Simultaneous Removal of NO_x and Hg in a Low Temperature Selective Catalytic and Adsorptive Reactor

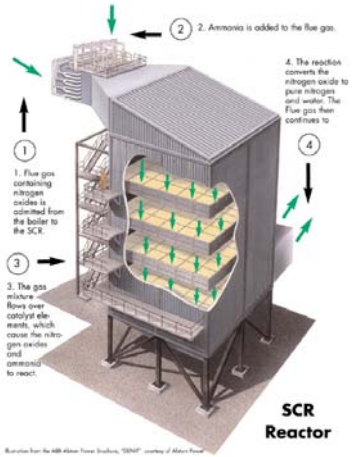
DoE Grant No. DE-FG26-06NT42712

Lei Ji, Juan He, Mohammed Khan,
Peter G. Smirniotis, Stephen W. Thiel, and Neville G. Pinto

Department of Chemical & Materials Engineering
University of Cincinnati
Cincinnati, OH, 45221

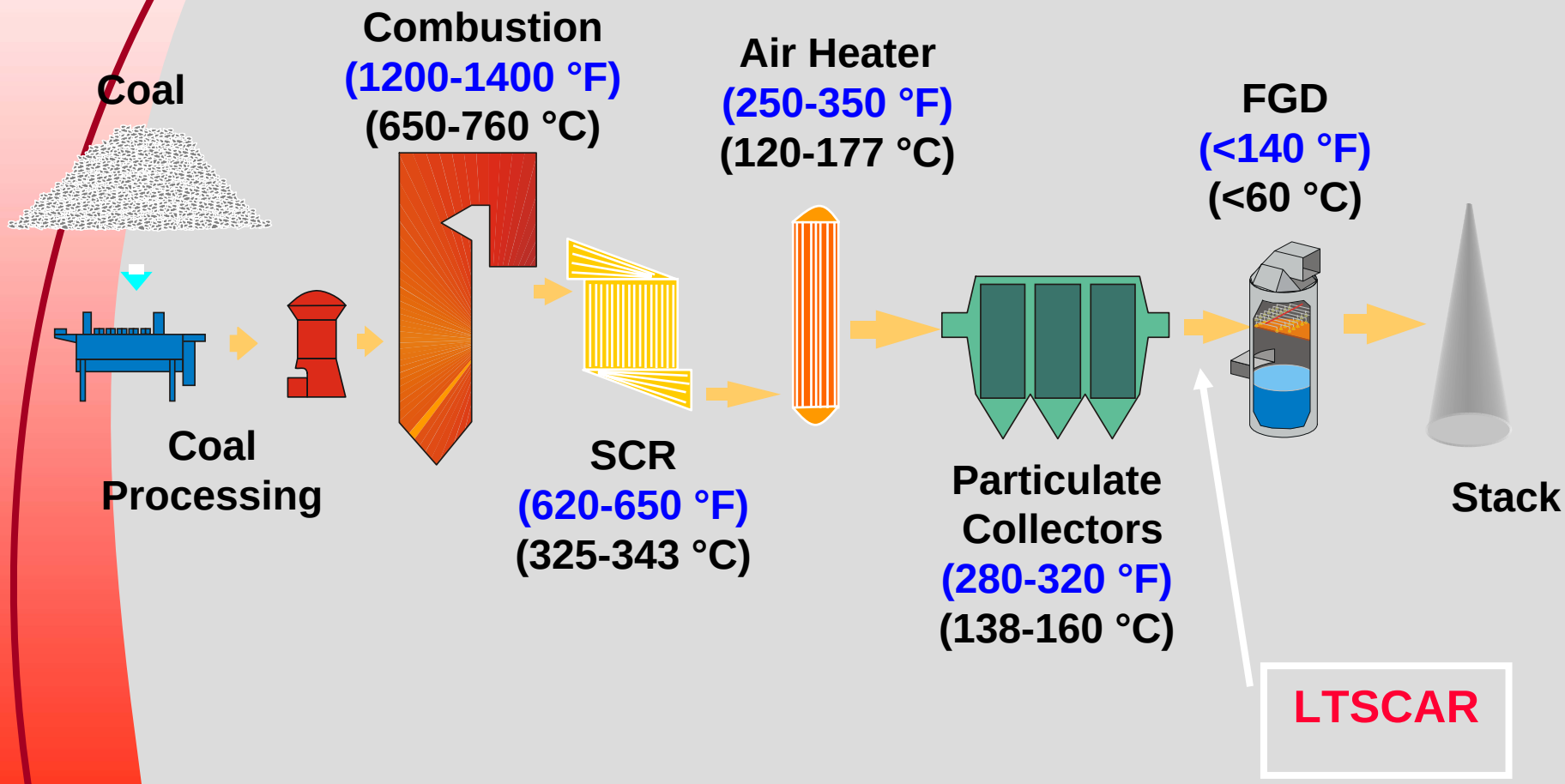
Project Goal

Simultaneous Removal of NO_x and Hg at Low T



Low Temperature Selective Catalytic and Adsorptive Reactor (LTSCAR)

Location of LTSCAR



UNIVERSITY OF Cincinnati

Project Objectives

- Develop catalysts for low temperature NO_x removal with carbon monoxide as reductant
- Engineer SO_2 and H_2O tolerance into catalyst
- Tailor adsorbents for the capture of Hg^0 and Hg^{2+} at high capacity in a LTSCAR
- Study speciation of Hg in LTSCAR
- Evaluate performance of the LTSCAR in simulated coal-fired utility flue gases

