Coal to Desired Fuels and Chemicals

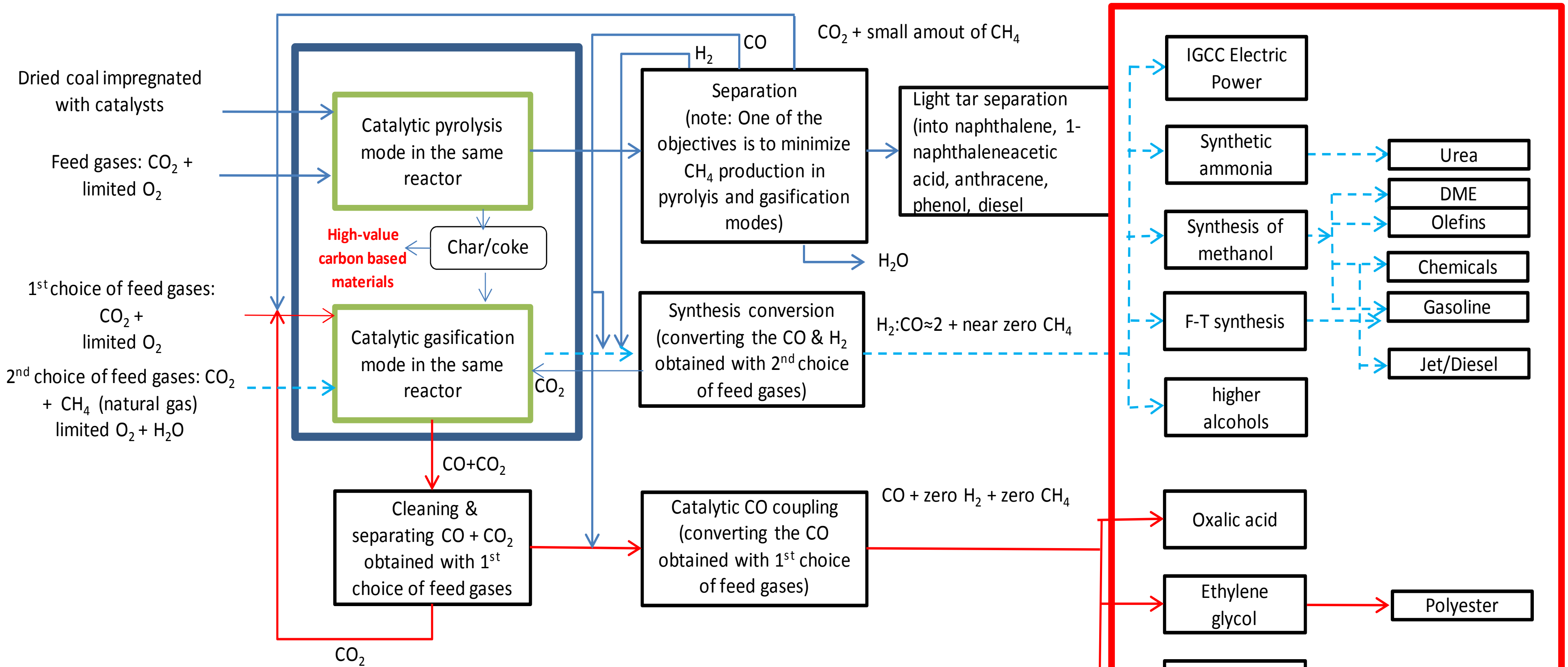
Maohong Fan

SER Professor in the Department of Chem. & Petroleum Eng.
UNIVERSITY OF WYOMING
mfan@uwyo.edu
Phone: (307) 766 5633


I'm dirty
I'm sticky
I'm smelly
Coal
Oil
Natural Gas
This stuff stinks like rotten eggs!
Without me, life isn't easy!
I'm picky
I'm rusty
I'm sneaky
Trona
Iron ore
Ce
58
140.12
Rare earth

Maohong Fan's Research Group

UW's Clean Coal Technology Development Map



Three Sample Projects to Be Presented

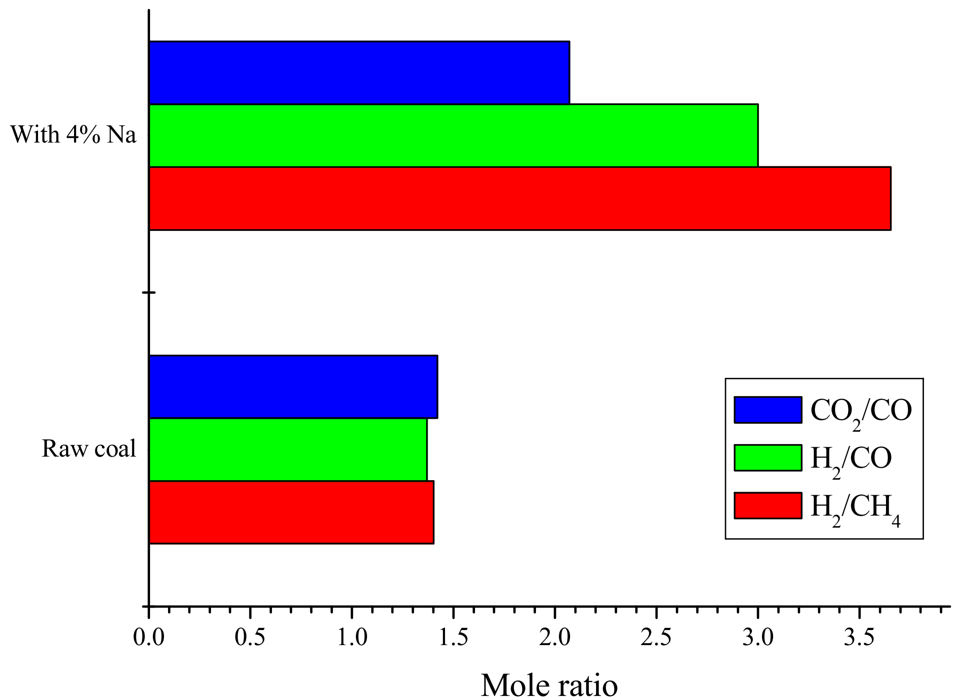
- Catalytic Coal Pyrolysis and Gasification
  - Na-Fe based
- Syngas to liquids
  - Ethylene glycol
- Environmental management
  - CO_2

