu_{.4}Pd_{.6}O_x)$/GDC	16.5	29.0

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

$CH_4 + H_2O = CO + 3 H_2$ $\Delta H_{298} = 206\ \mathrm{kJ\ mol^{-1}}$

2. Partial Oxidation

$CH_4 + \frac{1}{2} O_2 = CO + 2 H_2$ $\Delta H_{298} = -38\ \mathrm{kJ\ mol^{-1}}$

3. Dry Reforming

$CH_4 + CO_2 = 2 CO + 2 H_2$ $\Delta H_{298} = 247\ \mathrm{kJ\ mol^{-1}}$

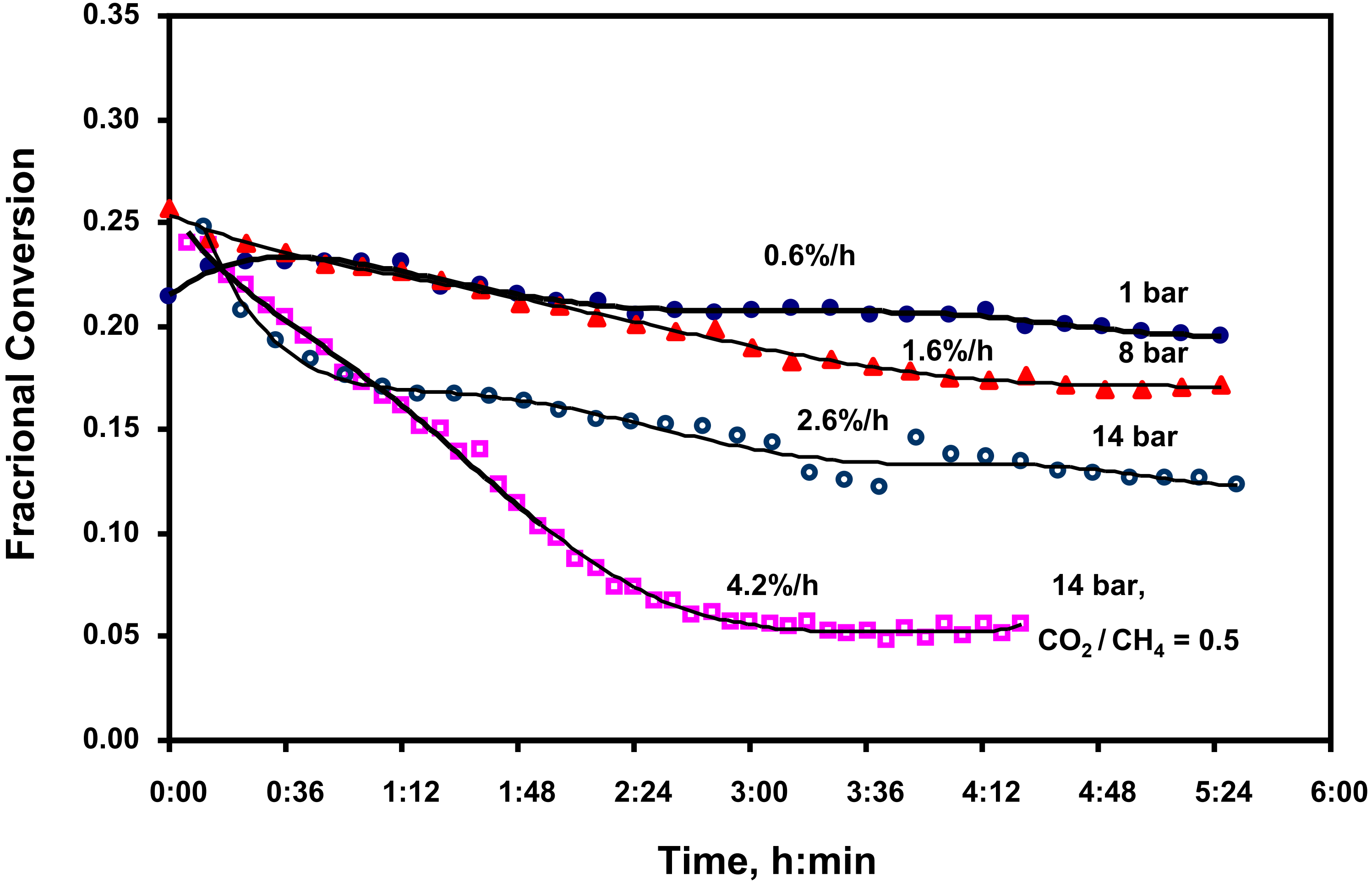
Challenges:

