Development of Low Cost Membranes (Ta, Nb & Cellulose Acetate) for H_2/CO_2 separation in WGS reactors

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OUTLINE

- Synthesis of low temperature Cu-Ce-Ni nanocatalysts for Water Gas Shift (WGS) reaction for hydrogen production using CO and steam **$CO + H_2O \rightarrow CO_2 + H_2$**
- Development of low cost metal (Ta/Nb)/Ceramic membranes for hydrogen separation

  a) Ta/Nb thin film deposition on porous ceramic disks using sputtering techniques

  b) Ta/Nb oxide powers deposition on ceramic disks followed by aluminothermic reduction

  $M_2O_5(s) + 10/3\ Al(s/l) \rightarrow 2M + 5/3\ Al_2O_3(s)$; (M=Ta or Na)
- Catalysts characterization, optimization of the reaction parameters using a gas flow reactor, and the study of CO conversion/reaction kinetics using a batch reactor
- Design of permeability testing system and H_2 permeability study

Catalysts Preparation – Sol-gel/Oil-drop Methods

<u>Step 1</u>: ***Boehmite Sol (γ-AlOOH) Preparation***

15mL aluminum tri-sec-butoxide is dissolved in 40 mL distilled water (at 75^{o}C) and 1M HNO_3 while adjusting pH value. The solution is refluxed for 14 hours.

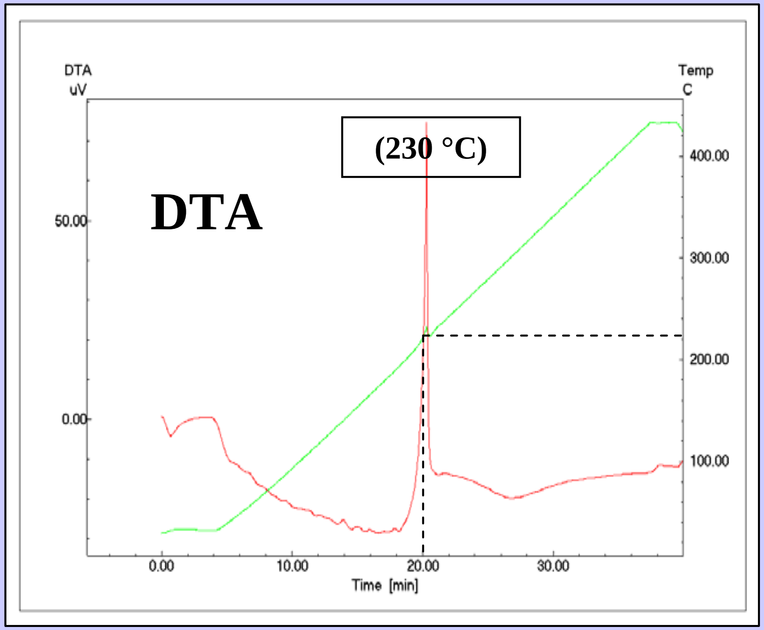
<u>Step 2</u>: ***Sol Gelation and shaping (Oil Dropping) the granules***

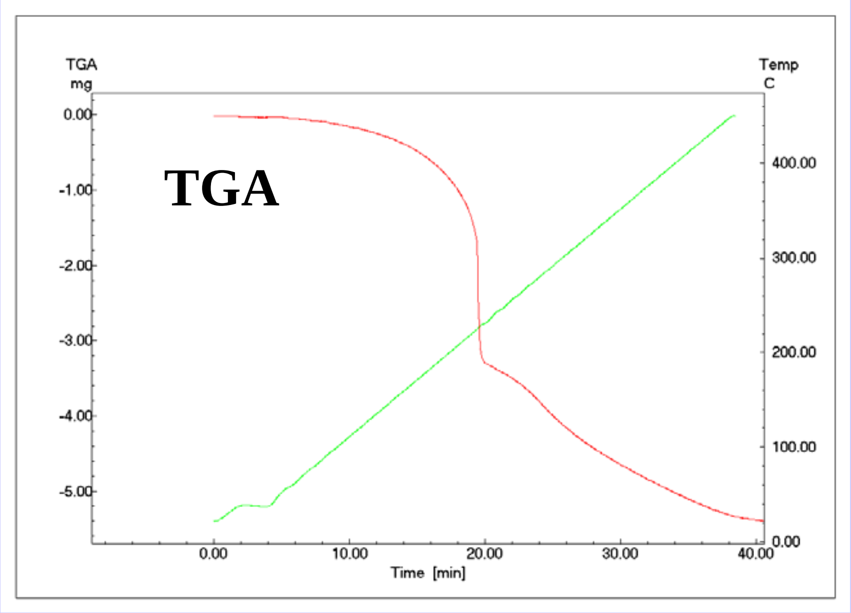
Metal nanoparticles were added to this solution and dropped using a syringe into the hot mineral oil top-layer at 90^{o}C and the gel was collected in the bottom layer of 10% ammonia solution. The soft sol-gel granules were collected from the ammonia and washed.

<u>Step 3</u>: ***Dry and Calcinations***

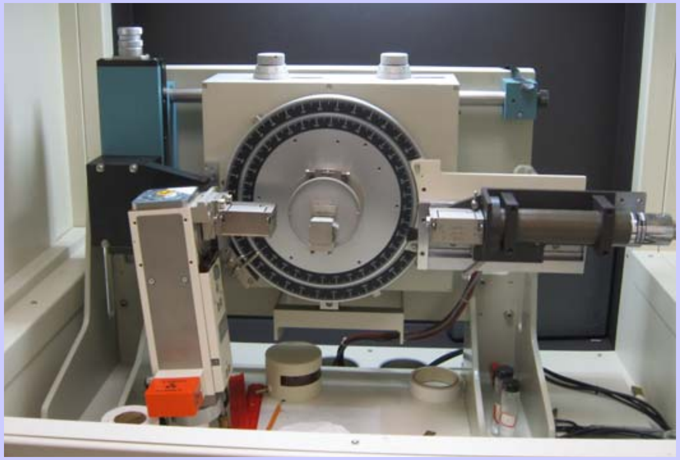
The catalyst granules were dried for about 48 hours in an oven kept at 50^{o}C . The granules were calcined at 450^{o}C for 4 hrs.