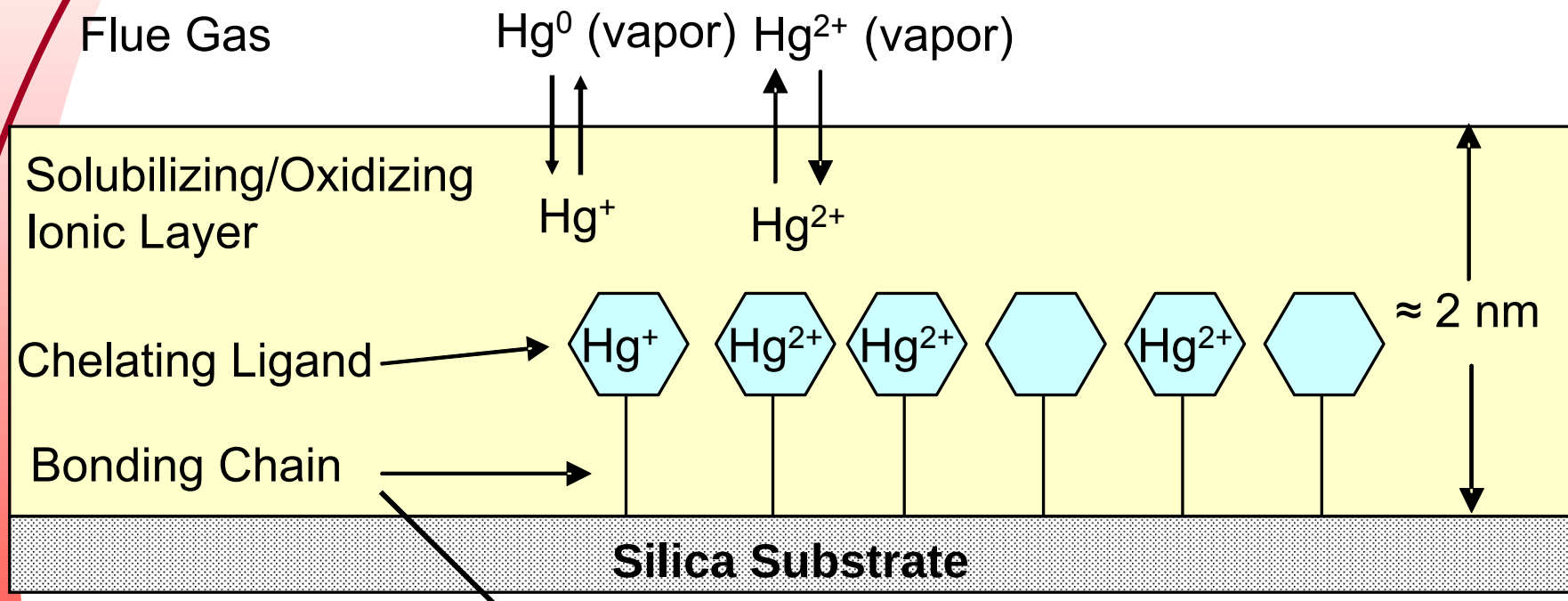
Project Objectives

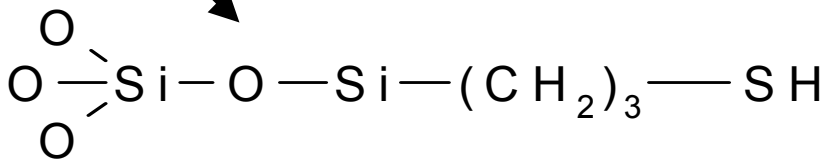
- Develop catalysts for low temperature NO_x removal with carbon monoxide as reductant
- Engineer SO_2 and H_2O tolerance into catalyst
- Tailor a novel existing adsorbent for the capture of Hg^0 and Hg^{2+} at high capacity in a LTSCAR
- Study speciation of Hg in LTSCAR
- Evaluate performance of the LTSCAR in simulated coal-fired utility flue gases

Thermally Stable Chelating Adsorbents for Hg^{2+} and Hg^{0} Capture

Adsorption Group:
Lei Ji, Juan He
Stephen W. Thiel, Neville G. Pinto

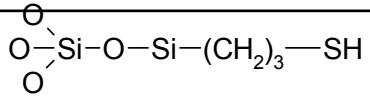
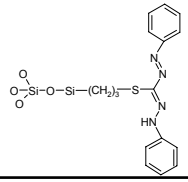
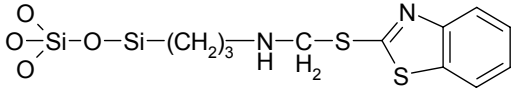
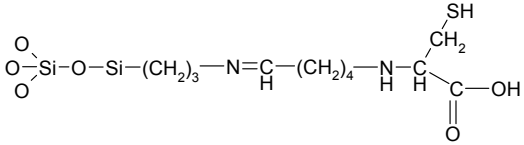
Chelating Adsorbent



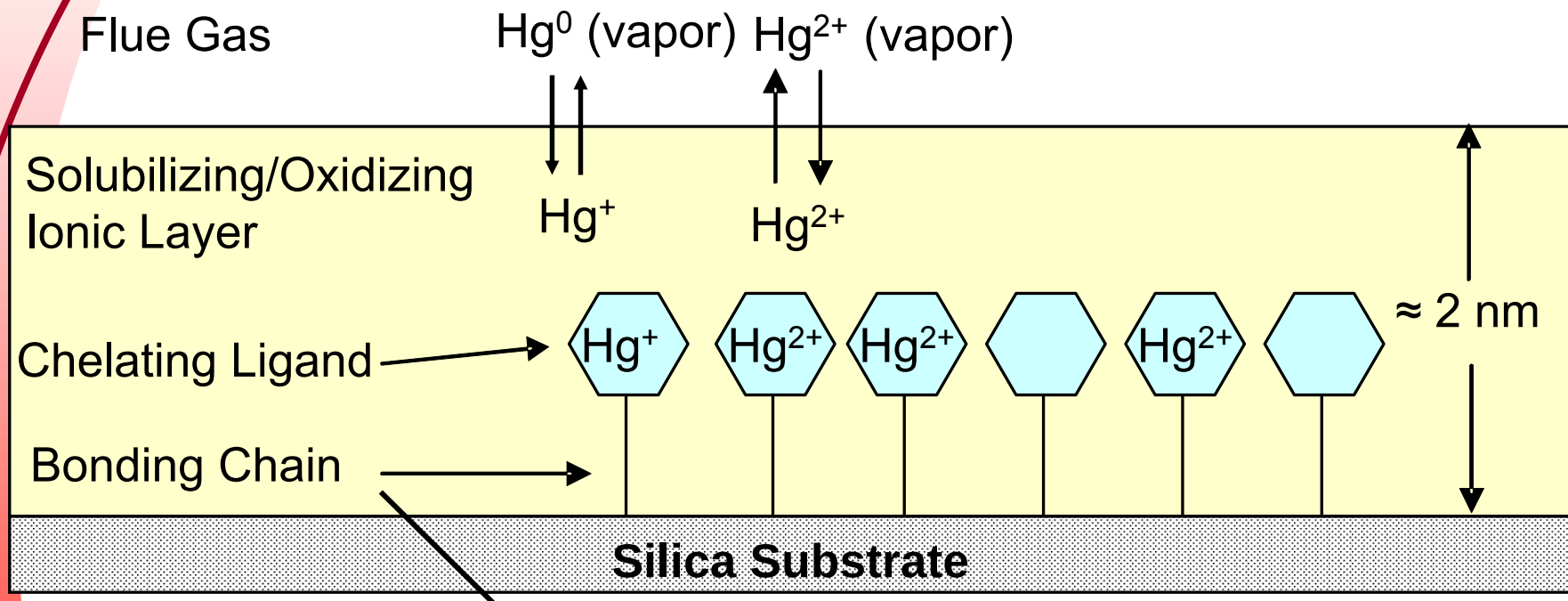


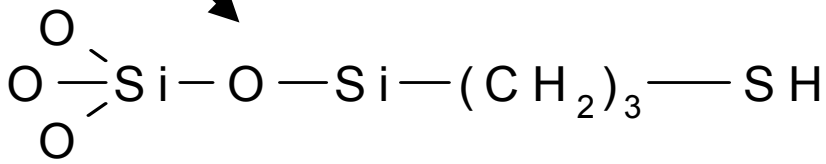
MPTS (3-mercaptopropyltrimethoxysilane)

Silica with Bonded Chelating Ligands

Chelating Ligand	Chemical Structure	Surface Coverage (mmol/g)	BET Area (m^2/g)	T_{up} (°C)
Pure Silica		-	291	-
MPTS		0.58	259	200
CPTS-DZ		0.17	215	180
APTS-MBT		0.22	245	190
Cysteine		0.33	235	135

Chelating Adsorbent

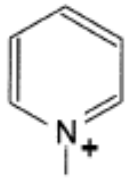




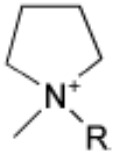
MPTS (3-mercaptopropyltrimethoxysilane)

Ionic Liquids Screened

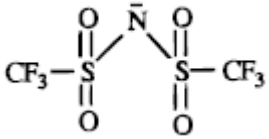
1-butyl-3-methylimidazolium
[bmim]



N-butylpyridinium
[bpy]



N-butyl-*N*-methylpyrrolidinium
[bmpro]