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

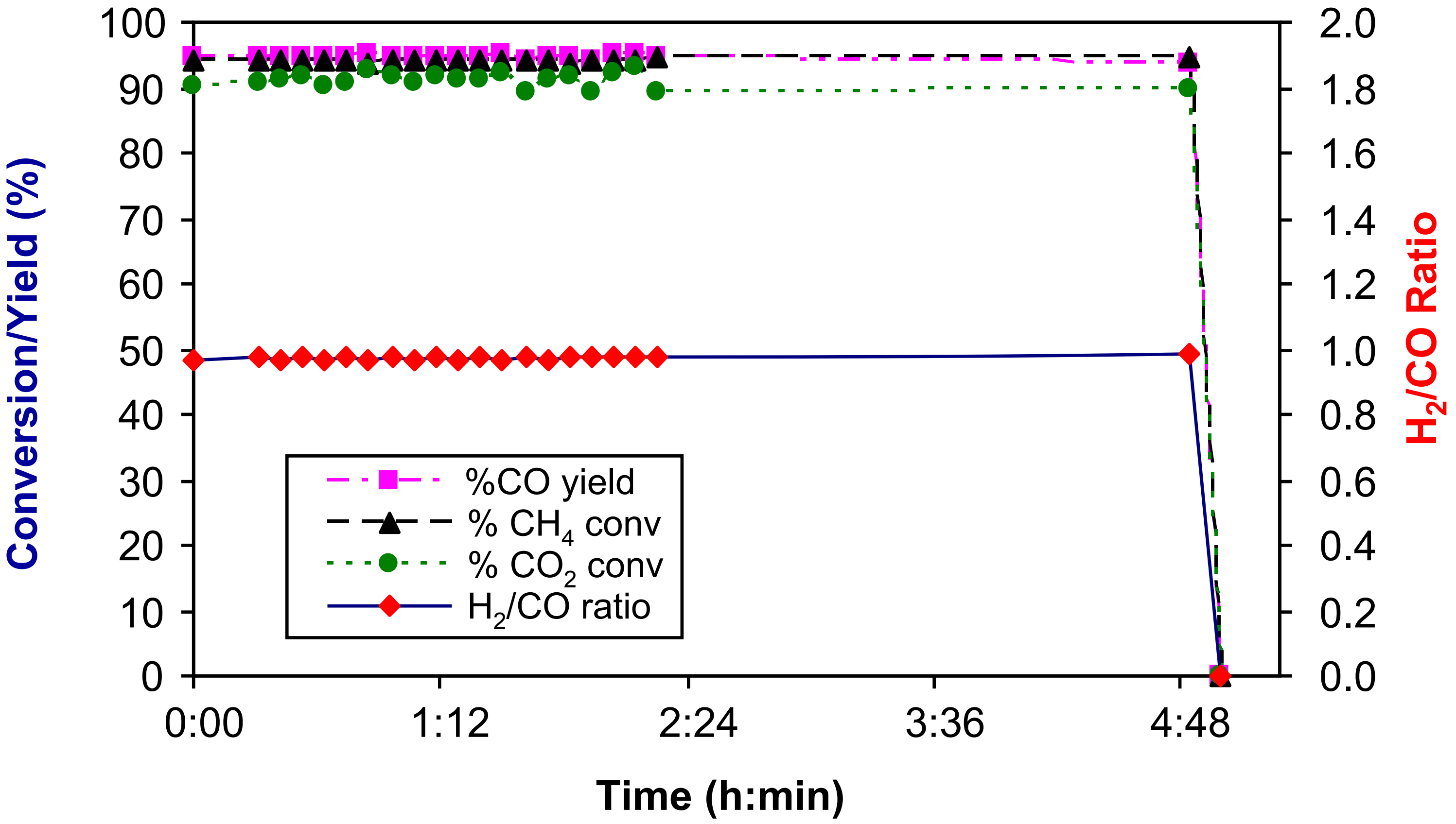
$\mathrm{CH_4 = 2H_2 + C}$ $\Delta H_{298} = 75\ \mathrm{kJ\ mol^{-1}}$