Catalysts Characterization





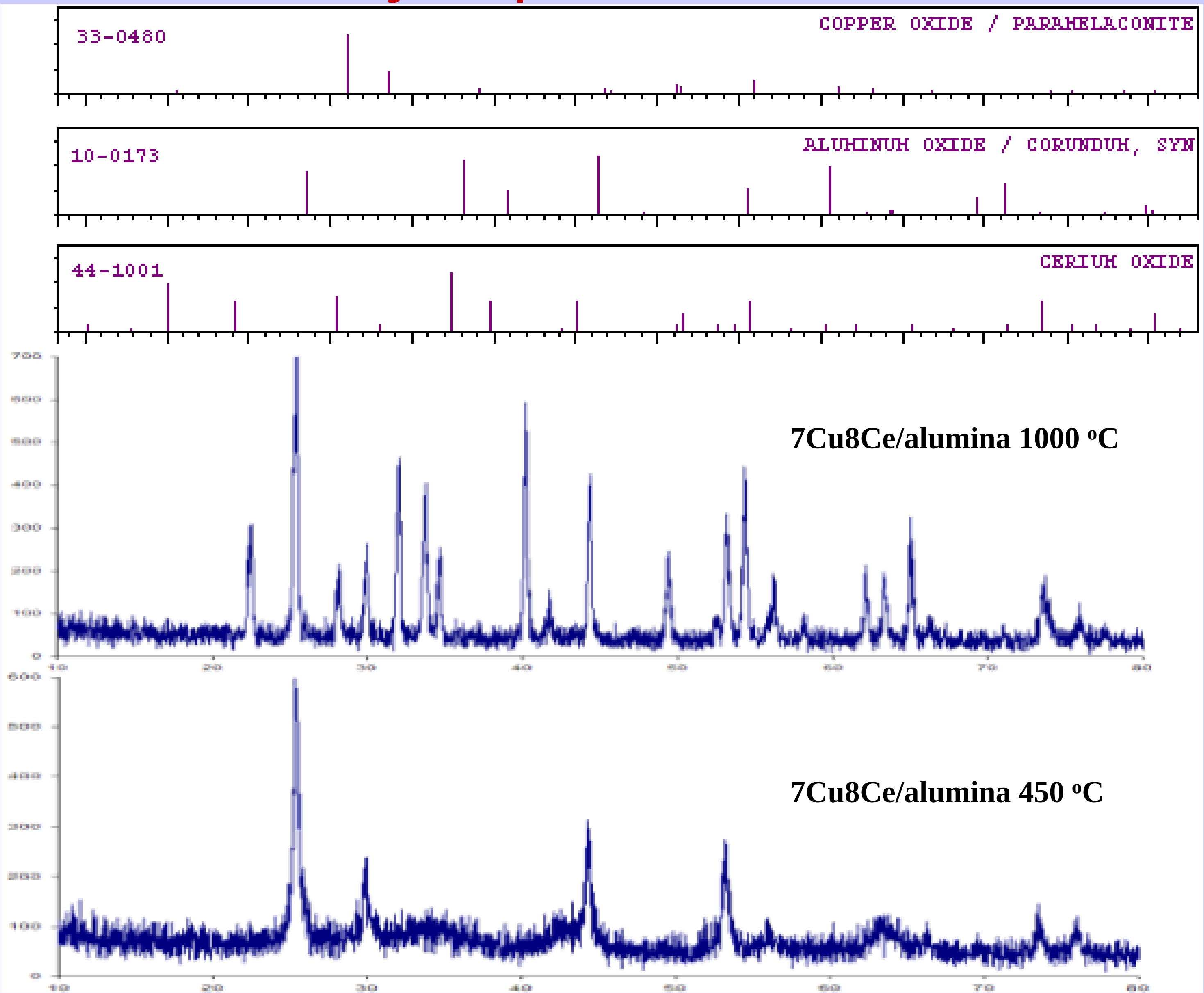
Thermal analysis of Cu(5%), Ce(7%) and Ni(8%) in alumina



XRD

SEM

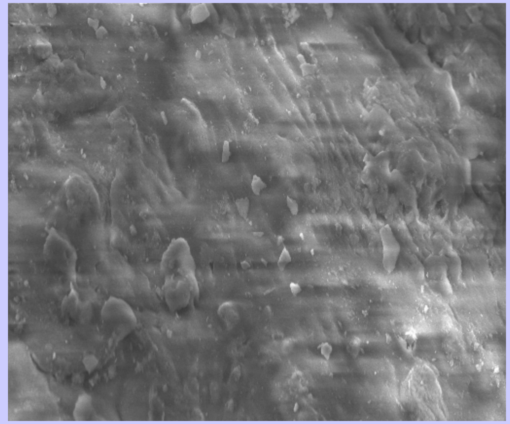
XRD Analysis for Cu/Ce/alumina



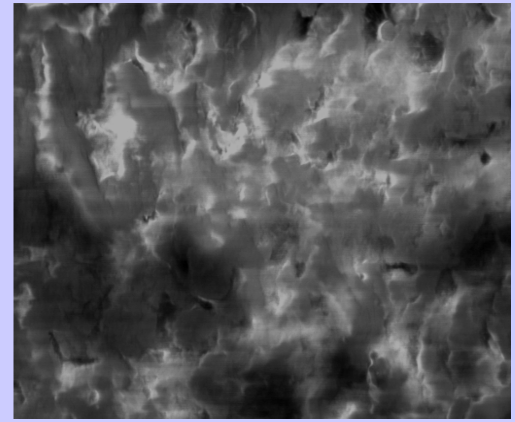
SEM Analysis of Granules

a) 20X mag.

b) 1000X mag.

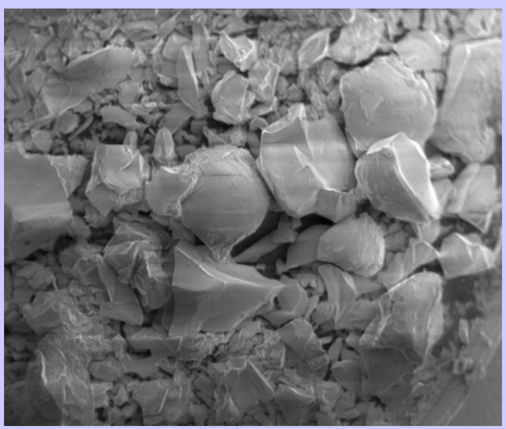


c) 5000X mag.