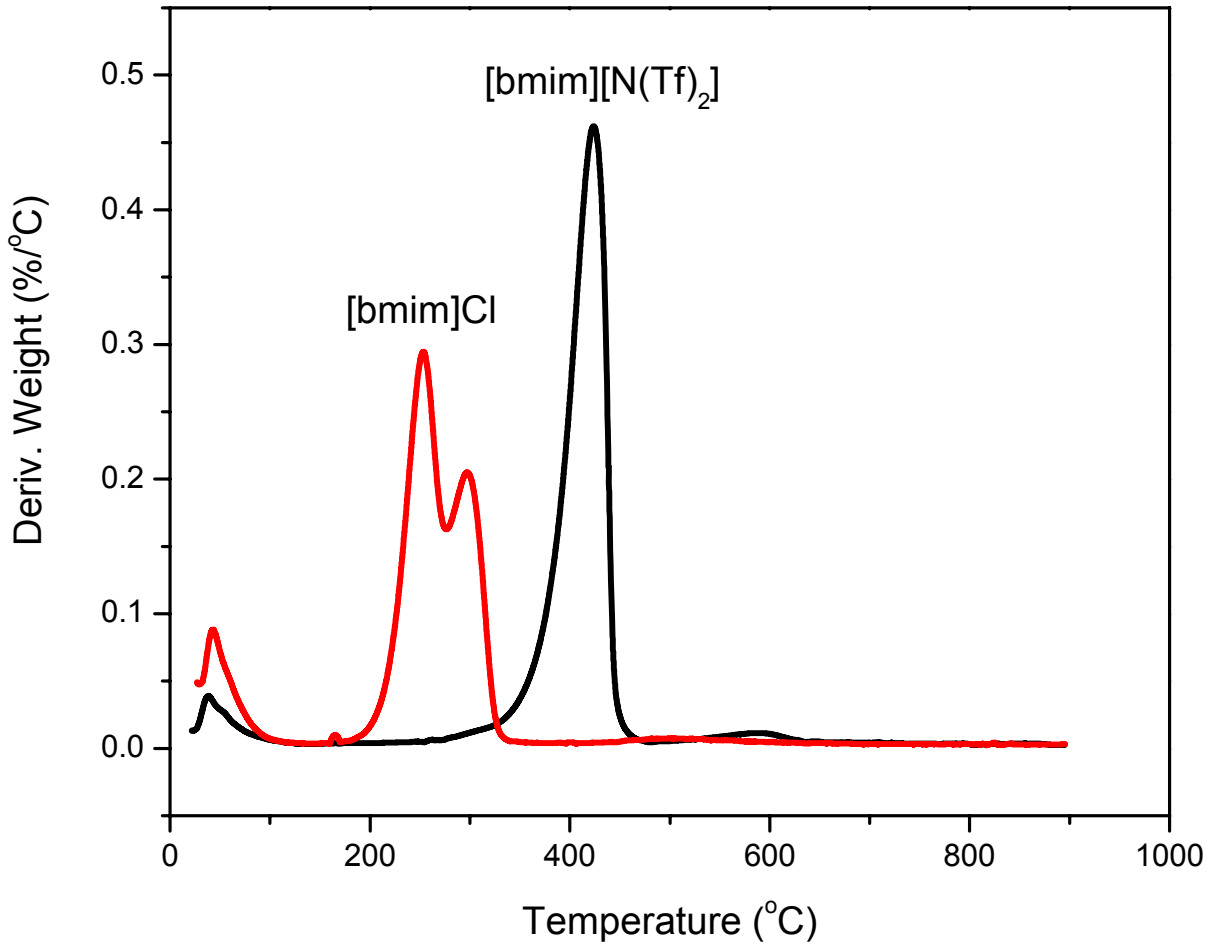


bis(trifluoromethane sulfonyl)imide
[$N(TF)_2$]

Cl^-

Chloride

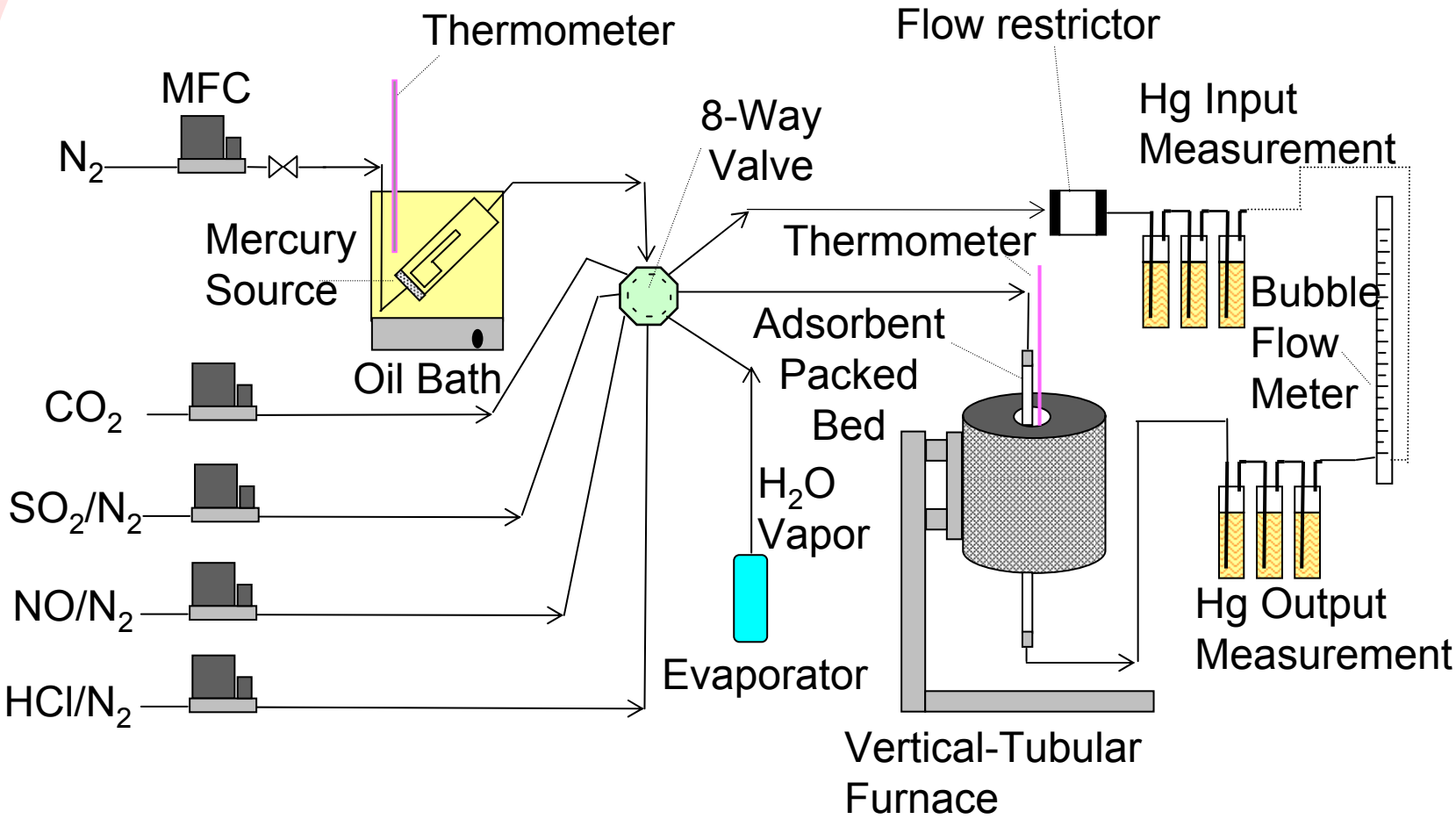
Thermal Stability



Thermal Stability

	Upper Temperature Limit (°C)	
	$N(Tf)_2$	Cl
[bmpro]	300	190
[bmim]	325	200
[bpy]	325	190

Apparatus (Fixed Bed)

