

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

Hong Lu, Lei Ji,

Peter G. Smirniotis and Neville G. Pinto

Department of Chemical & Materials Engineering

University of Cincinnati, Cincinnati, OH 45221-0012

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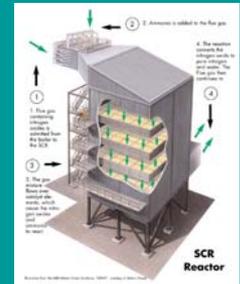
Objective and Rationale

Catalysis Group (Peter G. Smirniotis)
Promising Catalysts for NO_x Removal

Adsorption Group (Neville G. Pinto)
Novel Adsorbents for Hg²⁺ Removal



Goal of Collaboration
Simultaneous removal of NO_x and Hg at low T

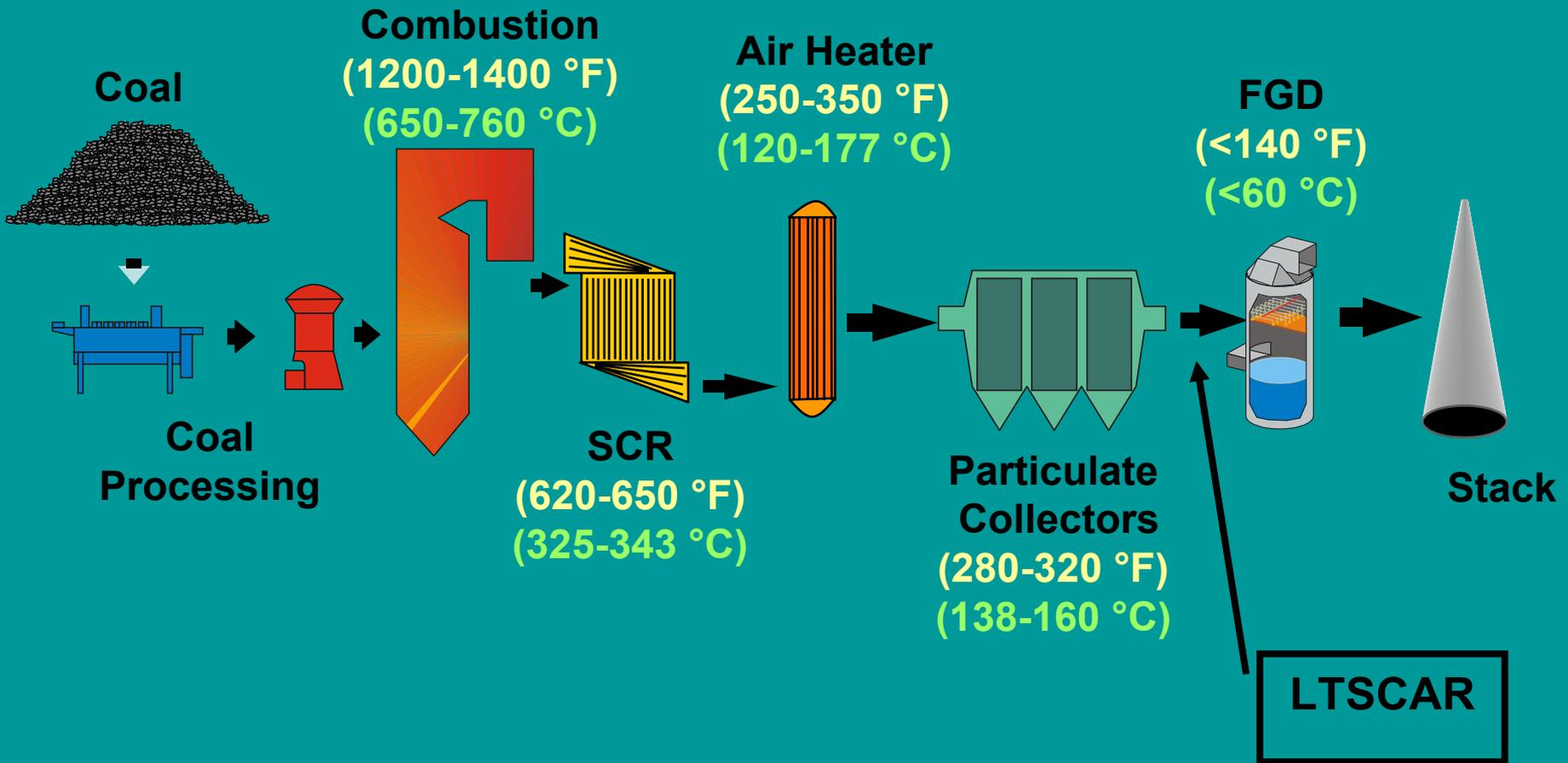


LTSCAR



- Project Objectives
- CO as reductant instead of NH₃
 - Match temperatures of operation for adsorption (↑) and catalysis (↓)
 - Capture Hg⁰ in addition to Hg²⁺ both at high capacity