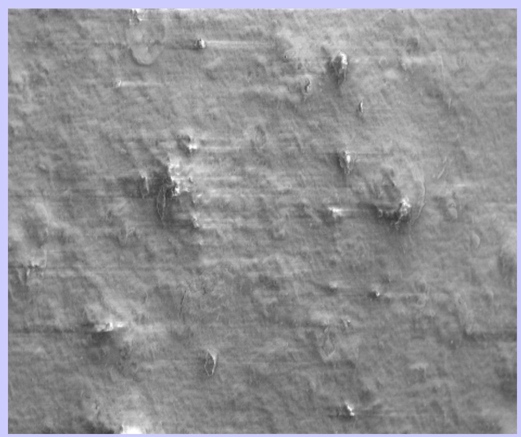


SEM - Cu(7%) and Ce(8%) nanocatalysts in sol-gel alumina

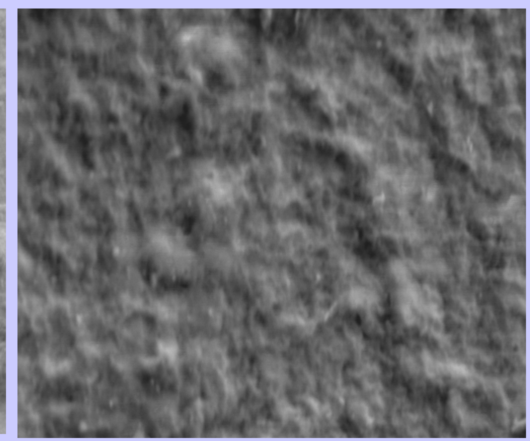
a) 20X mag.



b) 1000X mag.



c) 5000X mag.

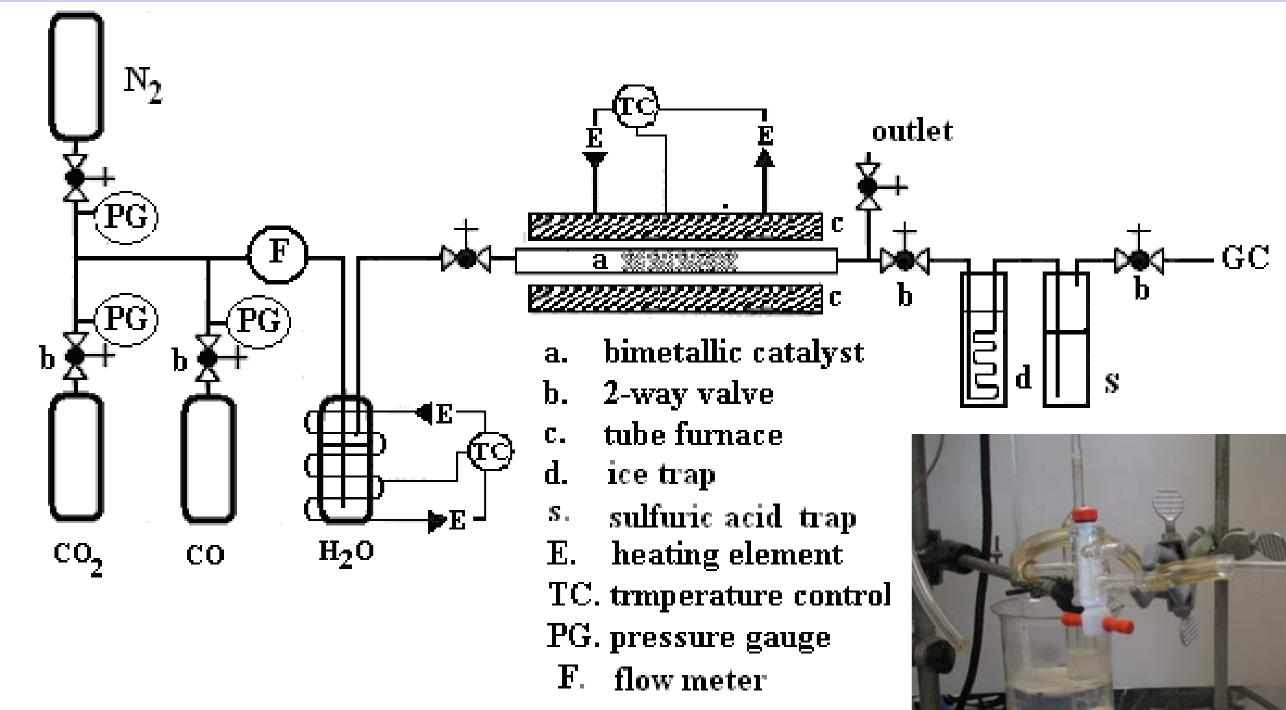


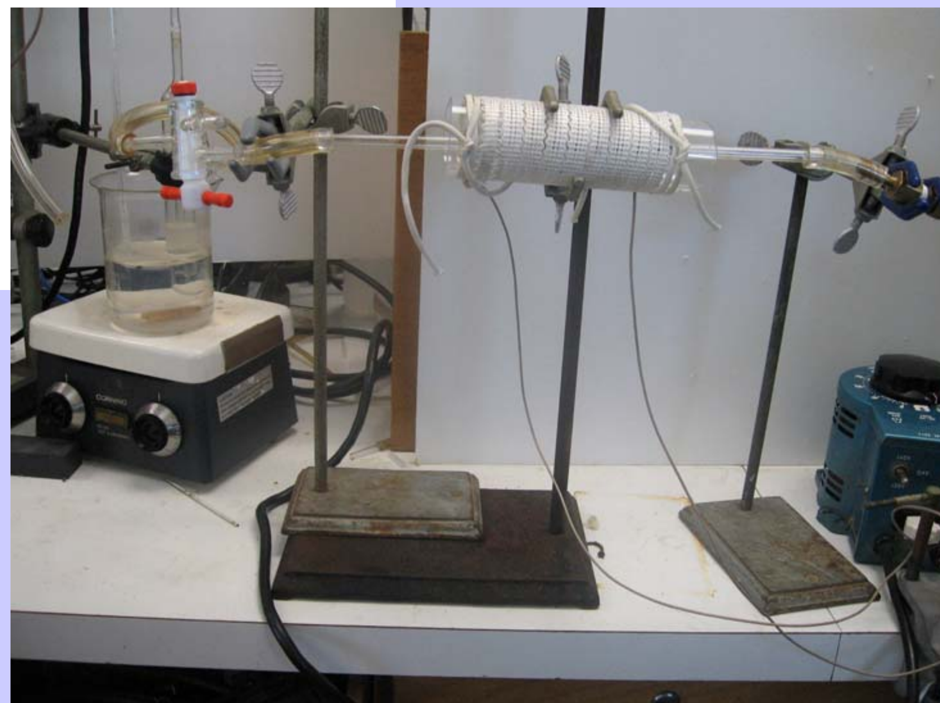
SEM - Cu(5%), Ce(7%), and Ni(8%) nanocatalysts in sol-gel alumina

SEM observations showed that Cu-Ce catalyst granules are larger with larger pores and have less mechanical strength compared to Cu-Ce-Ni.