$\mathrm{2\ CO = CO_2 + C}$ $\Delta H_{298} = -173\ \mathrm{kJ\ mol^{-1}}$

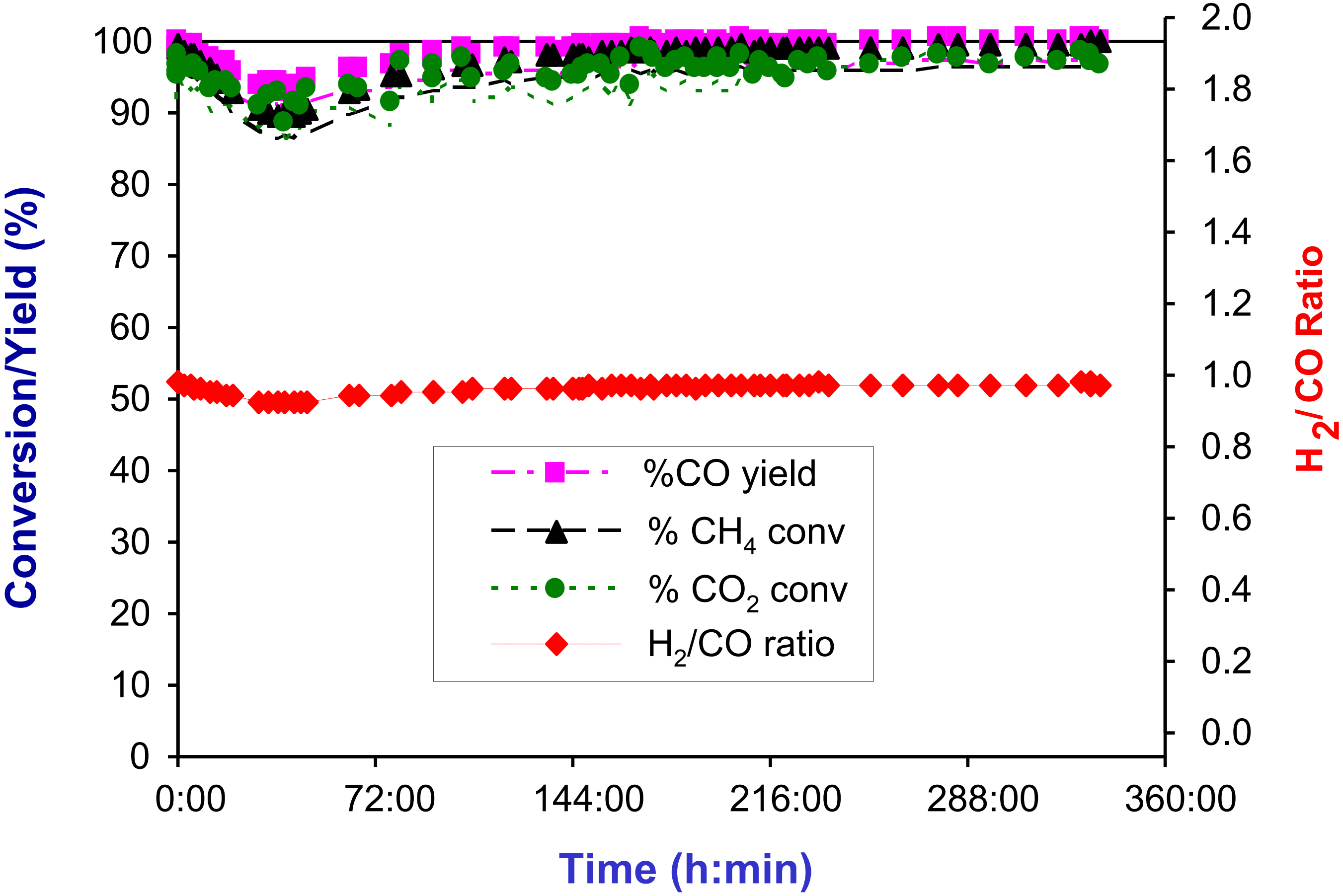
Effect of Pressure on Methane Conversion Over Pt/ZrO_2 Catalyst, CO_2/CH_4 = 1.14