Location of Low Temperature Selective Catalytic and Adsorptive Reactor (LTSCAR)



Outline

NO_x Removal

- Synthesis and characterization of NO_x catalyst
- SCR of NO with NH₃ and CO

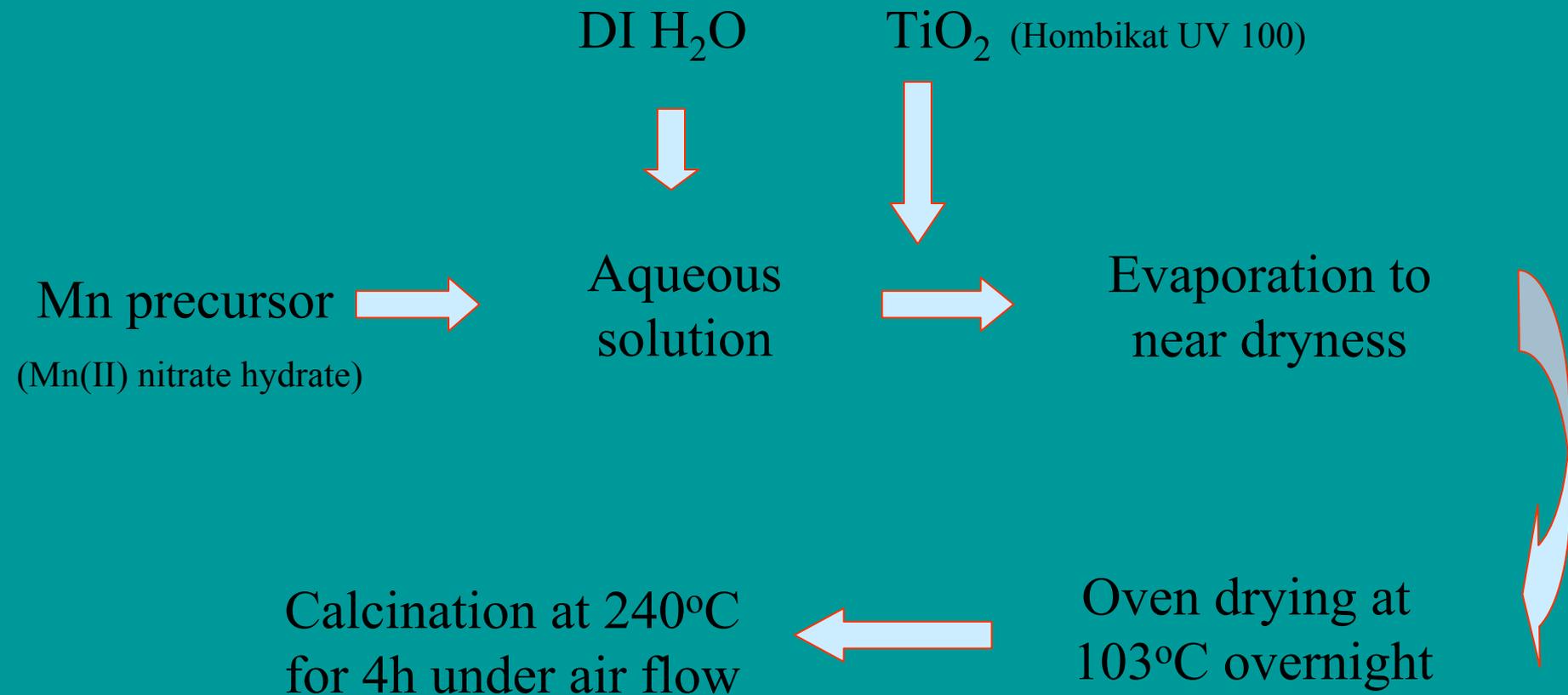
Hg Removal

- Structure of adsorbent
- Synthesis and characterization of thermally stable adsorbents
- Hg²⁺ Capture
- Hg⁰ Capture