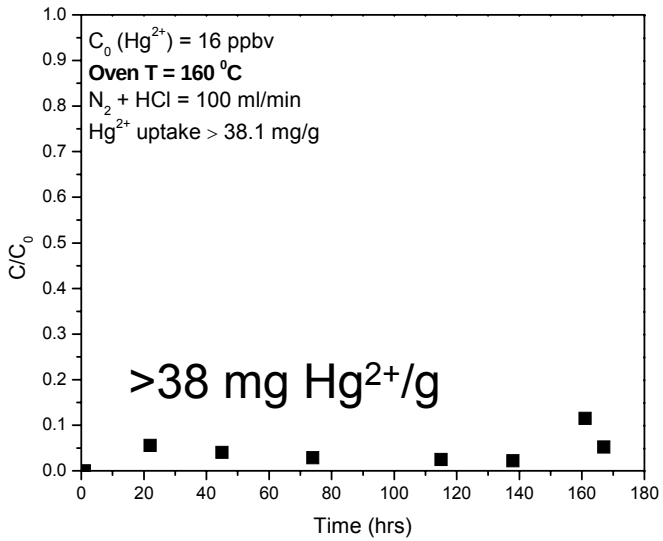


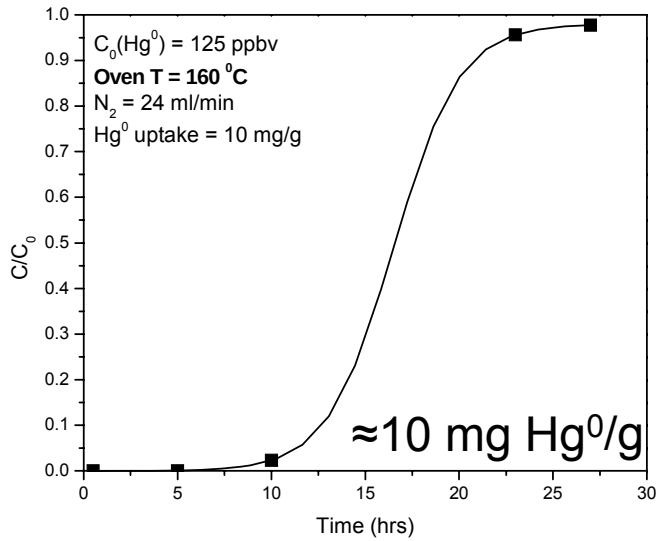
Mercury Capture – RTIL Coated Silica

	Hg^0 Capture (mg Hg^0/g Adsorbent)		**Hg^{2+} Capture** (mg Hg^{2+}/g Adsorbent)	
	$N(Tf)_2$	Cl	$N(Tf)_2$	Cl
[bmpro]	2.7	1.2	0	11
[bmim]	1.2	2.2	7.1	33
[bpy]	1.3	3.0	1.9	6.2

Adsorbent: 3.2 mg silica coated with 25% RTIL
Op. Temp: 160°C
Carrier Gas: 24 ml/min N_2 (Hg^0)
100 ml/min N_2 + 150 ppm HCl (Hg^{2+})

Mercury Capture - Fully Functionalized Adsorbent





Adsorbent : 3.2 mg of 25 wt% [bmim]Cl on MPTS-silica
Op. Temp: 160°C
Carrier Gas: 24 ml/min N2 (Hg0)
100 ml/min N2 + 150 ppm HCl (Hg2+)
Separate Experiments

UNIVERSITY OF Cincinnati

Summary

- Nanostructured chelating adsorbents effective for oxidized and elemental Hg capture at LTSCR temperatures
- Ionic liquid coatings alone are effective for Hg capture
- [bmim]Cl on MPTS-silica can capture both elemental and oxidized mercury
- Combined capture experiments in progress

Next Steps

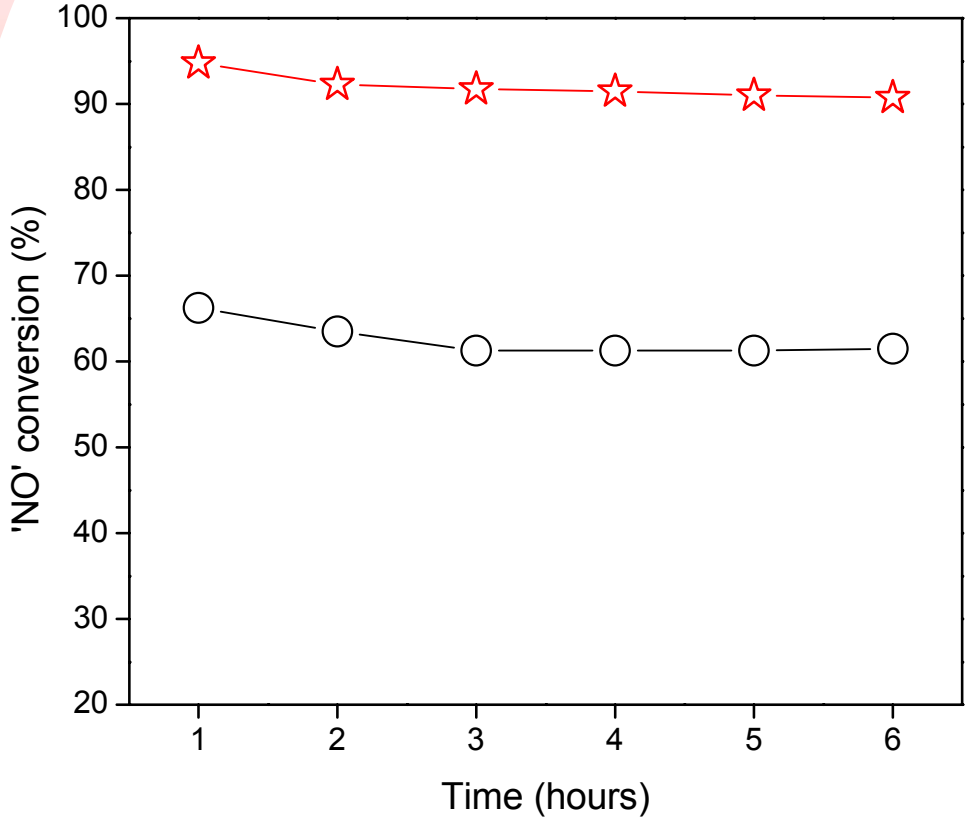
- Combined capture experiments
- Integration with LTSCR
  - Multiple beds
  - Mixed beds

CeO_2-TiO_2 Supported MnO_X DeNOx Catalyst for Hg^0 Capture

Adsorption Group
Lei Ji, Juan He, Stephen W. Thiel, Neville G. Pinto

Catalysis Group
Mohammed Khan, Peter G. Smirniotis

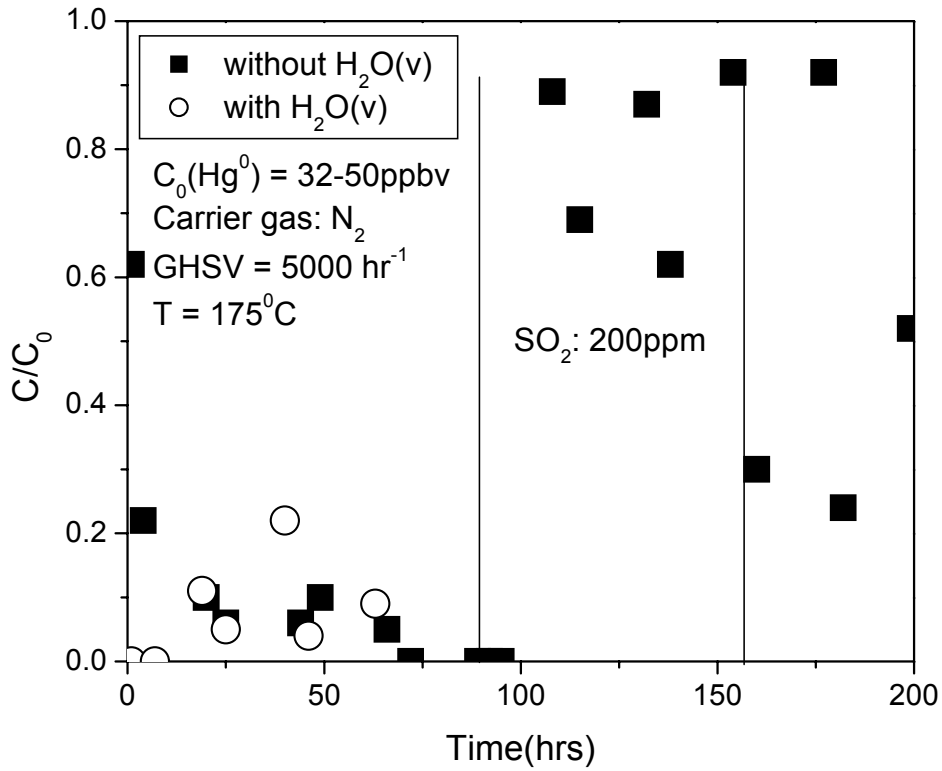
SCR of NO Using CO as Reductant



(○) 175 ^{0}C; (☆) 200 ^{0}C;
NO = CO= 400 ppm;
Oxygen = 2 vol%

Catalyst: 10 wt% MnO_2/TiO_2

Effect of SO_2 and H_2O on Hg^0 Capture



Adsorbent: 10 wt% MnO_2/TiO_2

12 mg Hg^0/g catalyst in absence of SO_2

New Catalyst/Adsorbent

- SO_2 sensitivity is key problem
- Strategy:
  - Add ceria to support to capture SO_2 and protect active sites
  - Look first at SO_2 and Hg adsorption
- 1:1 CeO_2-TiO_2
  - Co-precipitated – true mixed oxide
- 20 % MnO_x