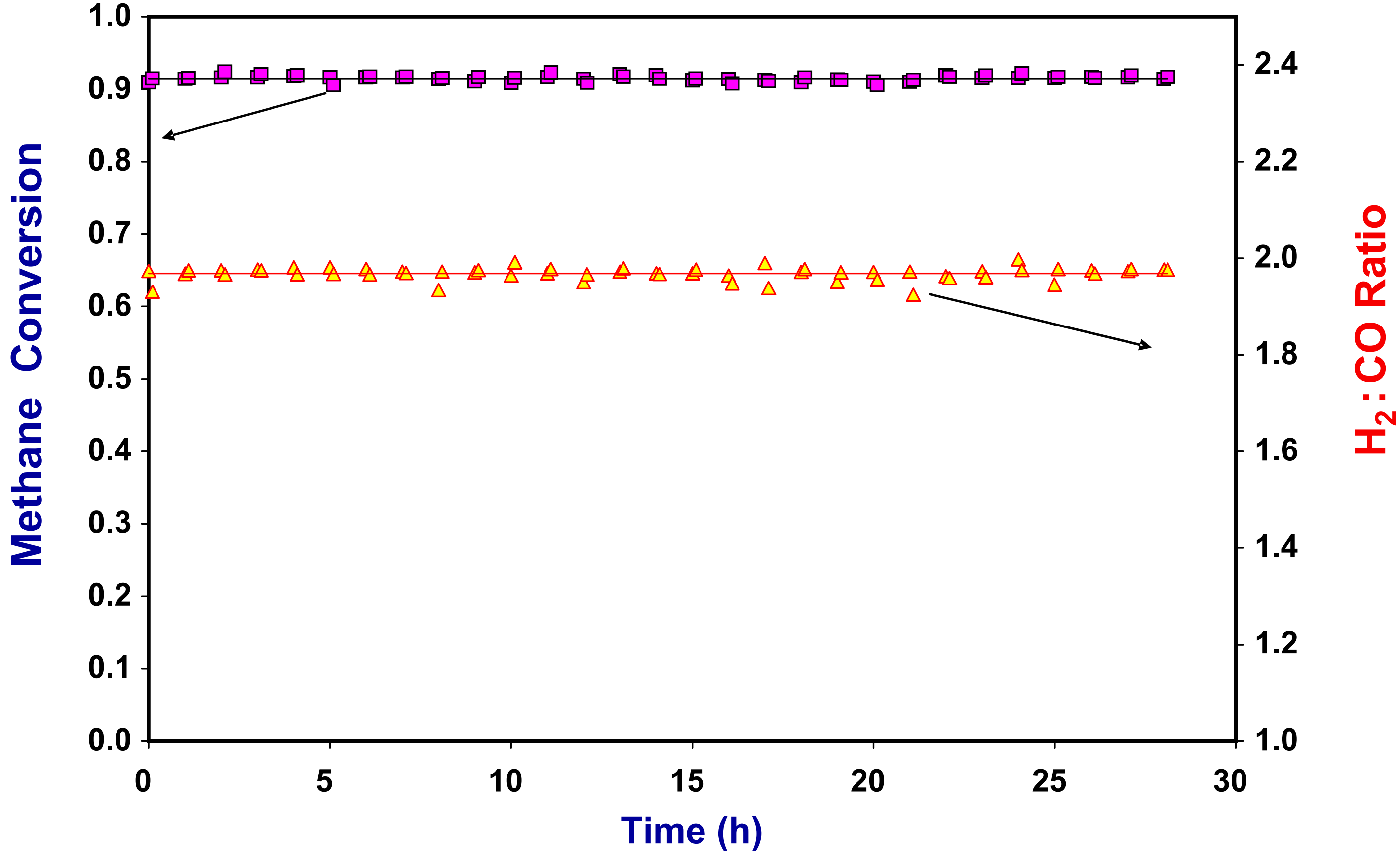
Carbon Formed on Commercially Available Catalysts Plugged the Reactor in less than Five Hours During Reforming of Methane with CO_2 at 750°C