Sample Project 1- Catalytic Coal Gasification

- Why catalyst?
  - Increase gasification or carbon conversion rate/kinetics
  - Decrease gasification temperature
    - Improve energy efficiency
    - Increase life span of gasifier
  - Change the composition of syngas
    - Obtain desired $CO:H_2$ ratio
    - Decrease CH_4 concentration in syngas

Catalytic Coal Pyrolysis and Gasification Setup

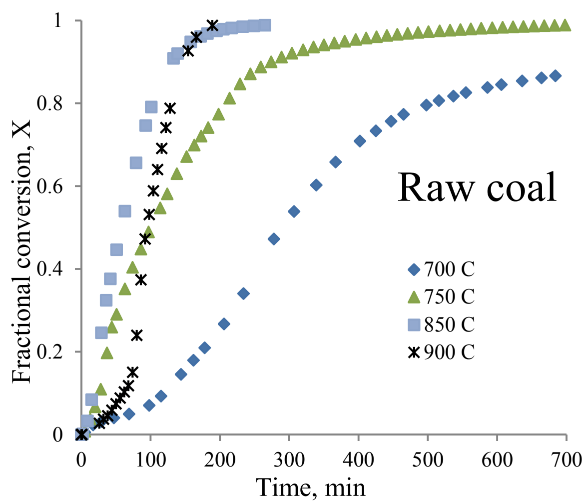
Effect of Na Catalyst on PRB Coal Pyrolysis

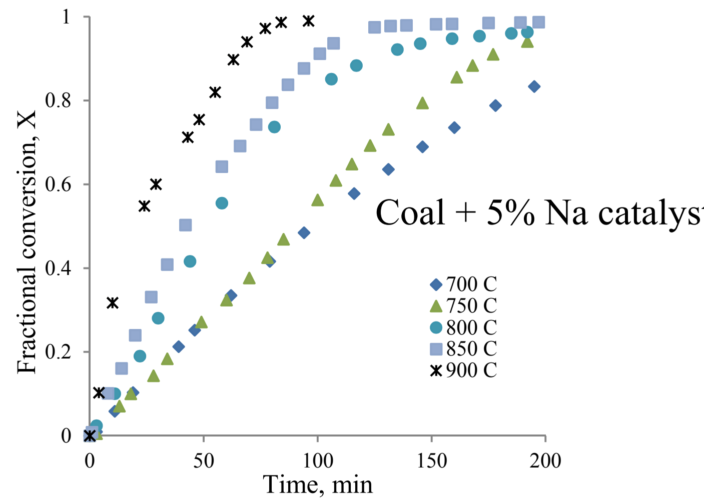


- Mole ratios of different gas products from catalytic coal pyrolysis at 600 ^oC [coal heating rate: 10 ^oC /min; pyrolysis time at 600 ^oC: 30min; flow rate of N_2 :15 ml/min]

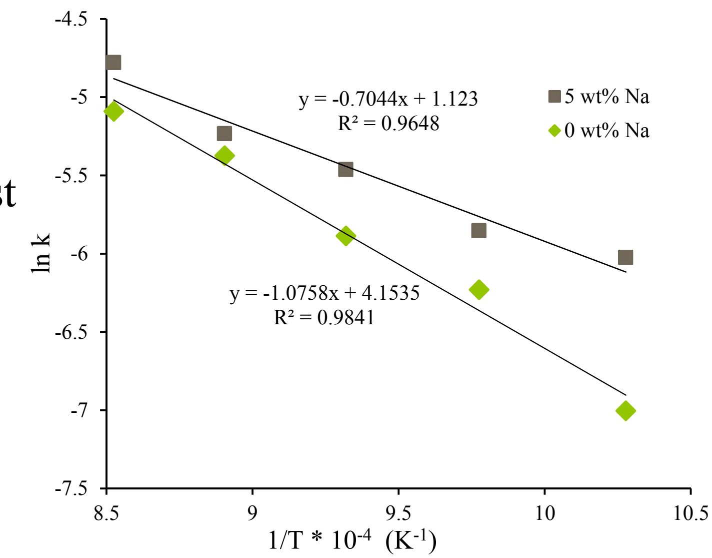
- Addition of Na_2CO_3 (as a catalyst) can increase
  - H_2/CH_4 ratio by ~170%
  - H_2/CO ratio by ~115%

Effect of Na Catalyst on PRB Coal Conversion (X) and Gasification Kinetics (k)

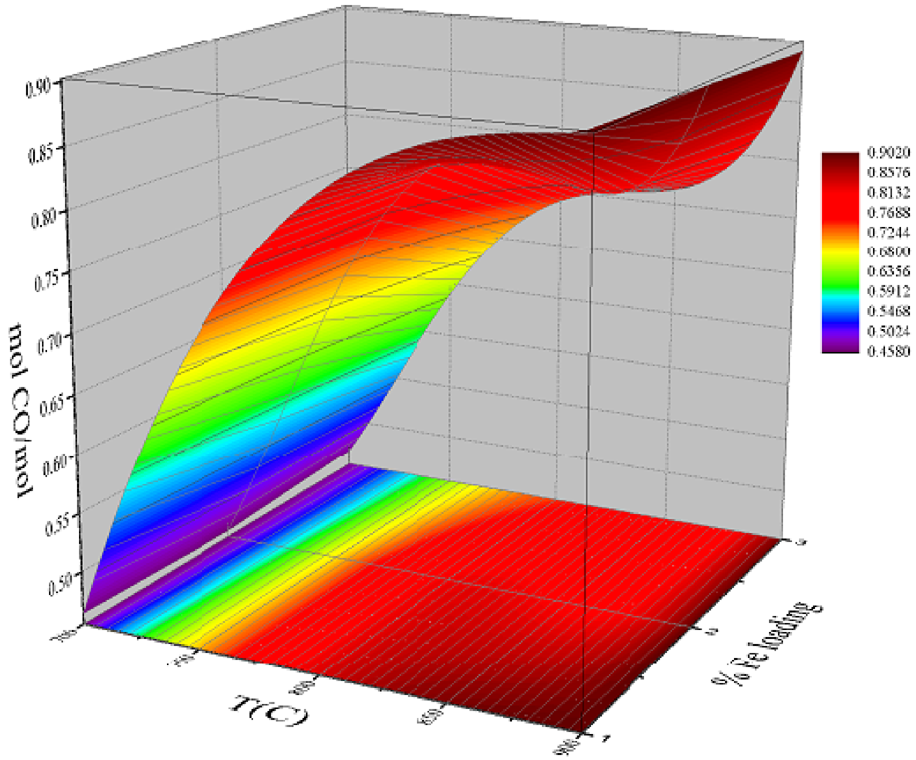




- Complete conversion at 750 ^{o}C
  - Only ~200 min needed with the use of Na catalyst
  - ~700 min needed without use of Na catalyst
- Activation energy [determined by lnk~(1/T) plot]
  - ~60 kJ/mol with catalyst
  - ~100 kJ/mol without catalyst