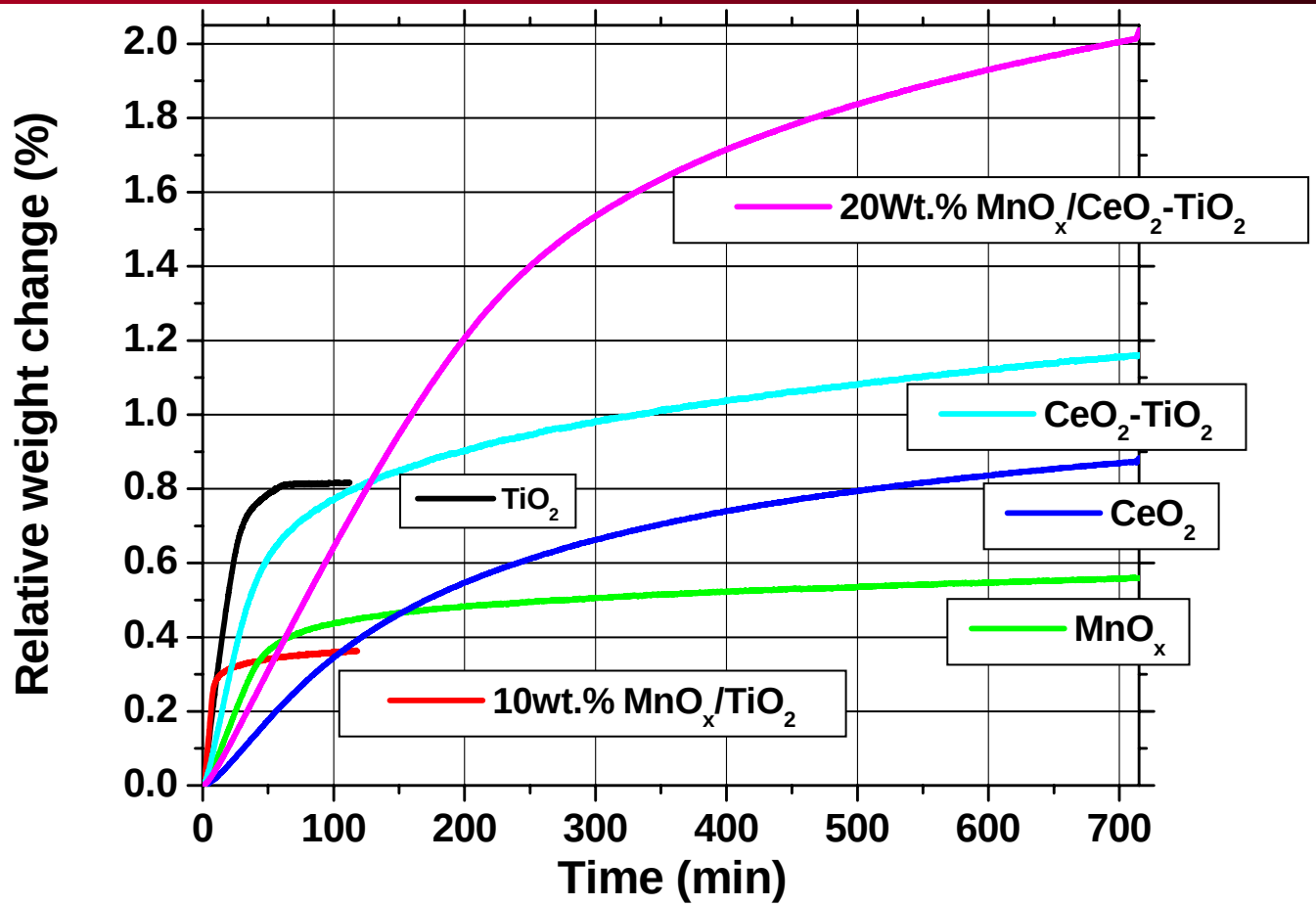
New Catalyst/Adsorbent Particle Characteristics

Sample	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Avg. Pore Dia. (Å)
TiO_2	309	0.36	44
20wt.% MnO_x/TiO_2	204	0.23	64
CeO_2-TiO_2 (1:1)	133	0.33	72.7
20wt.% MnO_x/CeO_2-TiO_2	103	0.23	67.5