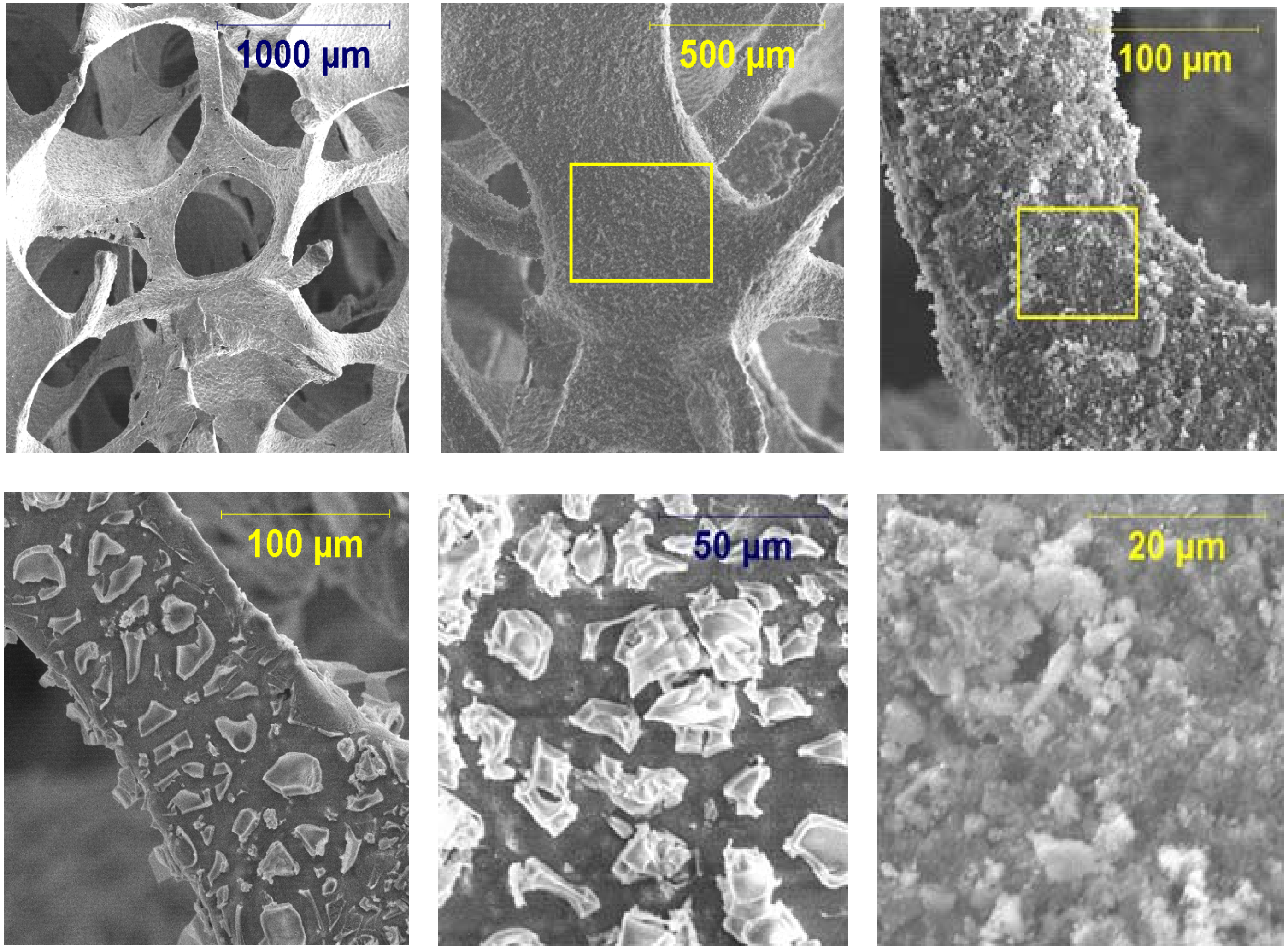
K-Promoted Ni-Based Catalyst Developed at NETL for Dry Reforming of Natural Gas Into Syngas at 760 º