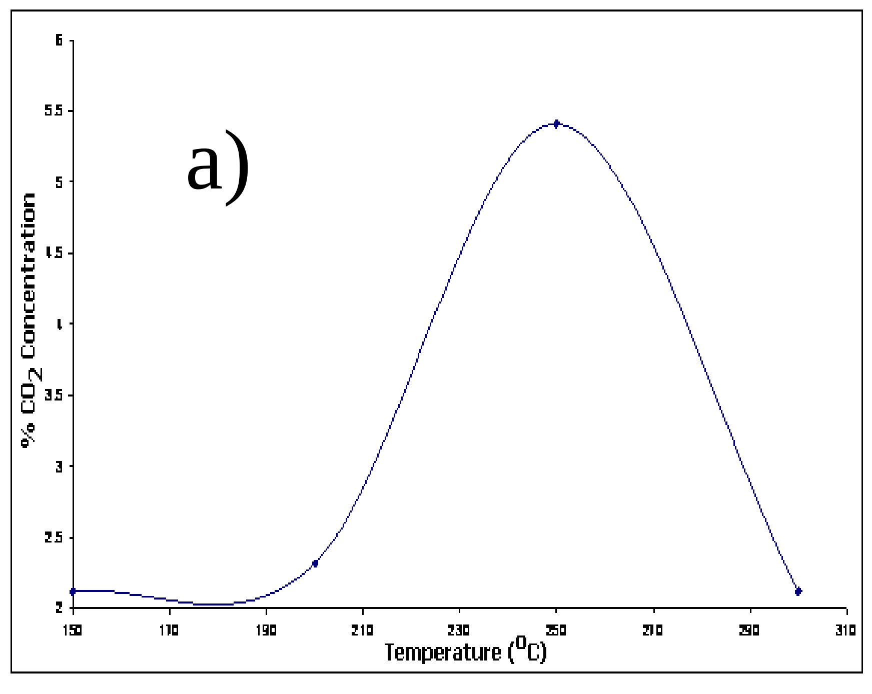
Gas-phase flow reactor

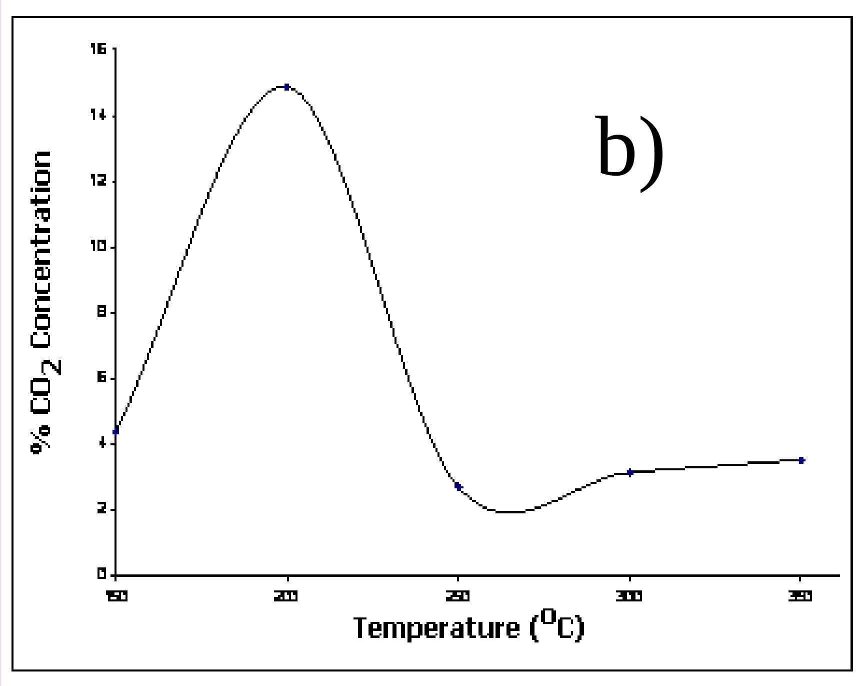
for optimizing reaction parameters





Gas-phase flow reactor Results





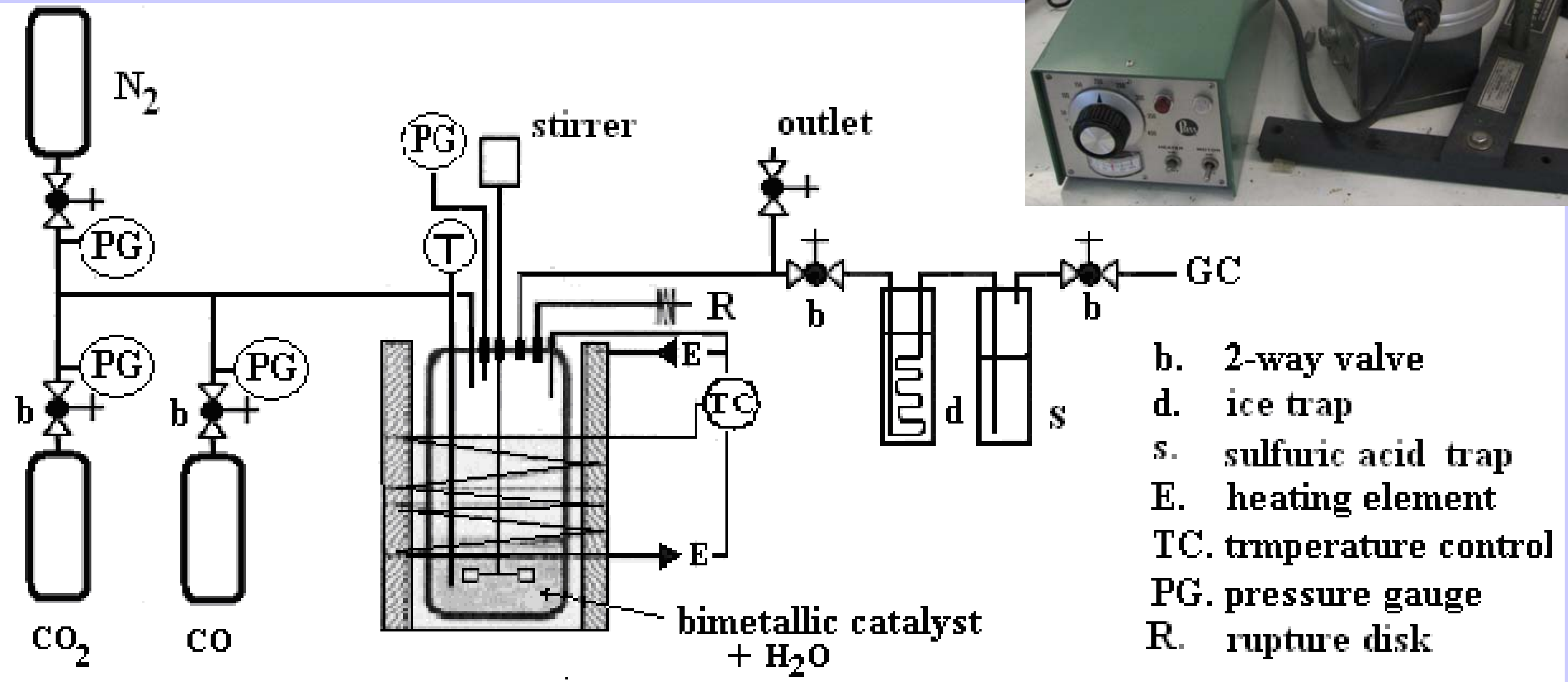
CO_2 production in a gas phase flow reactor with
a)Cu(7%)-Ce(8%) and
b)Cu(5%)-Ce(7%)-Ni(8%)