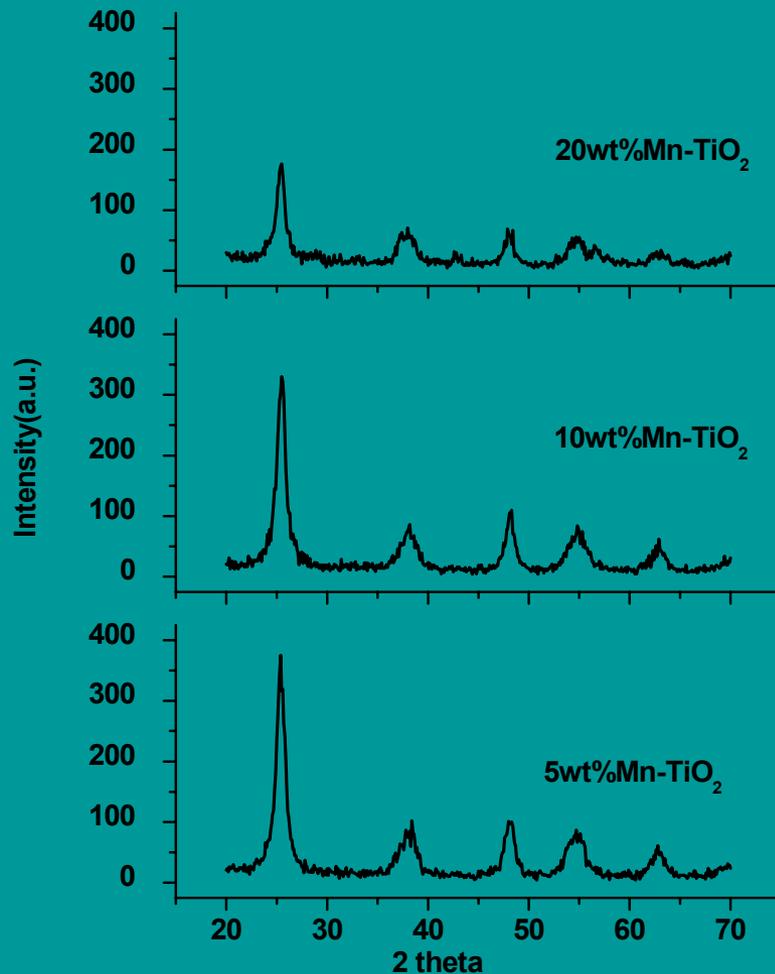
Low Temperature NO_x Removal

**Catalysis Group
(Peter G. Smirniotis)**

Catalyst Synthesis (Wet Impregnation)