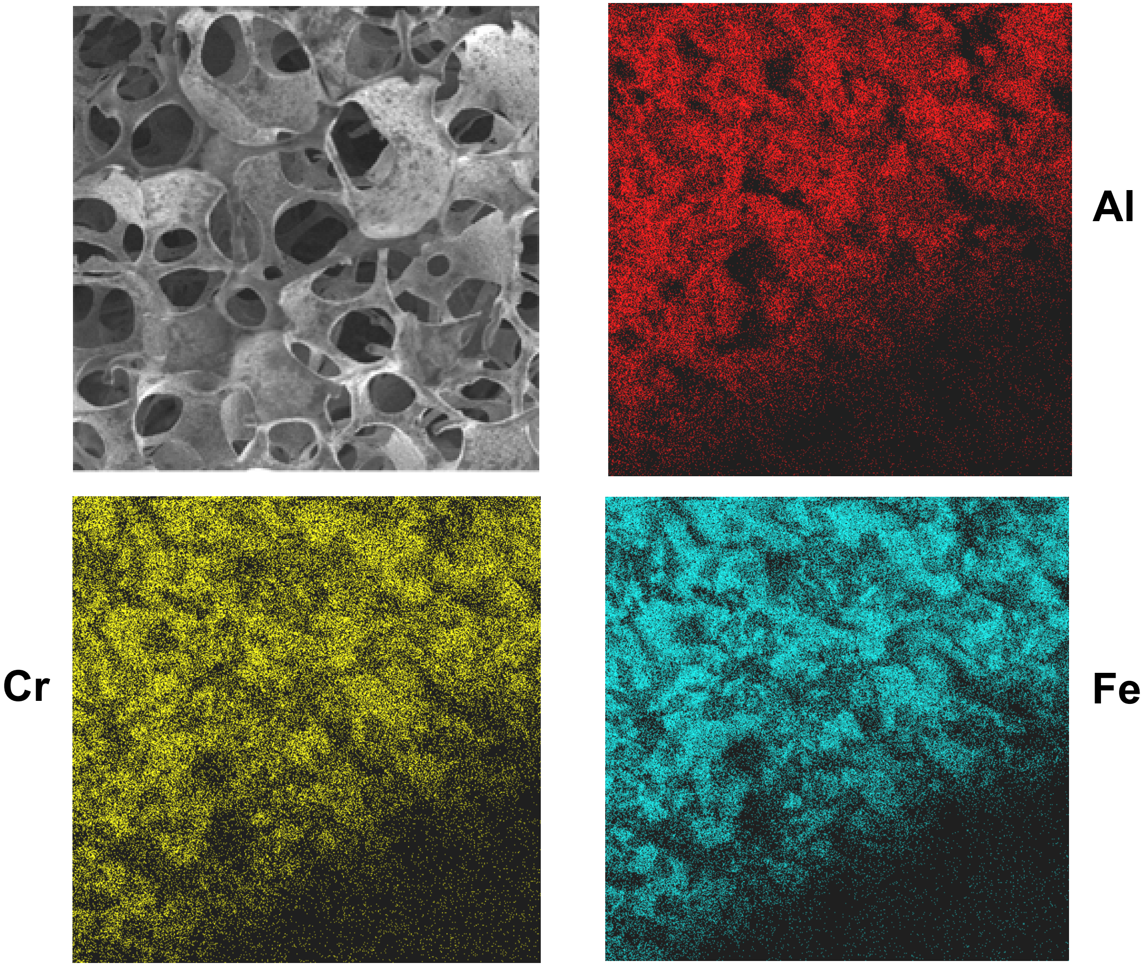
Partial Oxidation of Methane Over Metal-Foam-Supported Ni-MgO (#11) at 800°C, GHSV = 3731 h^{-1}, 29 Hours