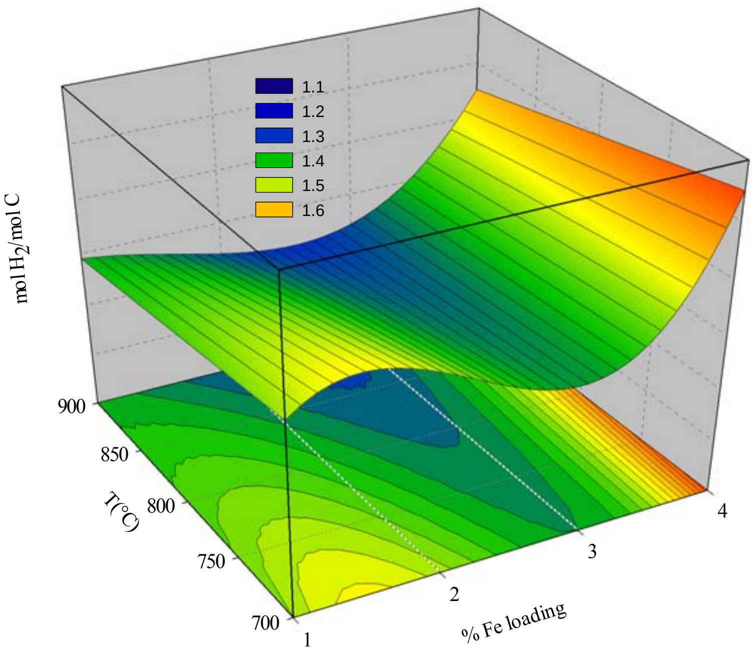
Effect of Composite Catalyst on CO Concentration in Syngas



Molar yield of CO per mole of carbon in the char vs. different loadings of Fe and temperatures

- Test conditions
  - Mass of DAF coal: 5 g
  - H_2O flow rate: 180 ml/min
  - N_2 flow rate: 4.1 ml/min
  - #1:1%-Fe+3%-Na
  - #2: 2%-Fe+2%-Na
  - #3: 3%-Fe+1%-Na
- Observations
  - Increase in temperature → significant increase in CO
  - Increase in Fe in composite catalyst → considerable decrease in CO

Effect of a Composite Catalyst's Composition and Temperature on H_2 Concentration in Syngas with Steam Gasification

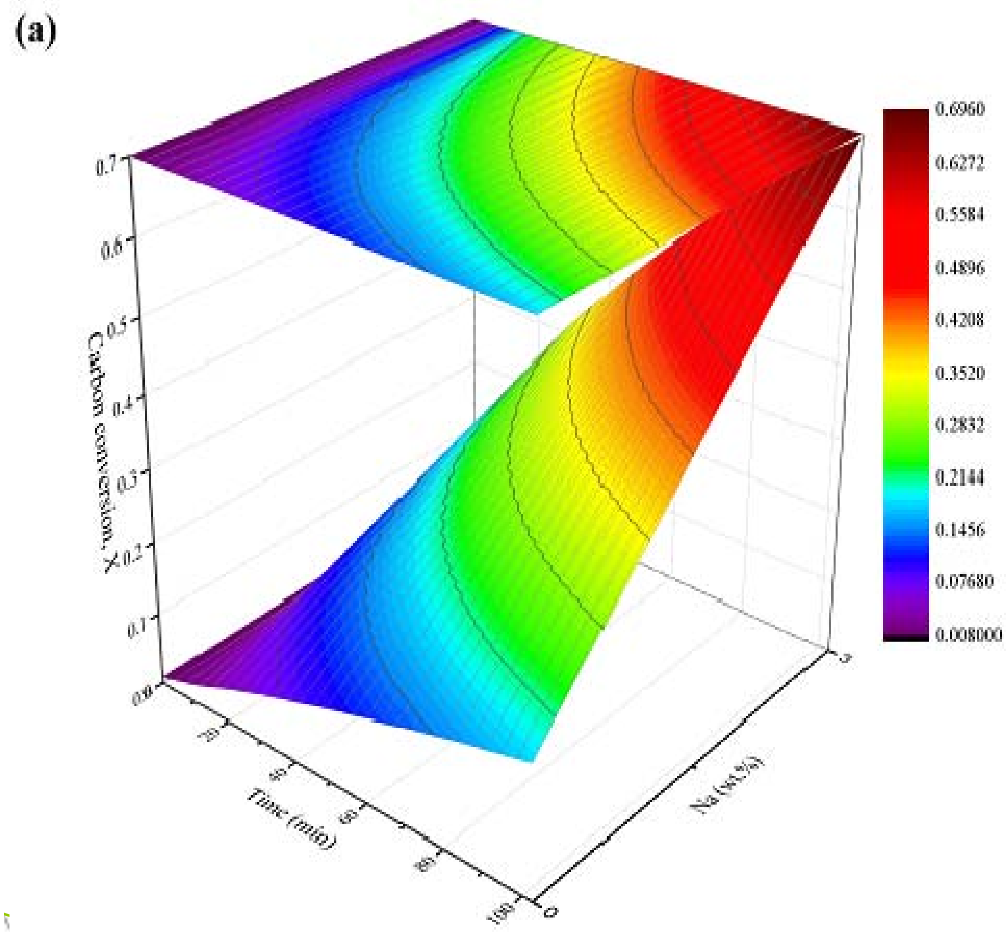


Molar yield of H_2 per mole of carbon in the char vs. different loadings of Fe and temperatures

Test conditions- Mass of coal: 5 g; #1: 1%-Fe+3%-Na; #2: 2%-Fe+2%-Na; #3: 3%-Fe+1%-Na: #4: 4%-Fe+0%-Na.