SO_2 Uptake

- Measured using TGA
- T = 175°C
- SO_2 concentration = 100 ppm

SO_2 Uptake

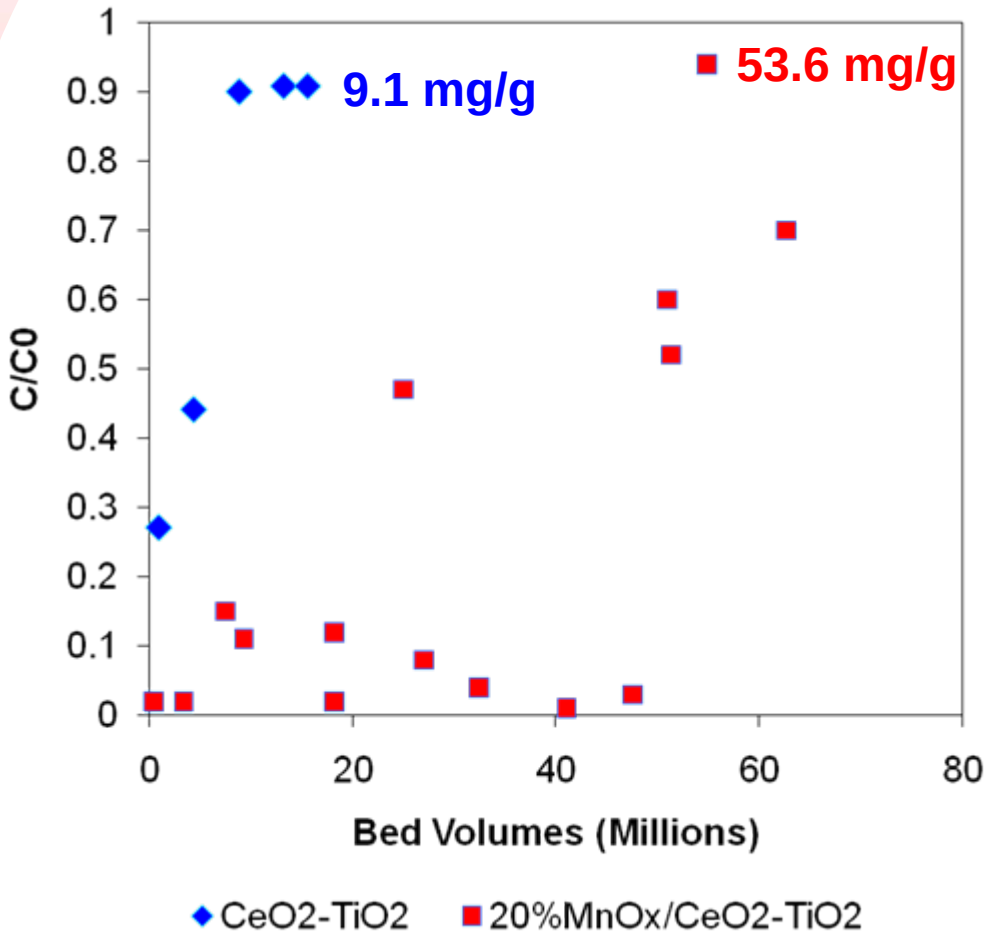


175°C, 100 ppm SO_2

XPS Characterization of Catalyst

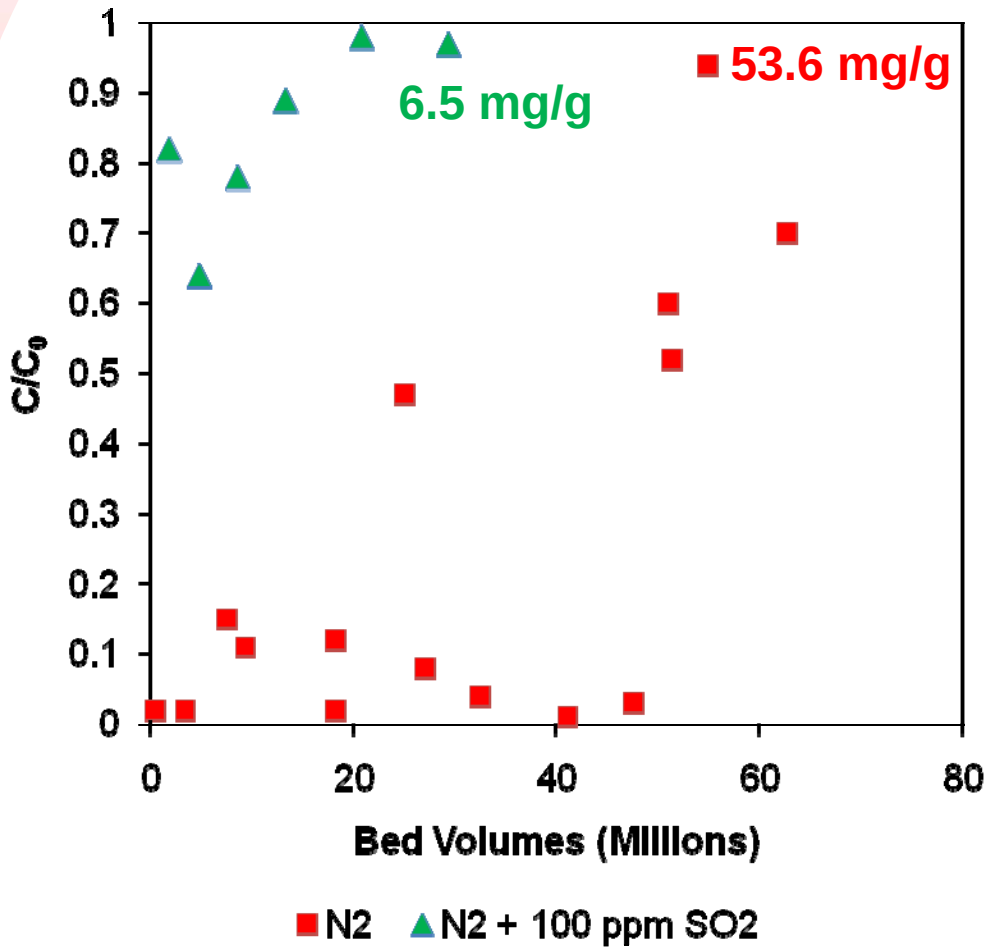
- Oxidation states as expected
  - Ce(IV) and Ti(IV)
  - Mn(III) and Mn(IV)
- No S detected in samples exposed to SO_2
  - SO_2 effects not due to sulfate formation
  - Working hypothesis:
    - Physisorption for SO_2
    - Desorption occurs due to vacuum required for XPS

Hg^0 Capture Using 20% MnO_x/CeO_2-TiO_2



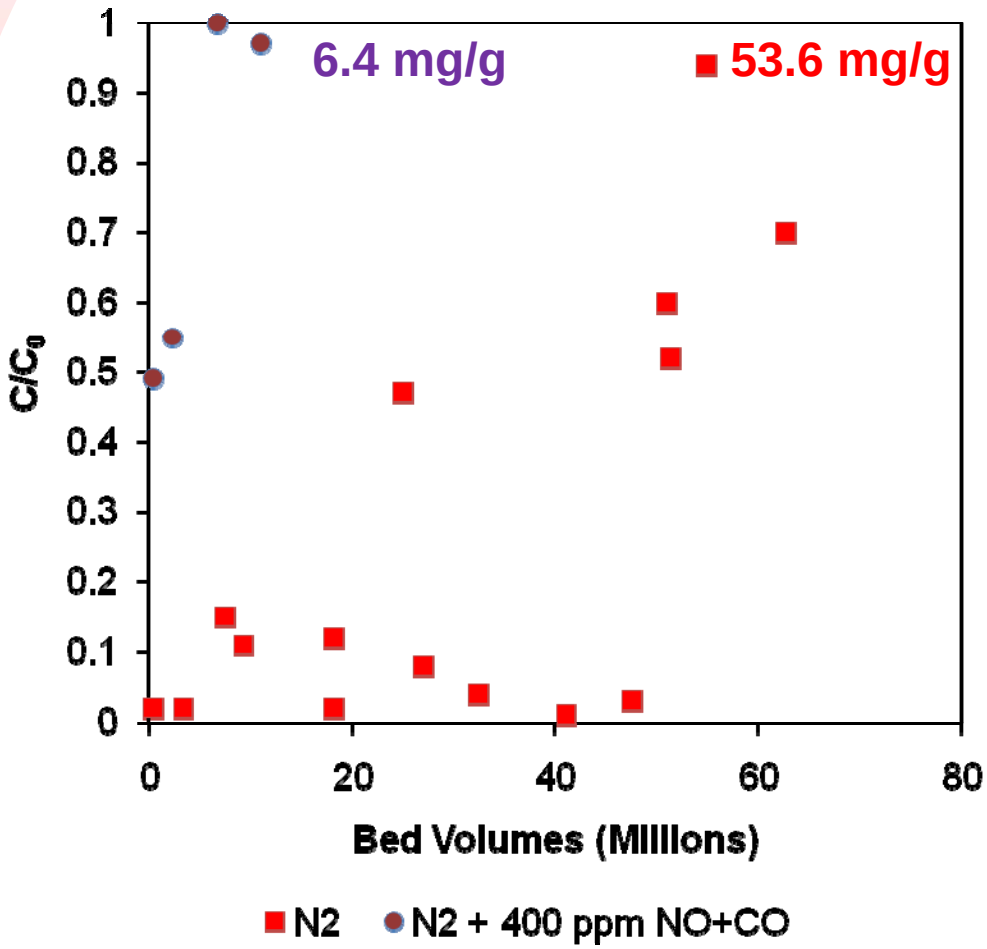
C_0 = 30-50 ppbv Hg^0
3.2 mg adsorbent
24 ml/min
175°C