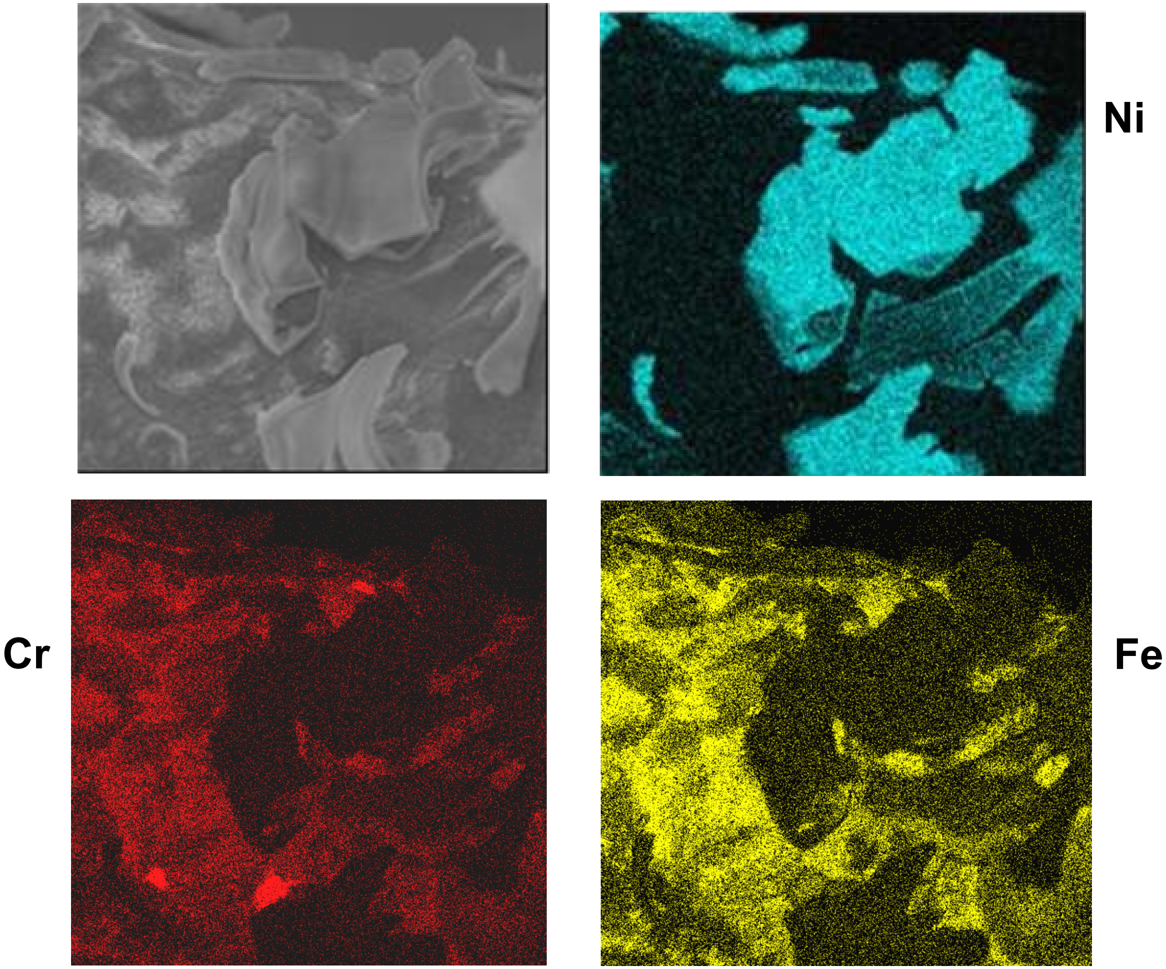
Metal Foam Supported Reforming Catalyst Developed at NETL



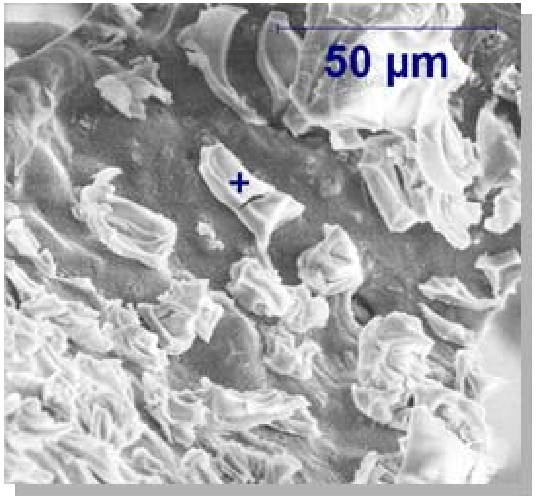
Secondary Electron Image (X55) and Corresponding Elemental Distribution (after reaction)