XRD Spectra of Mn-TiO₂



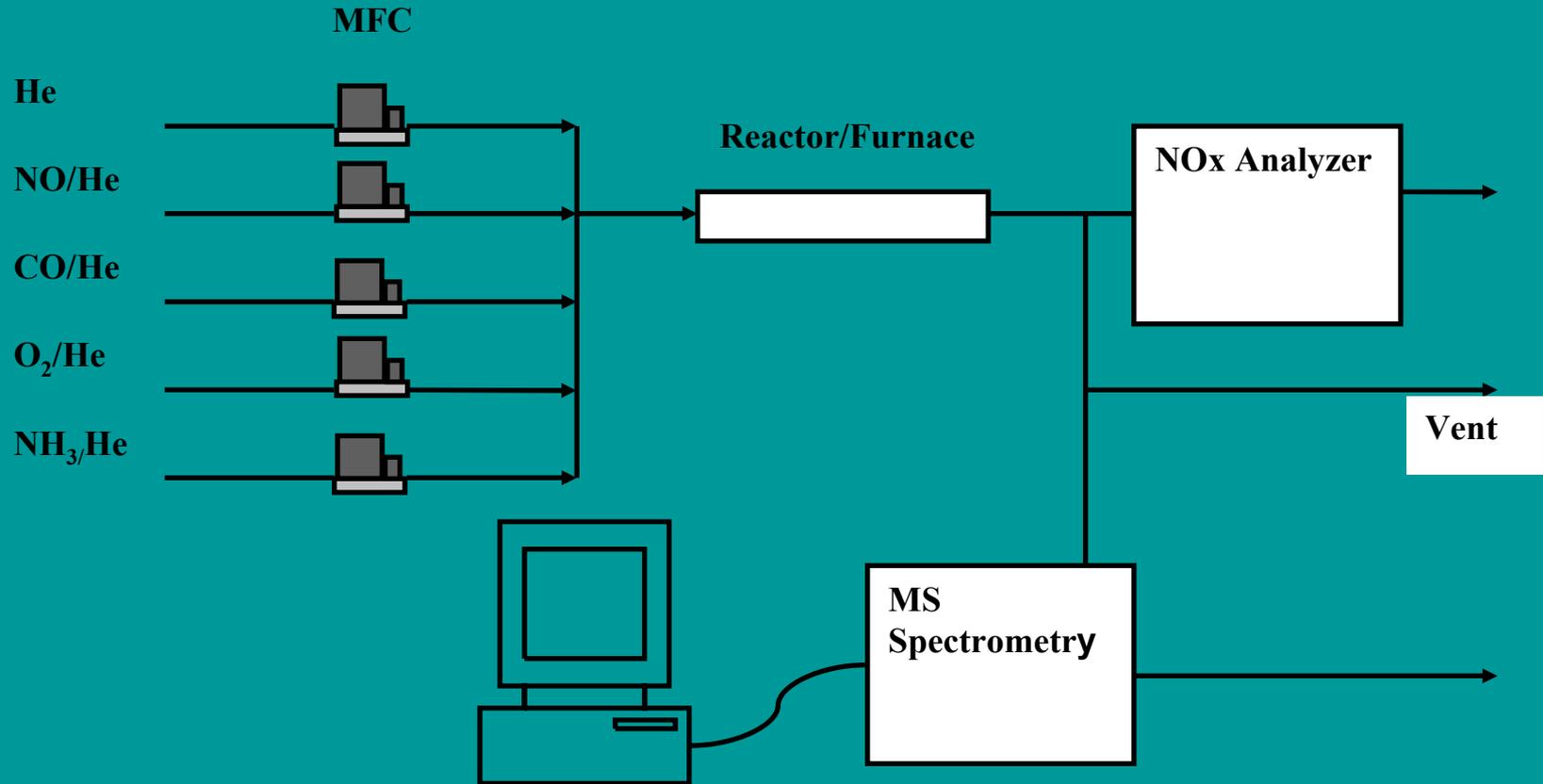
Anatase phase of titania was determined from the strongest peak located at 2 theta of 25.3°. There are no spectra that give sharp peaks that correspond to manganese oxide(s). We propose that this was caused by the high dispersion of manganese on the surface of titania. The peak intensity of titania decreased when manganese ratio of catalyst increased. This implies that manganese covered the titania surface in an amorphous state, which weakened the intensity of peaks coordinated with titania.