Effect of SO_2 on Hg^0 Capture



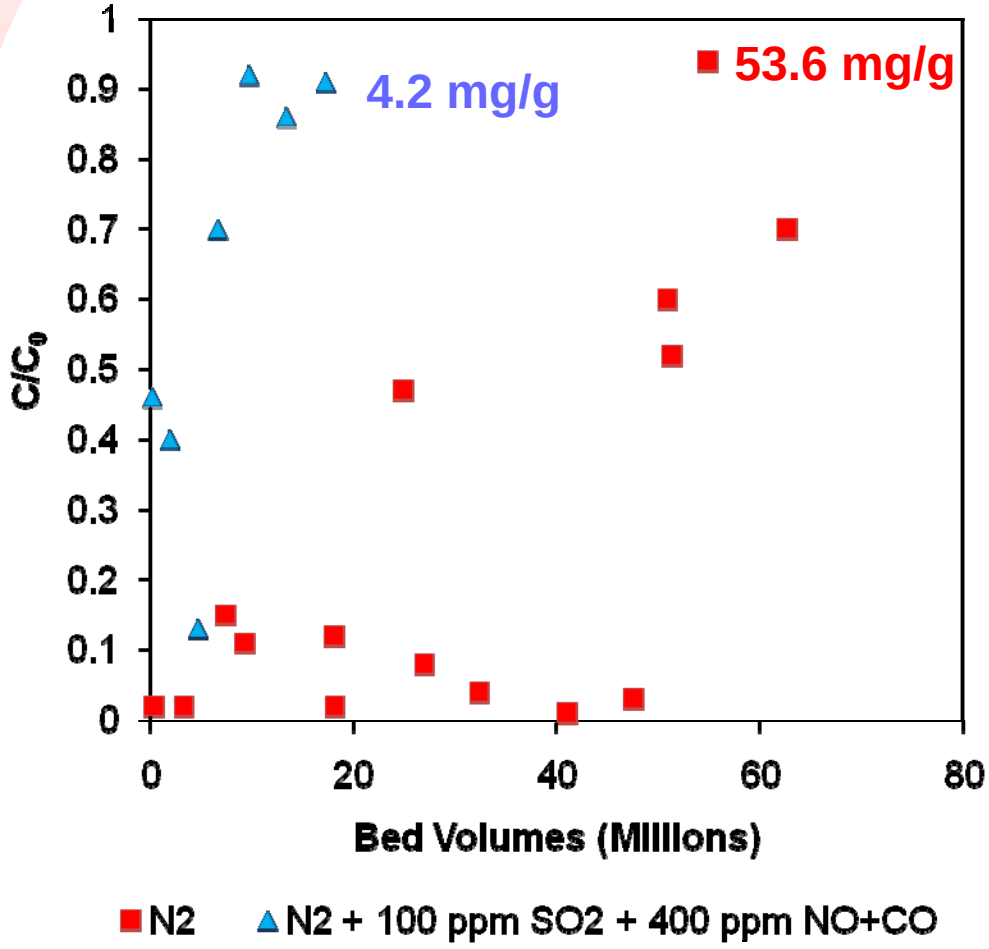
C_0 = 30-50 ppbv Hg^0
3.2 mg adsorbent
24 ml/min
175°C

Effect of NO+CO on Hg^0 Capture



C_0 = 30-50 ppbv Hg^0
3.2 mg adsorbent
24 ml/min
175°C

Effect of NO+CO+SO_2 on Hg^0 Capture



C_0 = 30-50 ppbv Hg^0
3.2 mg adsorbent
24 ml/min
175°C

Summary of Mercury Capacities

Catalysts	Mercury capacities (N_2)
10% $MnOx/TiO_2$	12.5 mg/g
20% $MnOx/CeO_2$-TiO_2	53.6 mg/g
CeO_2-TiO_2	9.1 mg/g

Effect of different gases 20% $MnOx/CeO_2$-TiO_2	Mercury capacities
N_2	53.6 mg/g
N_2 100 ppm SO_2	6.5 mg/g
N_2 400 ppm CO + 400 ppm NO	6.4 mg/g
N_2 CO NO SO_2	4.2 mg/g

Summary

- Significant mercury capacity was observed at 175°C and inert atmosphere using 20 wt % MnO_x/CeO_2-TiO_2 catalyst
- SO_2, NO + CO have adverse effect on mercury capture
- More SO_2 tolerant than MnO_x/TiO_2

Next Steps

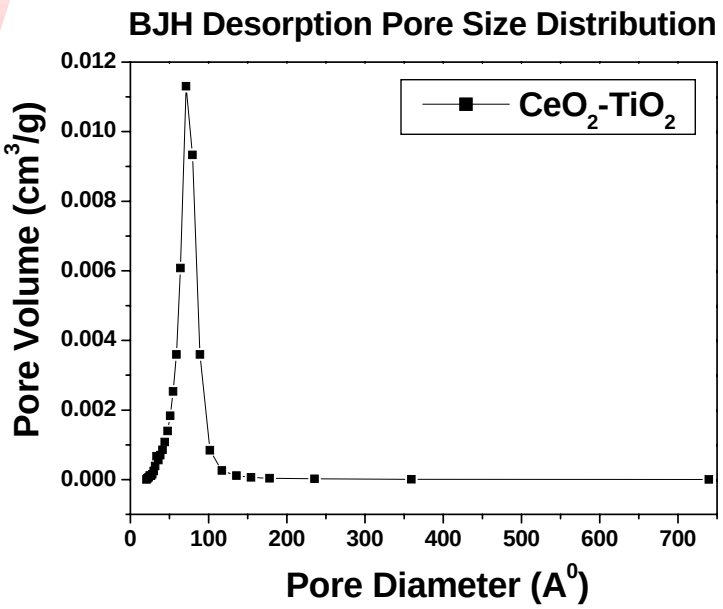
- Continue addressing sulfur tolerance
- LTSCR performance
- Combined LTSCR/Hg^0 capture

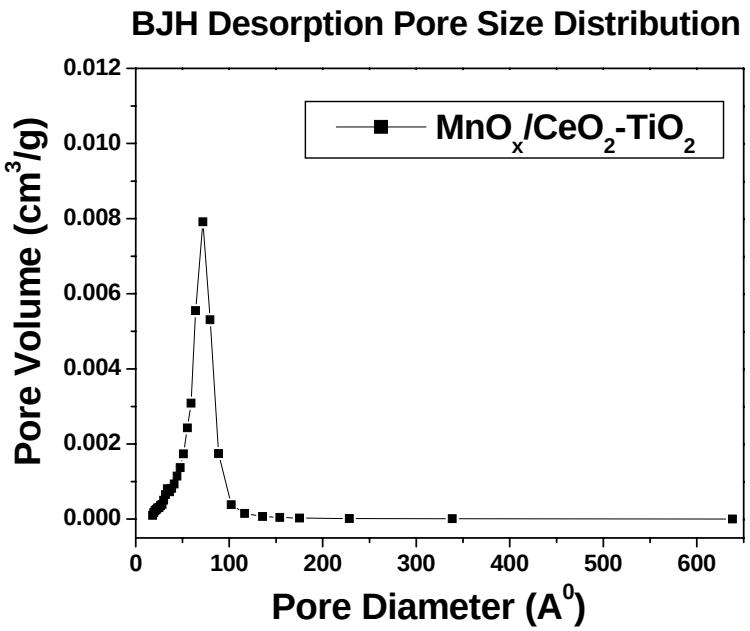
Acknowledgements

- US Department of Energy (Grant No. DE-FG26-06NT42712)
- Dr. James Boerio for assistance with the XPS analysis
- University of Cincinnati