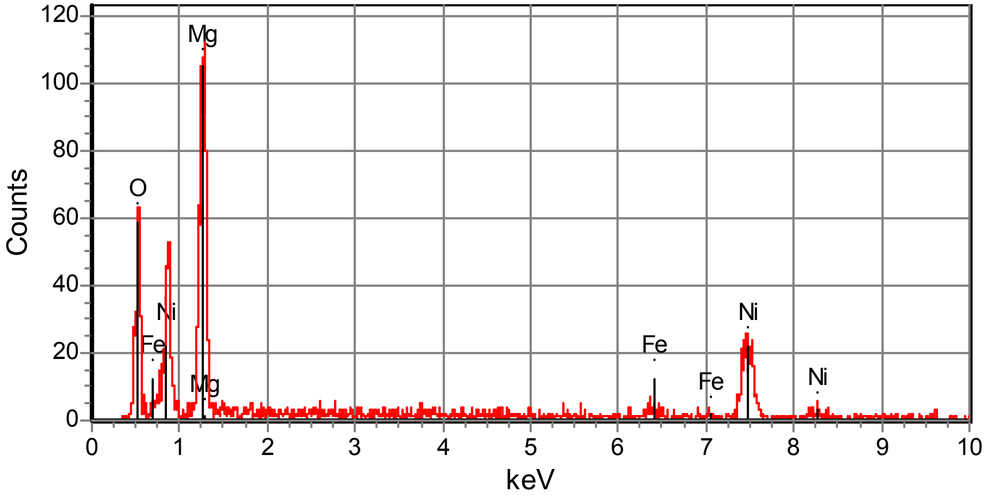


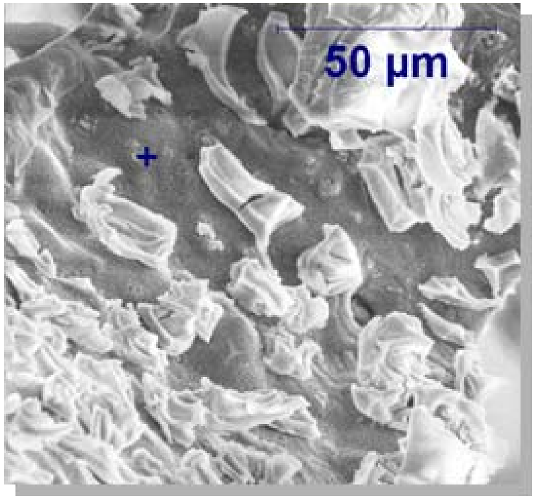
Secondary Electron Image (X1200) and Corresponding Elemental Distribution (after reaction)

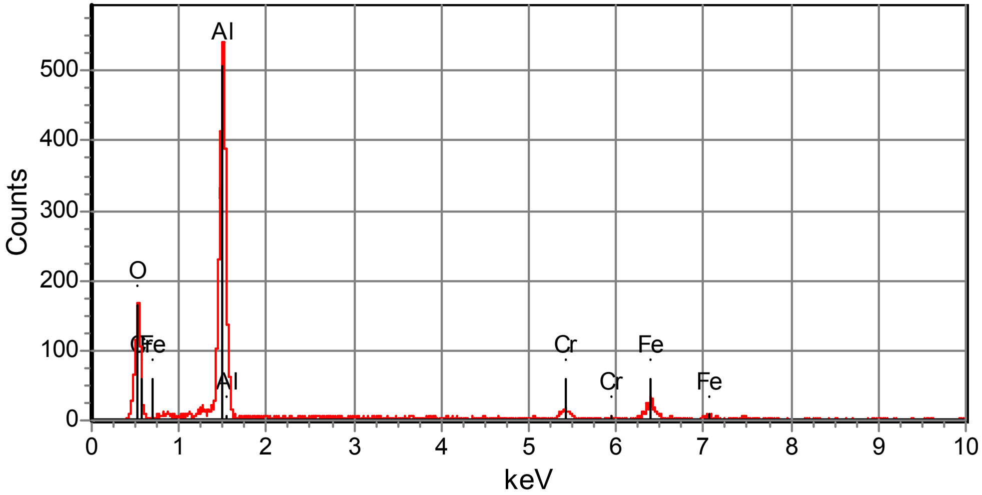


SEM-EDX Analysis of Metal Foam Supported Reforming Catalyst Developed at NETL









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_2/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_2 and Pt / $CeZrO_x$
- 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