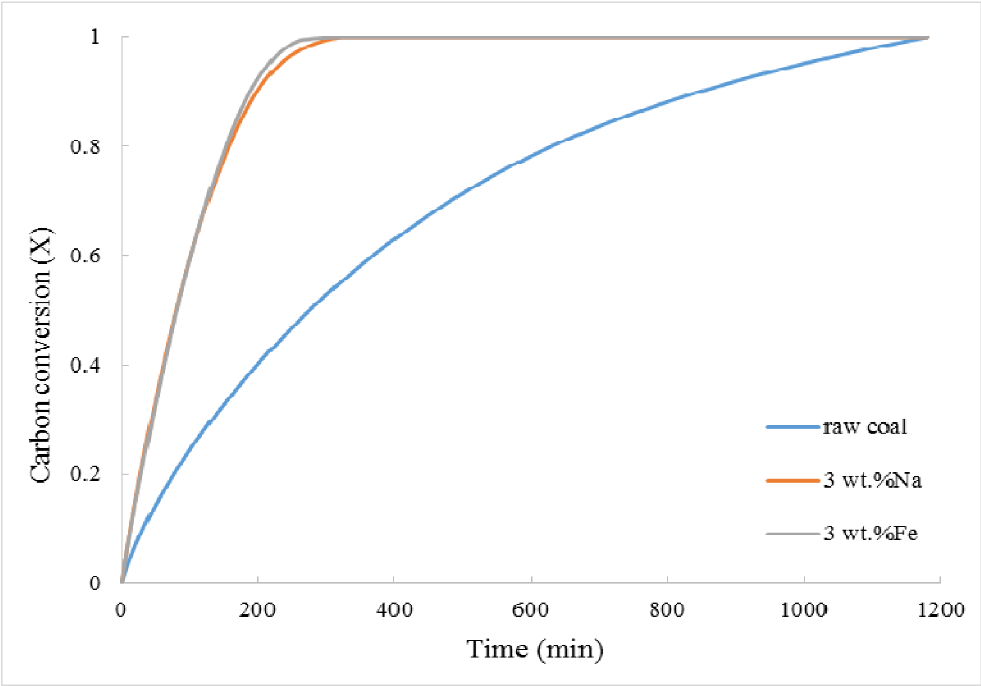
- Composite catalyst can take the advantage of two individual catalysts and overcome their challenges
- Molar yields of H_2 per mole of carbon
  - 3% Fe loading leads to the increase in H_2 production by 35% at 700 ^oC.

Effect of Na Catalyst on Carbon Conversion with CO_2 Gasification



- Test conditions
  - Gasification Temperature: 700 °C
  - Mass of DAF coal: 5 g
  - CO_2 flow rate: 180 ml/min
  - N_2 flow rate: 4.1 ml/min
- Observations
  - Addition of trona can significantly accelerate carbon conversion X (mole fraction) or coal gasification rate
  - Gasifying the same amount of coal with catalyst needs
    - less time
    - a smaller gasifier

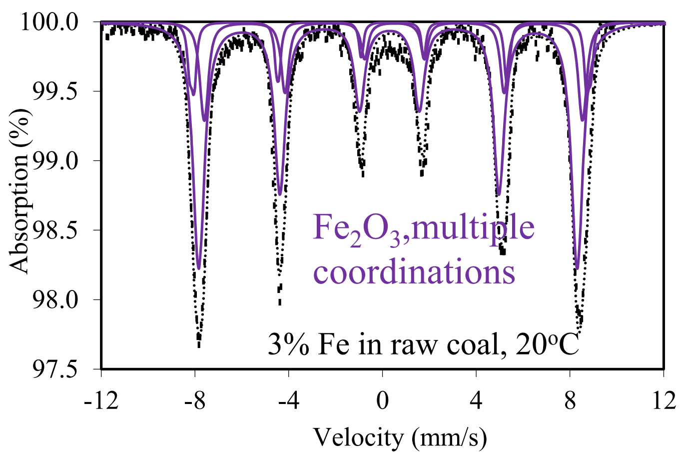
Effect of Catalyst on CO_2 Gasification (continued)

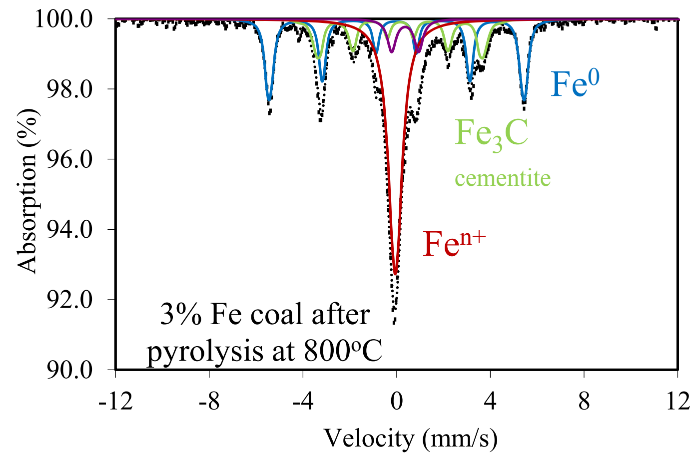


- **Pure CO** could be obtained
- 1,200 min is needed for gasifying the coal **without** presence of catalyst.
- **Only** 300 min is needed for gasifying the coal **with** the presence of catalyst.

Test conditions – Gasification temperature: 700 ^{o}C; mass of coal: 5 g; CO_2 flow rate: 180 ml/min; N_2 flow rate: 4.1 ml/min.