in alumina under CO and H_2O flow.

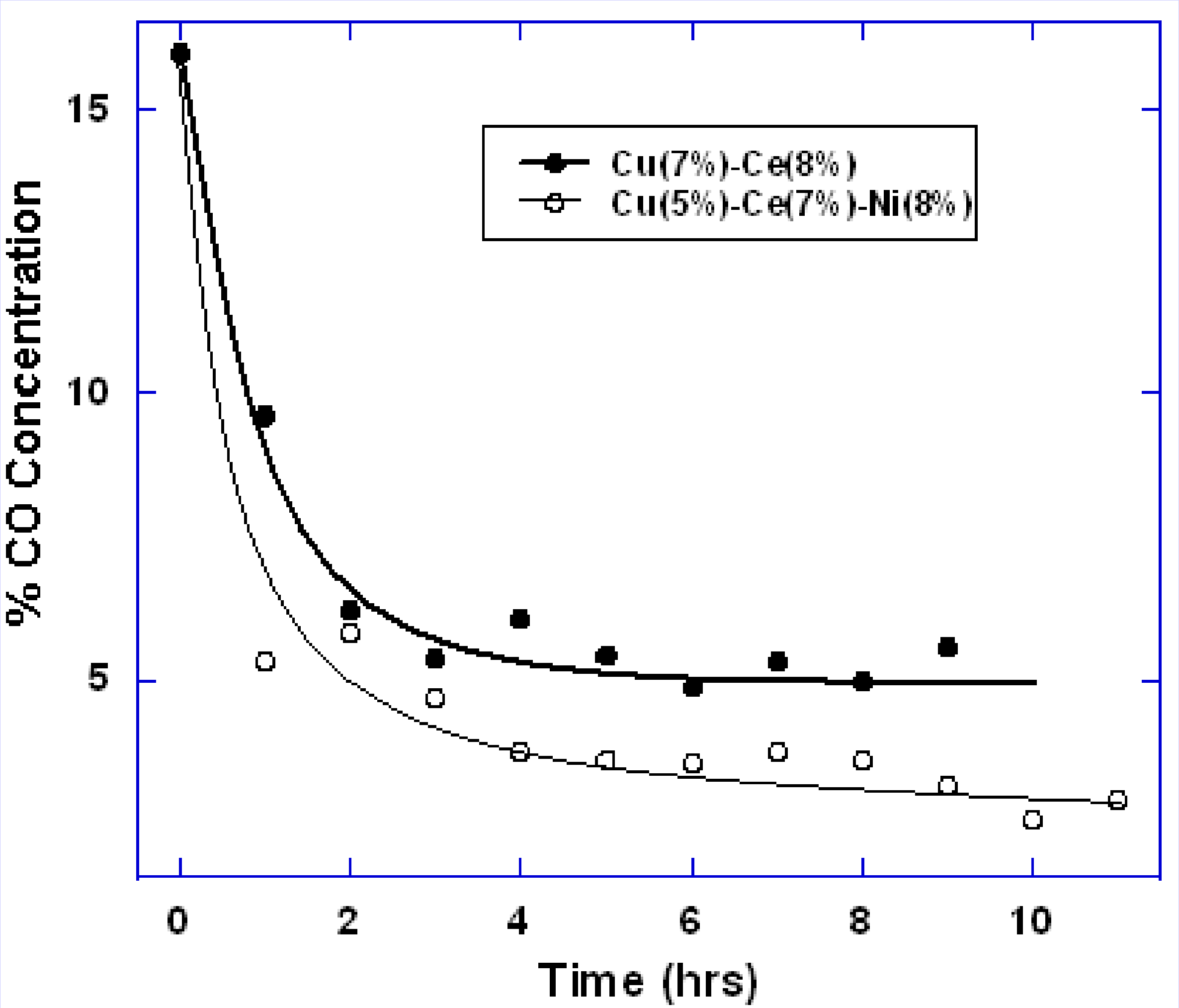
The optimum reaction temperatures for Cu-Ce and Cu-Ce-Ni catalysts are found to be ~ 250^{o}C and 200^{o}C, respectively.