BET Surface Area

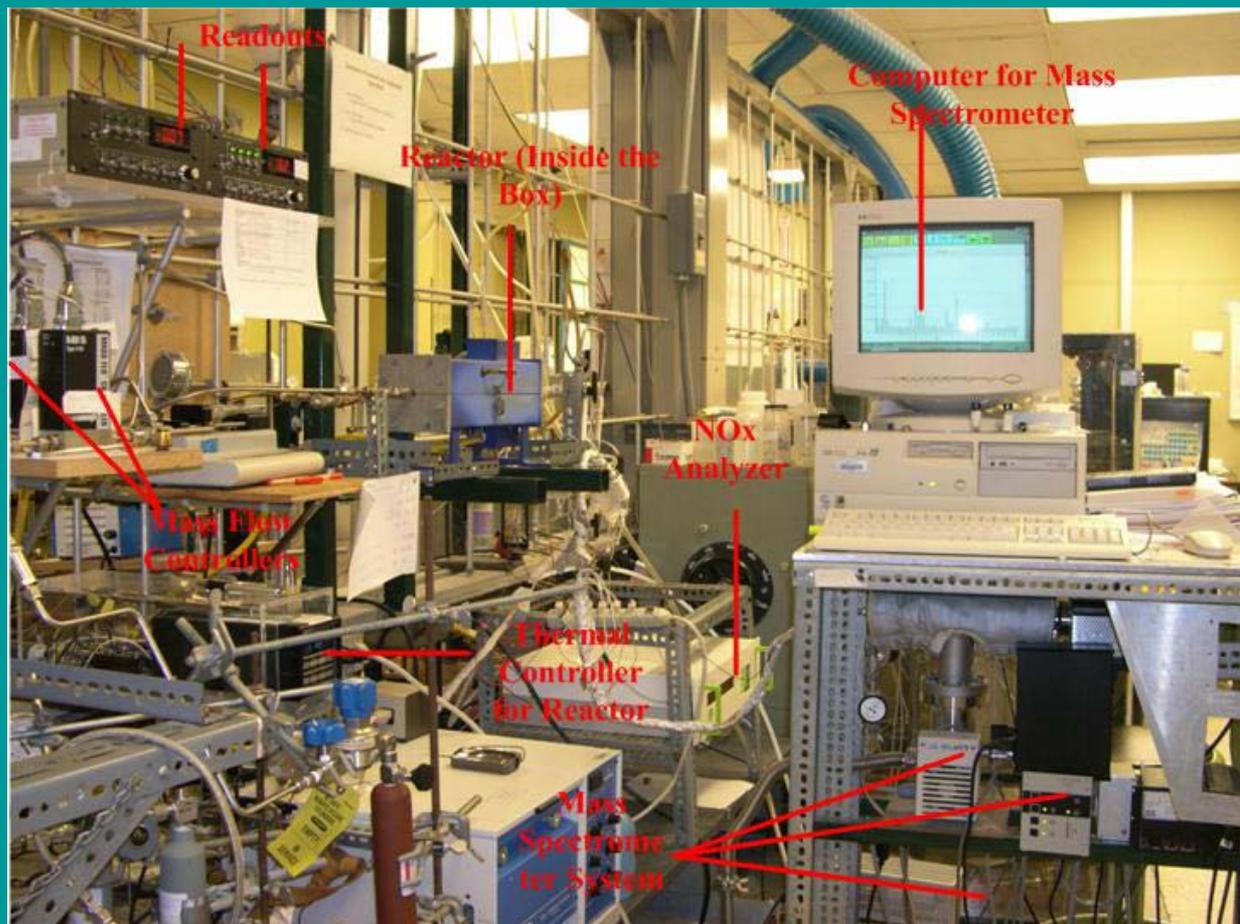
Catalyst Composition	Hombikat-TiO ₂	5wt%Mn-TiO ₂	10wt%Mn-TiO ₂	20wt%Mn-TiO ₂
BET (m ² /g)	325	259	236	198

BET surface areas of catalyst decreased with an increase in manganese. This might indicate some pore blockage by manganese.

Schematic of Experimental Setup for SCR



Experimental SCR Setup



SCR Experimental Conditions

- Fixed-bed glass reactor (I.D. 6 mm)
- 100 mg catalyst (25-45 mesh)
- Gas Mixture: NO, O₂, He
- Reductant: NH₃ or CO
- Pretreatment: 2 hours; 175°C; 40 sccm helium

Summary of Reaction Results with Ammonia as Reductant

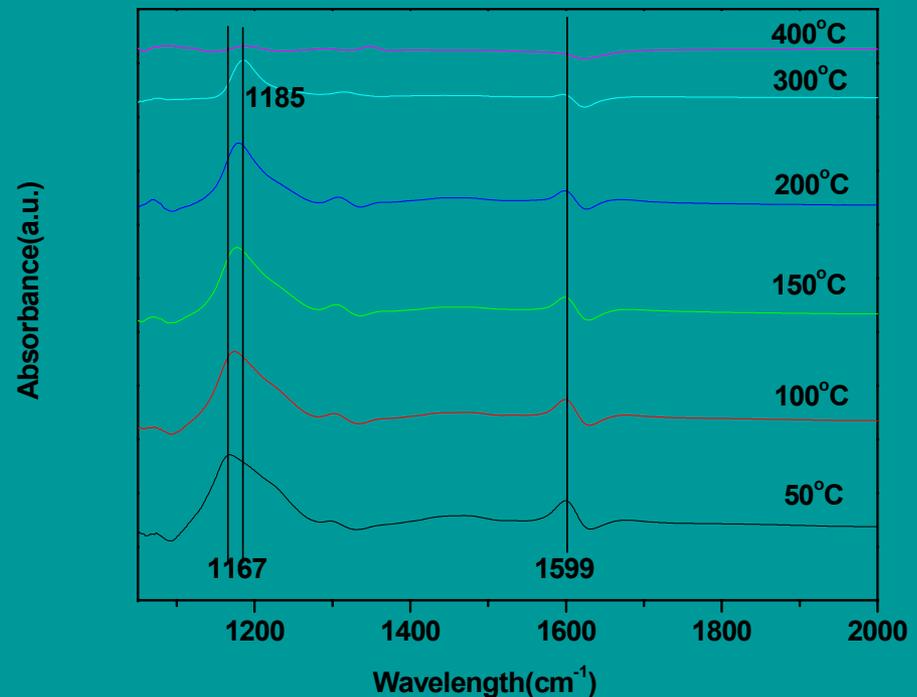
Mn Loading on TiO ₂ (wt%)	NO _x Conversion (%)	T _{rxn} (°C)	Total gas flow rate (sccm)	NO _x (ppm)	NH ₃ (ppm)	O ₂ (%)
20	59	100	140	400	400	2
20	94	140	140	400	400	2
10	96	140	140	400	400	2
5	56	140	140	400	400	2