The Mechanism of PRB Coal Gasification with Fe Catalyst: Mössbauer spectroscopy data





- During pyrolysis iron oxides are reduced to metallic iron Fe^0, Fe_3C and higher coordination iron Fe^{n+}
- After steam introduction Fe_3C is oxidized to Fe^0 and Fe(O)
- The catalytic mechanism on oxidized iron layer:

$Fe + H_2O \rightarrow Fe(O) + H_2$

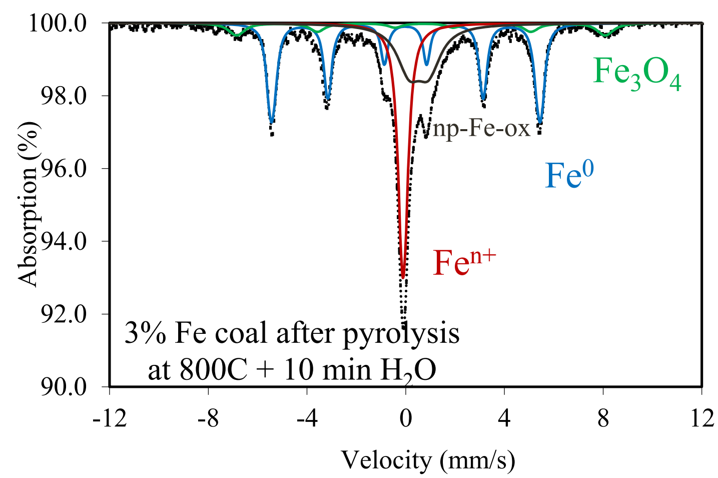
$Fe(O) + C \rightarrow C(O) + Fe$

$C(O) \rightarrow CO$

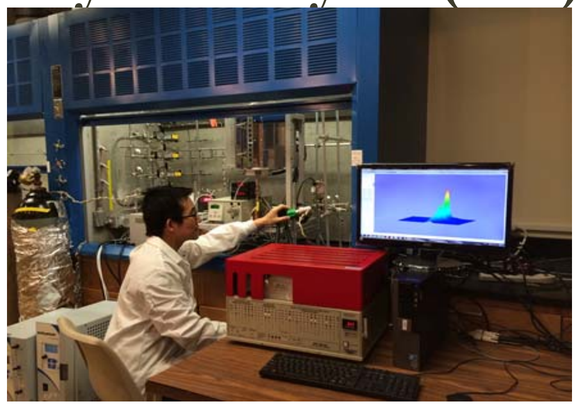
$3Fe(O) + H_2O \rightarrow Fe_3O_4 + H_2$

$Fe_3O_4 + CO \rightarrow 3Fe(O) + CO_2$

$CO_2 + C \leftrightarrow 2\,CO$



Sample Project 2- Catalytically Coverting Syngas to Ethylene Glycol (EG)



Syngas to ethylene glycol

$2CO + 2CH_3ONO \longrightarrow (COOCH_3)_2 + 2NO$

Methyl nitrite (MN) → *Dimethyl Oxalate (DMO)*

$2CO + 2CH_3CH_2ONO \longrightarrow (COOCH_2CH_3)_2 + 2NO$

Ethyl nitrite (EN) → *Diethyl Oxalate (DEO)*

$2NO + 0.5O_2 \longrightarrow N_2O_3$

$N_2O_3 + 2CH_3OH \longrightarrow 2CH_3ONO + H_2O$ — *Methyl nitrite (MN)*

$N_2O_3 + 2CH_3CH_2OH \longrightarrow 2CH_3CH_2ONO + H_2O$ — *Ethyl nitrite (EN)*

$(COOCH_3)_2 + 4H_2 \longrightarrow (CH_2OH)_2 + 2CH_3OH$

$(COOCH_2CH_3)_2 + 4H_2 \longrightarrow (CH_2OH)_2 + 2CH_3CH_2OH$

Dimethyl Oxalate (DMO) / Diethyl Oxalate (DEO) → *Ethylene glycol (EG)*

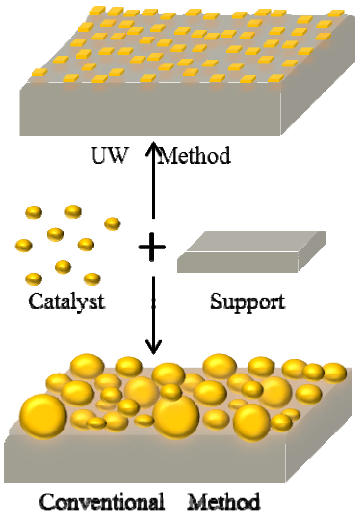
Methyl nitrite to Ethylene glycol

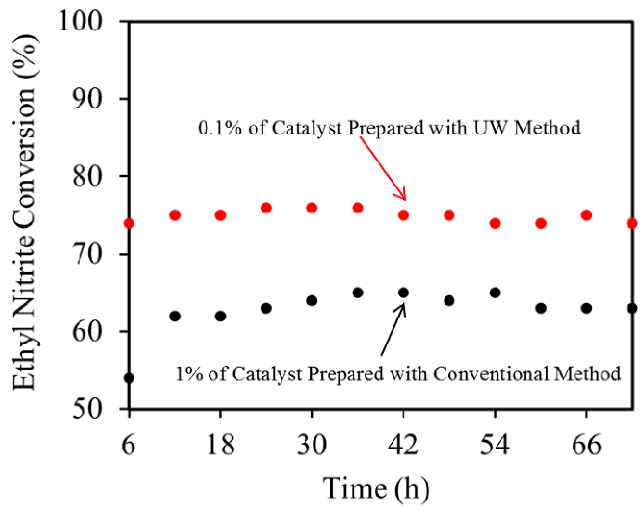
Ethyl nitrite to Ethylene glycol

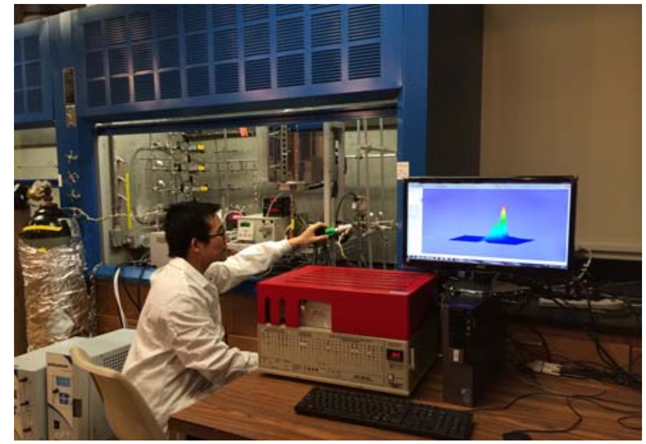
Disadvantages of methyl nitrite:
- Highly flammable
- Highly explosive
- Toxic
- Being controlled in the US

Advantages of ethyl nitrite:
- Less flammable
- Non-explosive
- Less toxic
- Transportation allowed