Gas-phase batch reactor

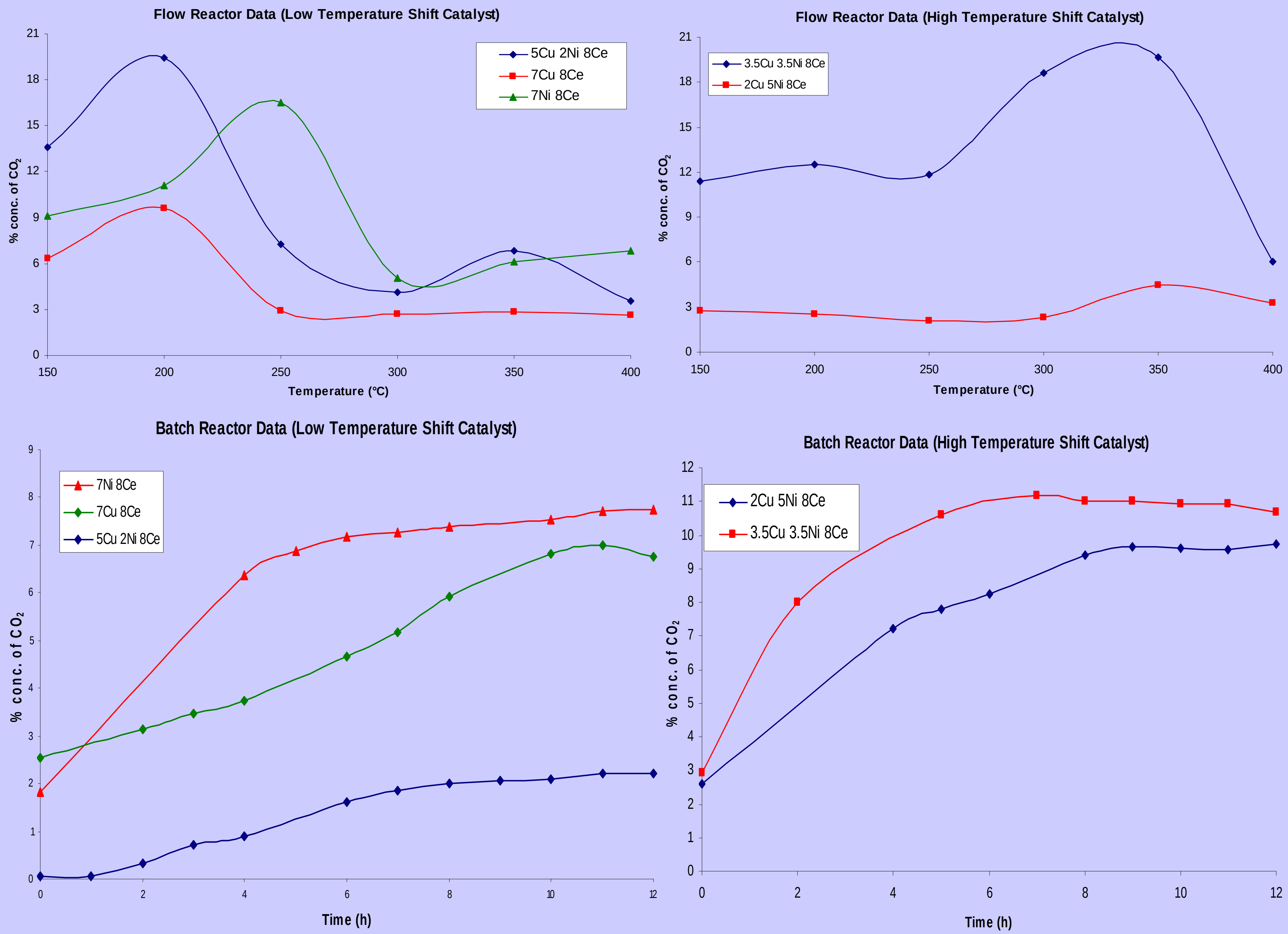
for kinetic study of WGS catalysts



Gas-phase batch reactor Results



After ~ 1 hr reaction ~43% CO is converted in case of Cu-Ce catalyst & ~62% CO in case of Cu-Ce-Ni catalyst. The overall CO conversions after 10 hrs reaction were 69% for Cu-Ce catalyst and 83% for Cu-Ce-Ni catalyst.


Flow Reactor Data (Low Temperature Shift Catalyst)
5Cu 2Ni 8Ce
7Cu 8Ce
7Ni 8Ce
% conc. of CO_2
Temperature (°C)
Flow Reactor Data (High Temperature Shift Catalyst)
3.5Cu 3.5Ni 8Ce
2Cu 5Ni 8Ce
% conc. of CO_2
Temperature (°C)
Batch Reactor Data (Low Temperature Shift Catalyst)
7Ni 8Ce
7Cu 8Ce
5Cu 2Ni 8Ce
% conc. of CO_2
Time (h)
Batch Reactor Data (High Temperature Shift Catalyst)
2Cu 5Ni 8Ce
3.5Cu 3.5Ni 8Ce
% conc. of CO_2
Time (h)

BET Surface Area & Pore Sizes of Catalysts

Catalyst	Specific Surface Area (m^2/gm)	Average Pore Size (Å)
Cu(2%) Ni(5%) Ce(8%) HT (2)	233.7	15.89
Ni(7%)Ce(8%) LT (1)	214.8	18.01
Cu(3.5%) (Ni(3.5%)Ce(8%) HT (1)	183.7	17.95
Cu(7%)Ce(8%) LT (2)	156.3	20.11
Cu(5%) Ni(2%)Ce(8%) LT (3)	141.8	17.97

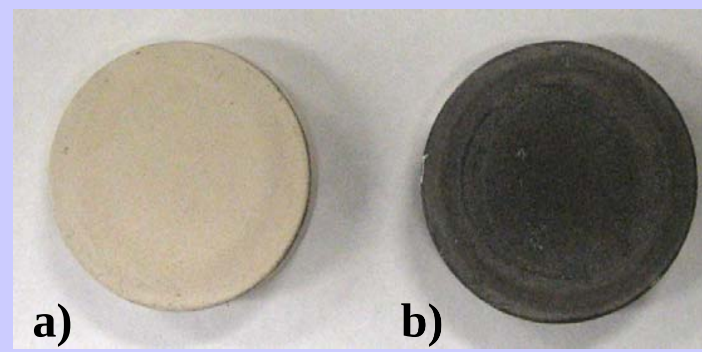
Preparation of H_2 Separation Membranes

Method 1: Sputter Deposition of Na & Ta metal thin films on ceramic disks (11/8” dia & 0.281” thick) with porosities: 0.16 µm, 0.5µm, and 0.8µm. The thickness of the coated metal films is ~ 400 nm.

Method 2: **Aluminothermic method**

$M_2O_5 + 10/3\ Al \rightarrow 2\ M + 5/3\ Al_2O_3$; (M = Na and Ta)