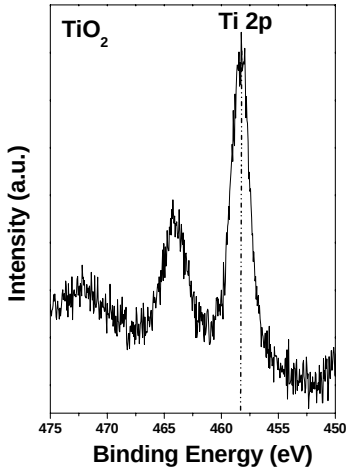
Supporting Material

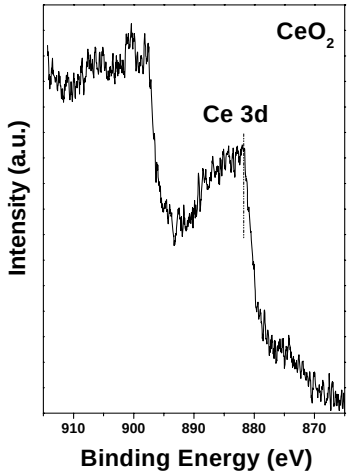
Physical Characteristics

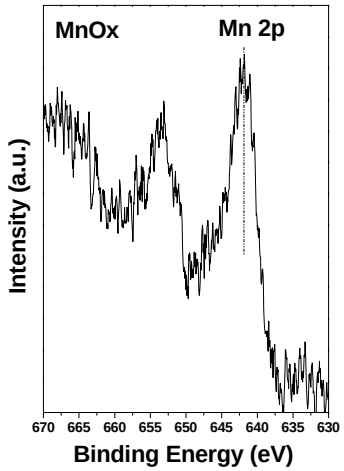


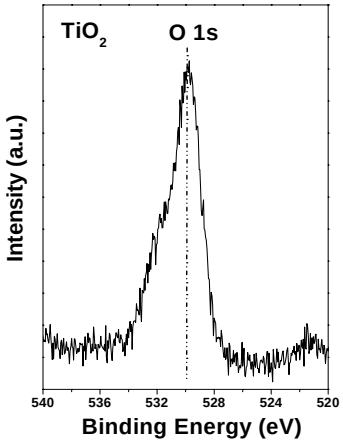


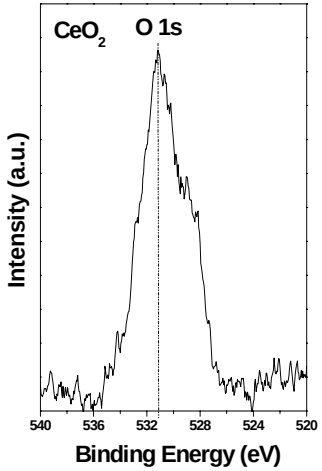
XPS: Pristine TiO_2, CeO_2, MnO_2

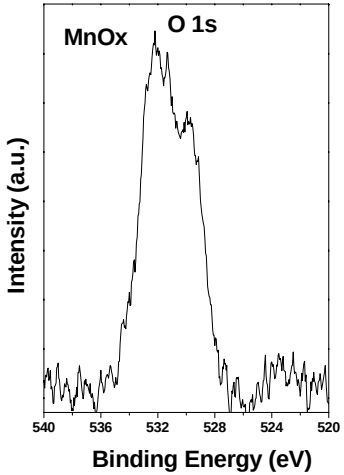




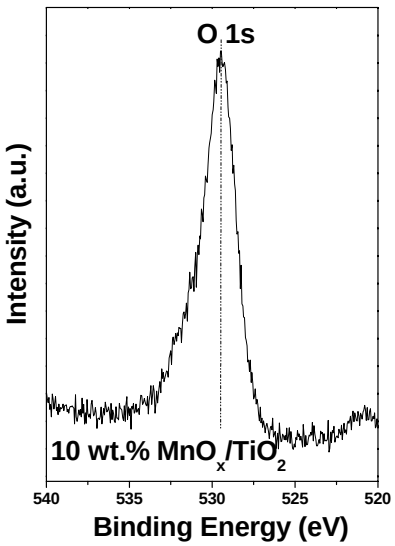


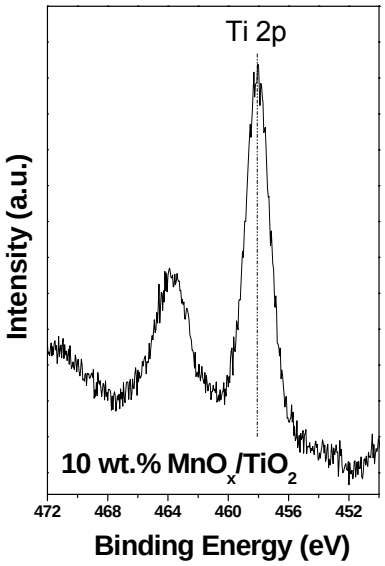


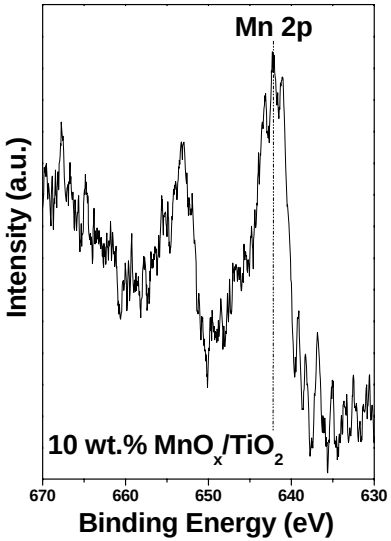




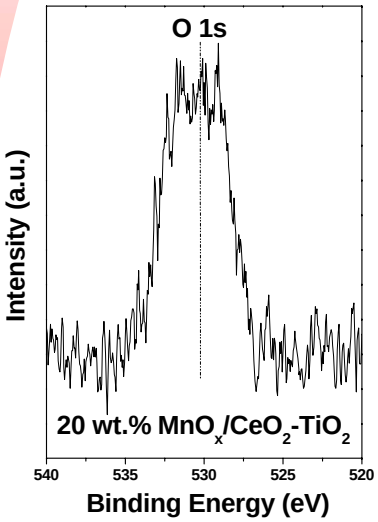
XPS: 10 wt % MnO_x/TiO_2

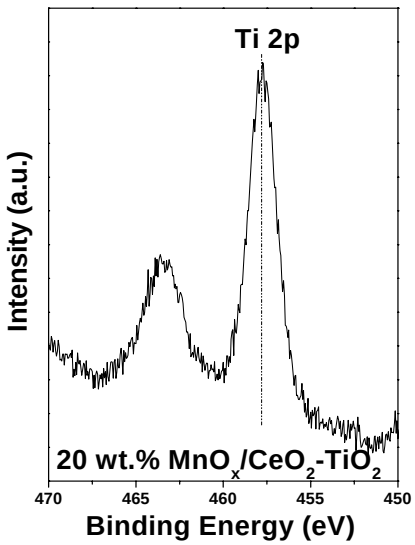


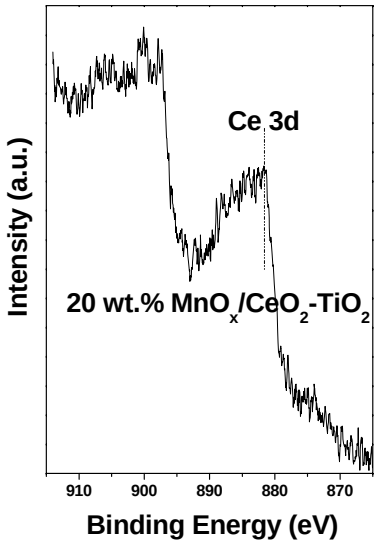


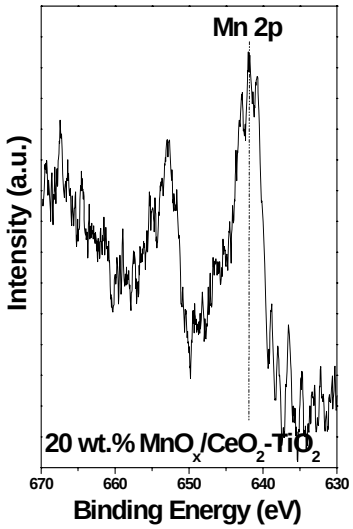


XPS: 20 wt % MnO_x/CeO_2-TiO_2









XPS: Core Level Binding Energies

Sample	Binding energy (eV)			
	O 1s	Ti 2p	Mn 2p	Ce 3d
TiO_2	529.8	458.3	-	-
MnO_x	532.2	-	641.9	-
CeO_2	531.2	-	-	881.8
CeO_2-TiO_2	530.35	457.6	-	882
10 wt.% MnO_x/TiO_2	529.5	458	642.2	-
20 wt.% MnO_x/CeO_2-TiO_2	530.2	457.7	641.9	881.5