1st Step of Syngas to EG: (CO +EN) → DEO

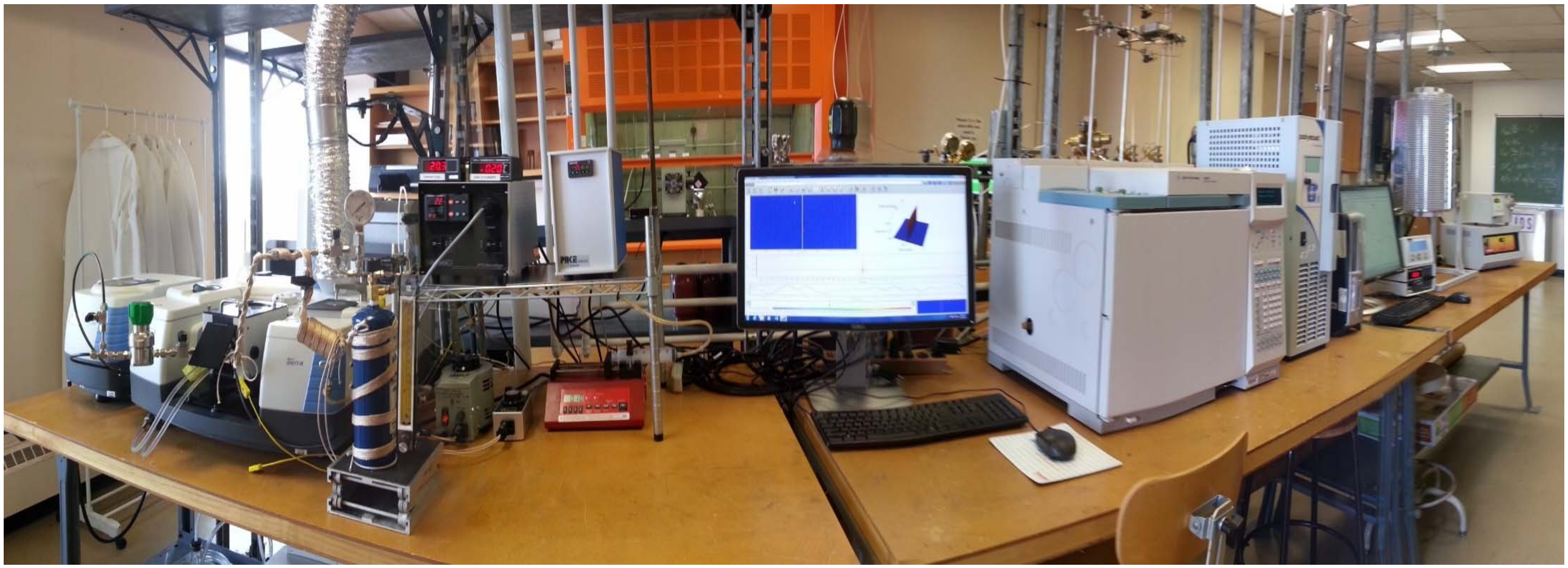






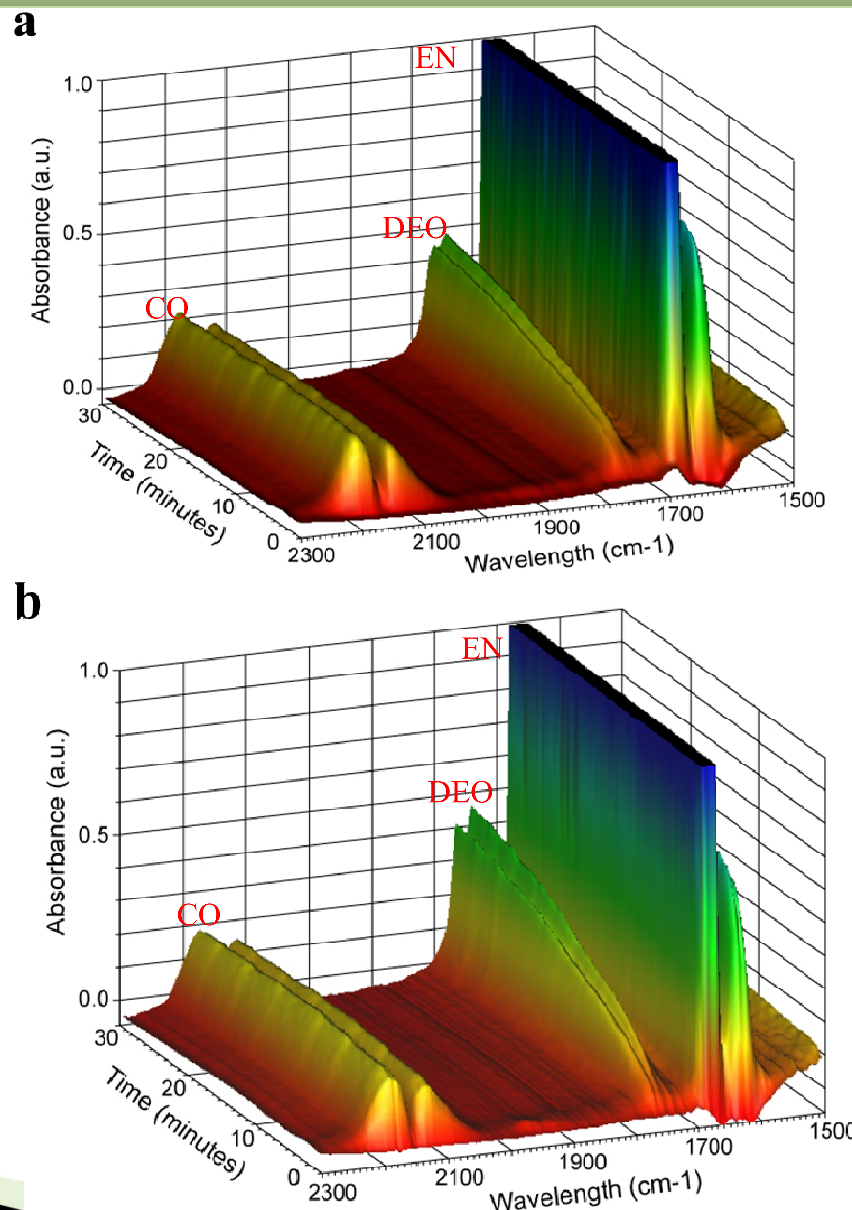
- UW DEO synthesis catalyst
  - 0.1% DEO production catalyst prepared at UW can perform better than 1% that prepared with conventional method.
  - Cost-effectiveness of UW catalyst is 9 times or 900% better than that of conventional ones.