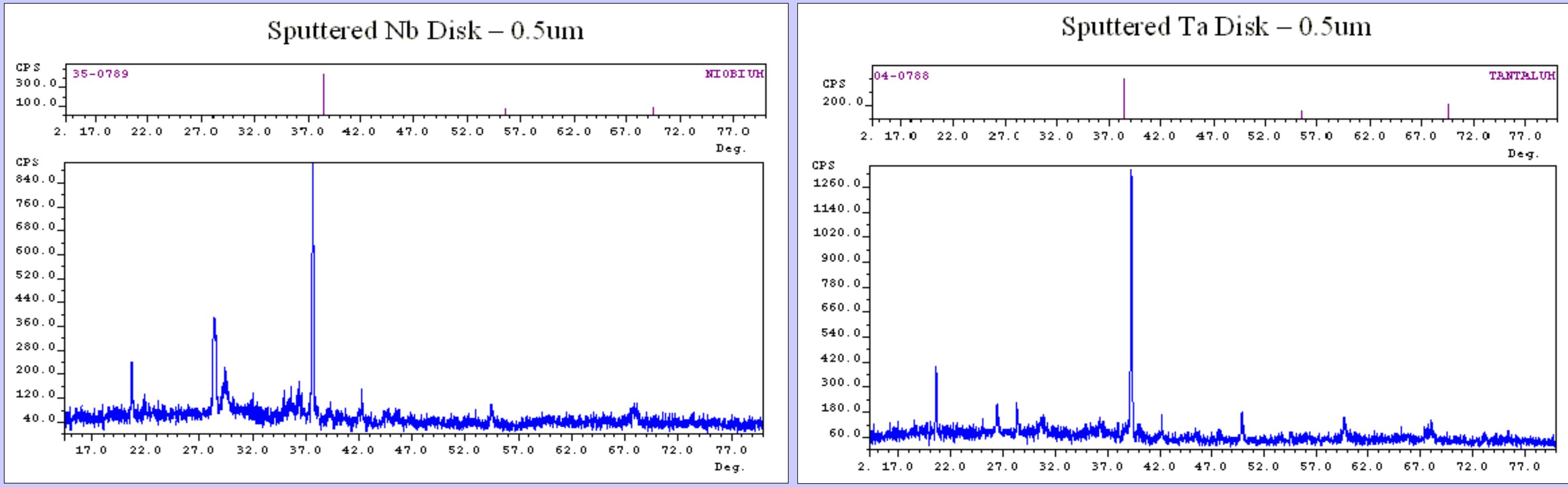
Samples of Nb_2O_5 & Al , or Ta_2O_5 & Al in a molar ratio of 1:11 were mixed and grounded using a motor and pestle for 15 min to obtain a fine particle homogenous mixture. 0.2 g of sample was added to 10 mL acetone, sonicated, deposited on the disks and slowly heated up to 1200°C for 8 hrs to complete the aluminothermic reaction. DTA of M_2O_5 (M = Nb and Ta) and Al mixtures shows reduction of M_2O_5 to M at the temperature ~ 950°C.



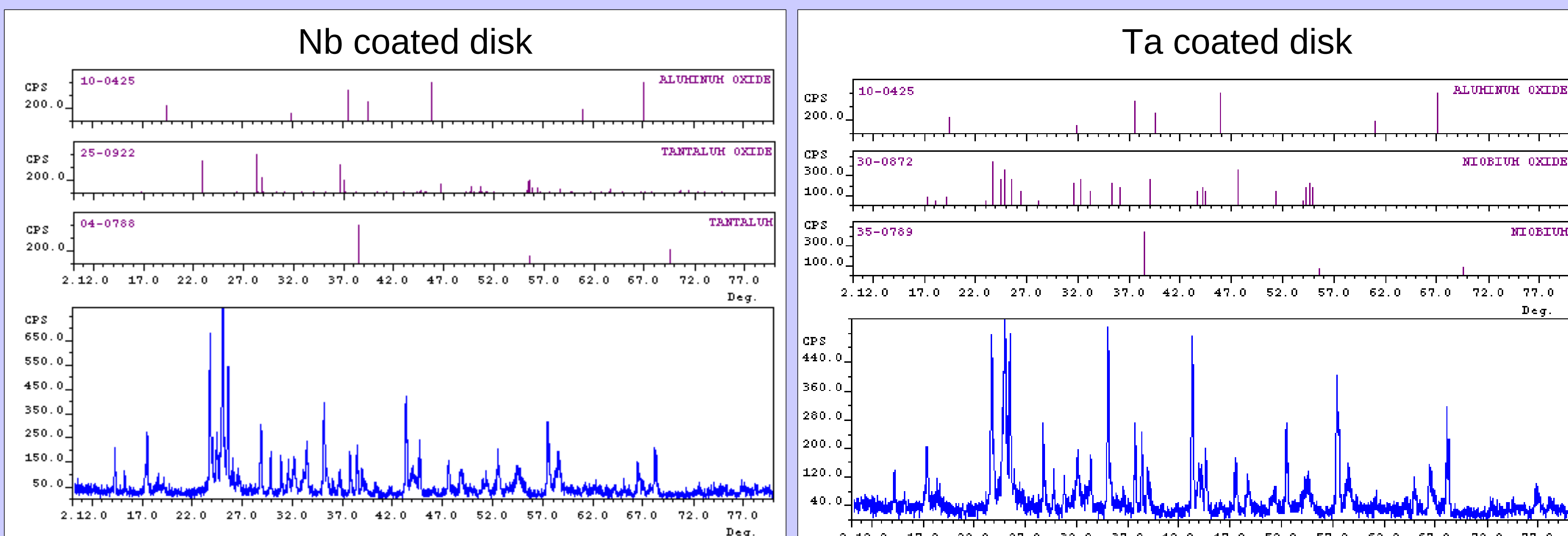
Ceramic disks:

a) blank

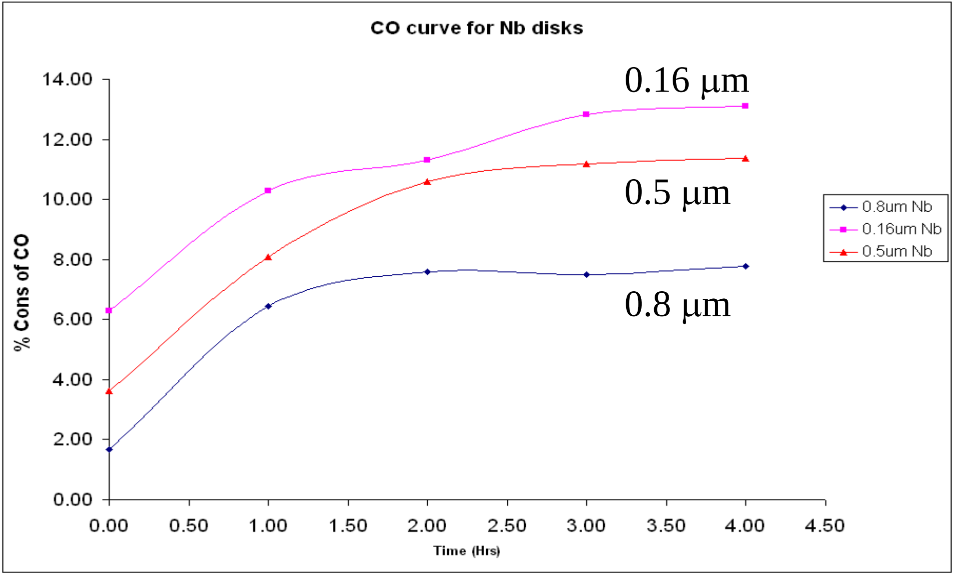
b) Nb sputter deposited

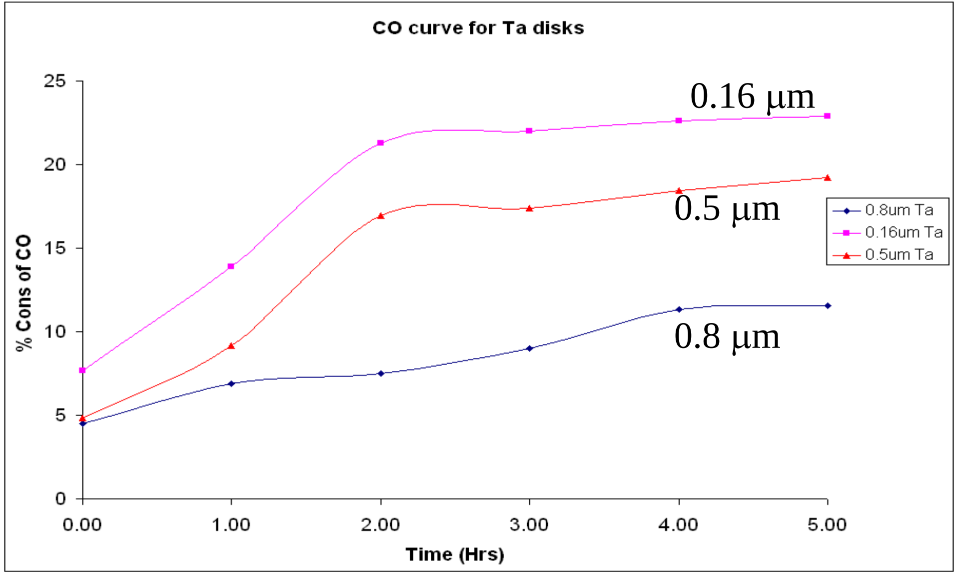


PXRD of sputtered Nb and Ta disk surfaces



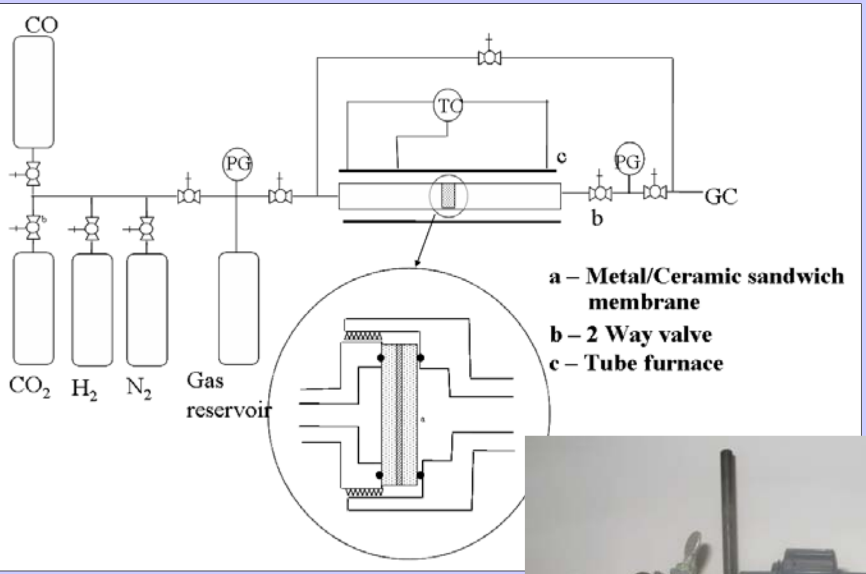
PXRD of aluminothermically coated Nb and Ta disk surfaces

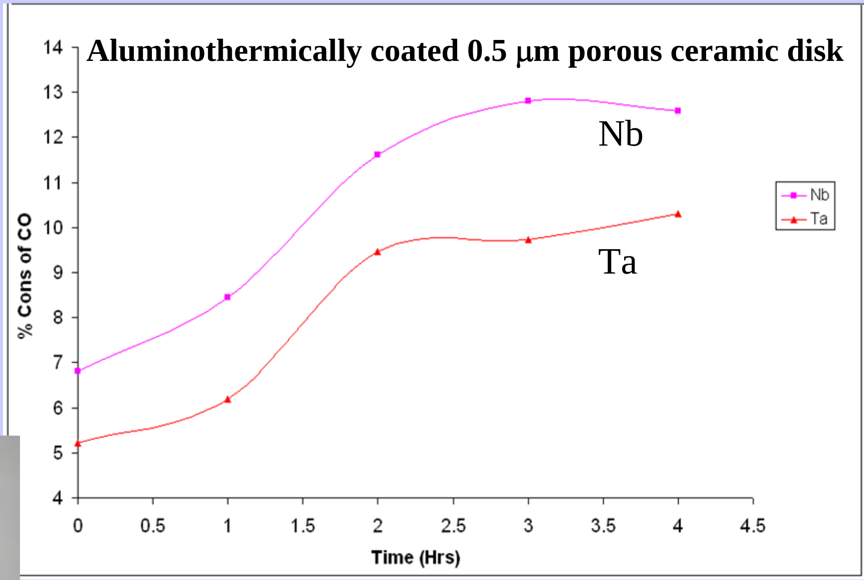




Nb sputtered disks

Ta sputtered disks





Since H_2 is difficult to quantify in GC, we assumed H_2 permeability is inversely proportional to the %CO concentration.

Conclusions

We have set up the facilities for preparing nanocatalysts using sol-gel/oil-drop methods and made Cu-Ce-Ni/Al_2O_3 granular WGS catalysts.

Gas-phase flow and batch reactors were designed for optimizing catalytic reaction parameters and to study of the reaction kinetics. Among LT-WGS catalysts Cu(7%)Ce(8%)/alumina and among HT-WGS catalysts Ni(3.5%)Cu(3.5%)Ce(8%)/alumina gave the best CO conversion.

We have designed a H_2/CO/CO_2 permeability testing system, and Nb/Ta thin film membranes were prepared using sputtering and aluminothermic reduction techniques.

XRD of sputtered disks show metallic phases of Nb and Ta films and Al_2O_3 disk while chemically coated disks shows more phases: M, M_2O_5, Al_2O_3 and alloy.

Sputtered disks show increasing H_2 permeability with porosity of the ceramic disk. Nb has a higher permeability than Ta at a given disk porosity in sputtered membranes, but chemically coated disks showed lower H_2 permeability for Nb.

Future Plans

- Prepare Cu-Ce-Fe/alumina WGS nanocatalysts
- Prepare Cu-Ce-Ni/silica catalysts with various compositions and compare to the alumina supported catalysts.
- Design a stainless steel testing system for permeability studies at higher pressure/temperature.