Integrated in-situ FTIR Based Set-up for Studying EG Reaction Mechanism



In-Situ FTIR Observation of DEO Synthesis with and without Uses of a Promoter

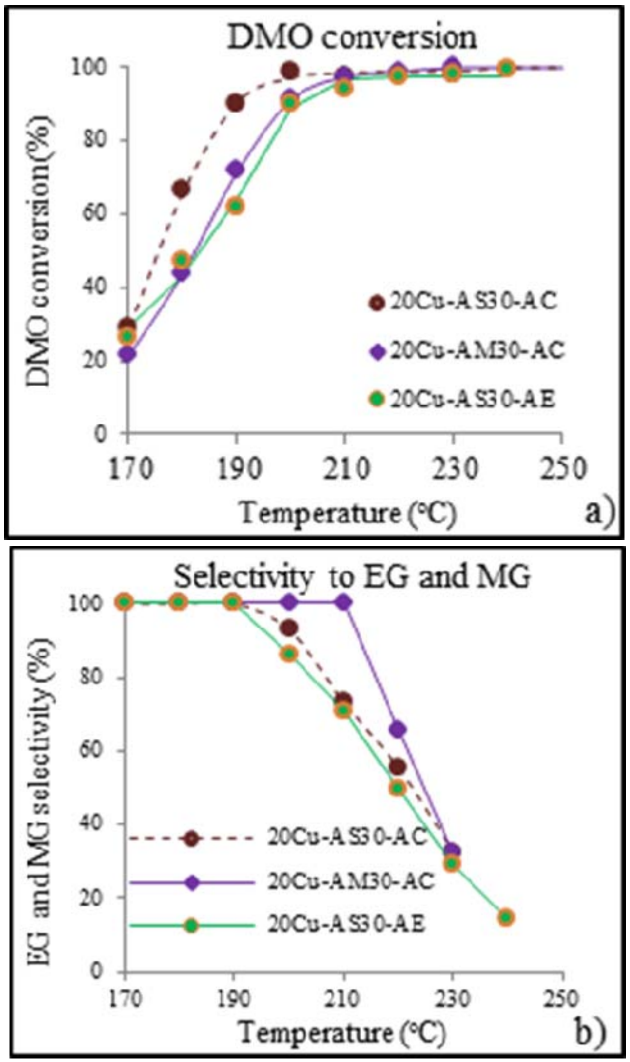
140 ^{o}C;1 atm;
CO: EN;1.4 :1.



Without promoter

With a promoter (0.8 wt-%)

2^{nd} Step of Syngas to EG: DMO→EG

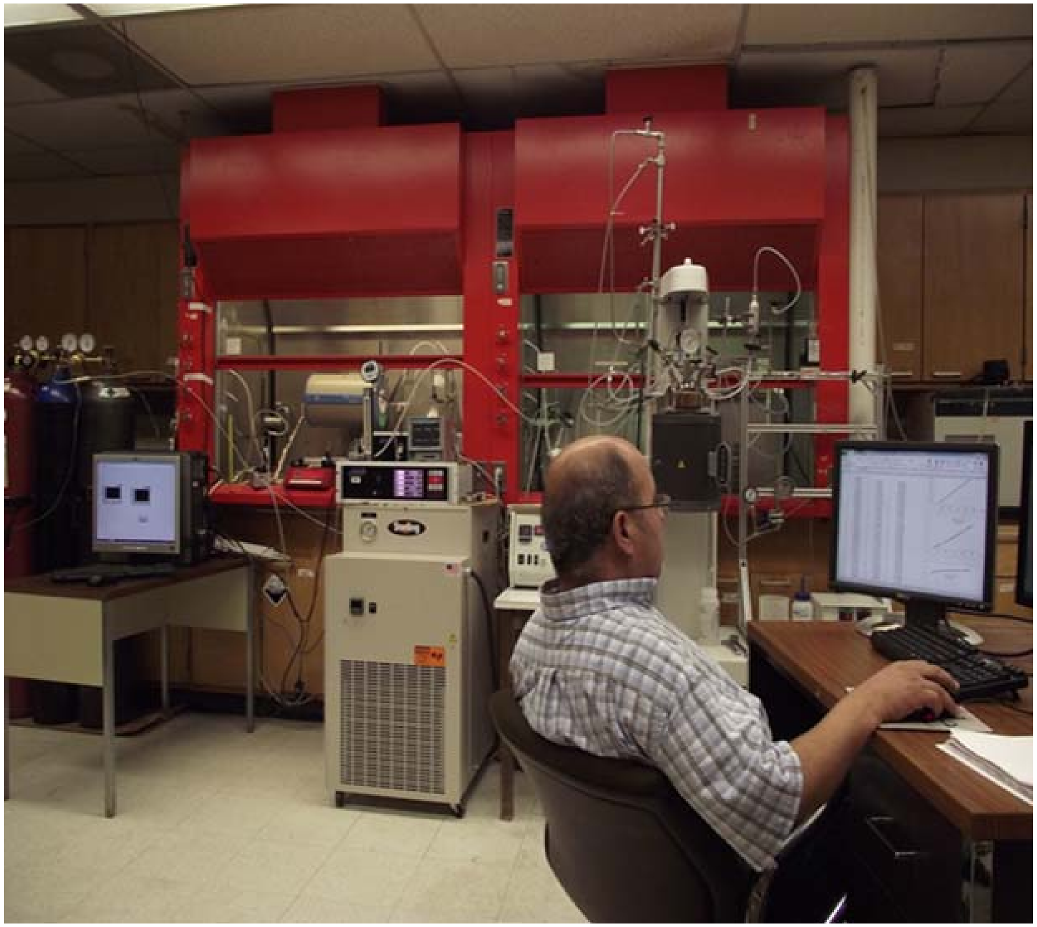


- UW's AC based catalysts achieve higher DMO conversion and EG + MG (methyl glycolate) selectivity in lower temperature range (< 200 °C)
- UW's 20Cu-AS30-AC is the best catalyst
  - 100% CO conversion
  - 90% EG + MG

Sample Project 3- New CO_2 Capture Technologies

- Sorption based CO_2 capture technology
  - Advantages
    - Easy in operation
    - Applicable to gases with a wide range of CO_2 concentrations
      - Absorption: for pre-combustion CO_2 capture
      - Adsorption: for flue gas with low CO_2 concentration
  - Shortcoming
    - Slow CO_2 desorption rates (especially for absorption based technology) → high desorption energy consumption
      - the largest obstacle for reducing overall CO_2 capture cost since about 70% of overall CCS capital is spent on CO_2 desorption step
    - What to do? *Using catalysis*

Catalytic CO_2 Capture
set-up



Sample Project 3- Catalytic Based CO_2 Capture

Background

- Carbonates for CO_2 capture
  - Mechanism (reversibility of the following reaction)
    - $Na_2CO_3 + H_2O + CO_2 \rightleftarrows 2NaHCO_3$

      Or : $CO_3^{2-} + H_2O + CO_2 \leftrightarrow 2\ HCO_3^-$
  - Advantages
    - Stoichiometric CO_2-H_2O ratio: almost equal to that in actual flue gas
    - Na_2CO_3: inexpensive, stable, easily available
  - Disadvantage
    - More difficult than amines based CO_2 capture technology in CO_2 desorption or sorbent regeneration step

Catalytic Based CO_2 Capture - Inorganic

CO_2 Desorption Rate Constants (k) with and without Uses of a Catalyst

- Test Conditions
  - Mass of spent CO_2 sorbent ($NaHCO_3$):50-100 mg
  - $NaHCO_3$/Catalyst (called NHF)
  - N_2 flow rate: 100 mL/min
- Observations
  - Rate constants [k (min^{-1})] increased significantly at the same temperature due to use of the catalyst (e.g., $k_{pure-NaHCO3} = 0.005\ min^{-1}$, while $k_{90\%\ wt.\%NHF} = 0.19\ min^{-1}$, $k_{50\%\ wt.\%NHF} = 0.20\ min^{-1}$, $k_{10\%\ wt.\%NHF} = 0.06\ min^{-1}$ at 100 °C)
    - CO_2 desorbs much faster due to use of catalyst
    - Reduce operating and capital costs

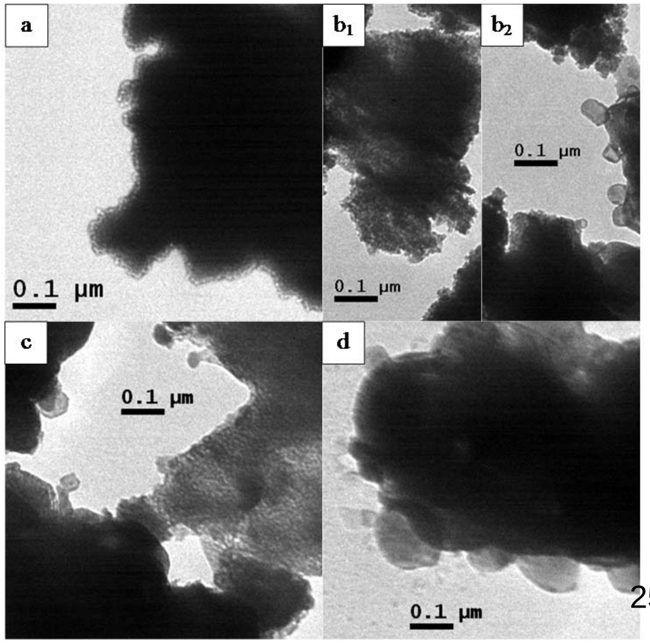
Sample	Temperature (° C)	m	k (min^{-1})	R^2
Pure $NaHCO_3$	100	0.9	0.005	0.9992
	120	1.0	0.02	1.0000
	140	1.2	0.06	0.9991
	150	1.2	0.13	0.9991
	160	1.2	0.29	0.9999
90 wt.% NHF	100	0.7	0.19	0.9996
	110	0.6	0.25	0.9994
	120	0.4	0.49	0.9995
	130	0.4	0.89	0.9990
	140	0.3	1.32	0.9975
50 wt.% NHF	100	0.6	0.20	0.9989
	110	0.4	0.32	0.9989
	120	0.1	0.46	0.9994
	130	0.1	0.59	0.9997
	140	0.1	0.84	0.9995
20 wt.% NHF	100	0.5	0.06	0.9997
	110	0.5	0.13	0.9998
	120	0.5	0.23	0.9998
	130	0.5	0.35	0.9998
	140	0.5	0.50	0.9998

Catalytic Based CO_2 Capture - Inorganic

Arrhenius Parameters

Sample	R^2	A (min^{-1})	E_A (kJ/mol)
Pure $NaHCO_3$	0.9988	$9.66 \times 10^9 \pm 3.16 \times 10^8$	86 ± 2.5
90 wt.% NHF	0.9529	$2.65 \times 10^8 \pm 2.43 \times 10^7$	64 ± 5.8
50 wt.% NHF	0.9493	$4.86 \times 10^5 \pm 4.06 \times 10^4$	44 ± 3.5
20 wt.% NHF	0.9899	$4.02 \times 10^8 \pm 1.72 \times 10^7$	69 ± 2.8

- Reduction in desorption activation energy also implies better adsorption
  - $\Delta H_R = E_{A,R} - E_{A,-R}$



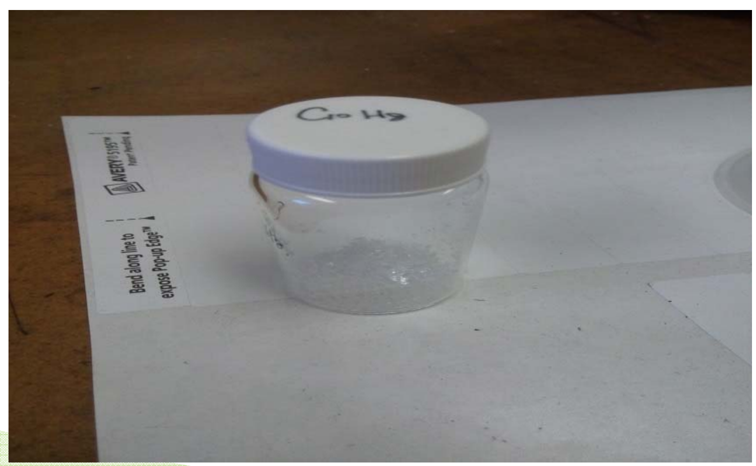
a – catalyst

b – 20 wt.% NHF

c – 50 wt.% NHF

d – 90 wt.% NHF

Sample Project 4: Naphthalene synthesis



Thanks to