GHSV = 50,000 h⁻¹

$$\text{NO conversion} = (\text{NO}_{\text{in}} - \text{NO}_{\text{out}}) / \text{NO}_{\text{in}} * 100\%$$

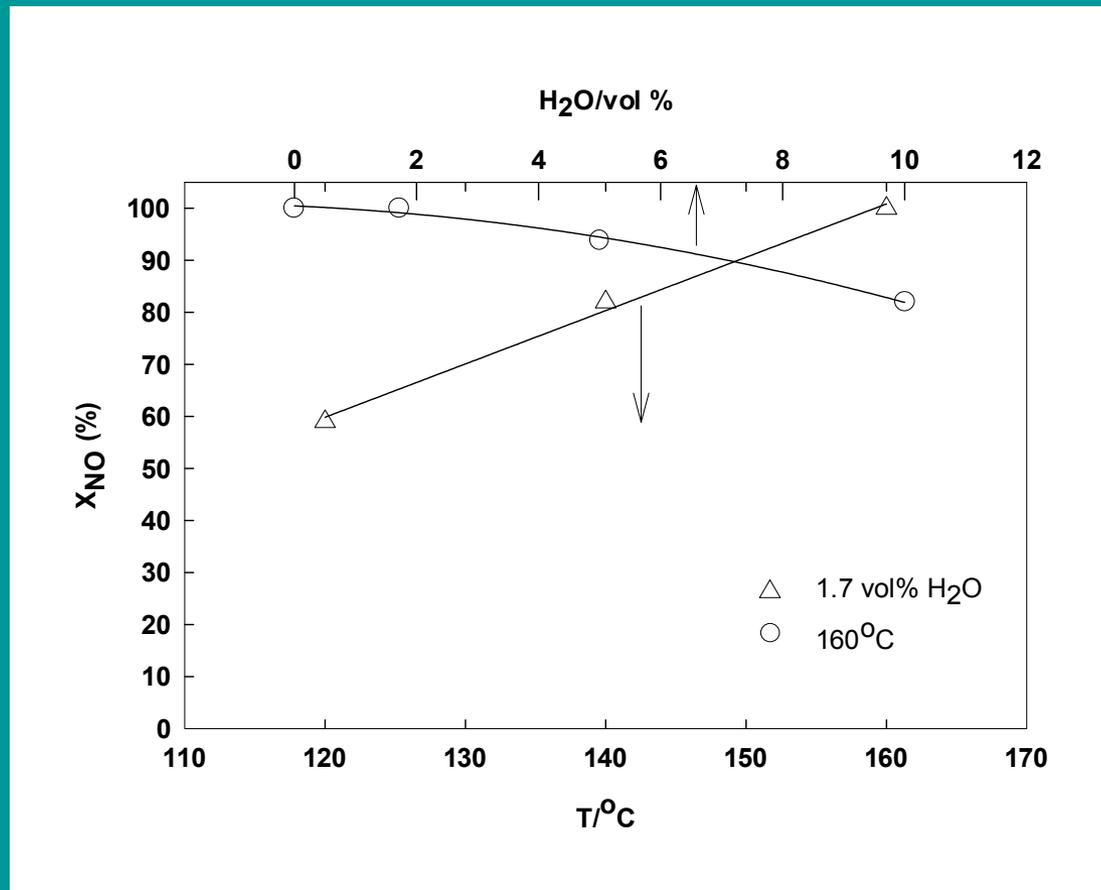
NH₃-TPD Spectra of 5wt%Mn-TiO₂ at Different Temperatures

- Ammonia adsorbs on titania in coordinated form over Lewis acid sites. It shows 5wt%Mn-TiO₂ has peaks at 1167cm⁻¹ and 1599cm⁻¹. Peak at 1167cm⁻¹ corresponds to $\delta_s(\text{NH}_3)$ coordinated Lewis acid sites that play an important role in low-temperature SCR for NO (Pena¹ et al, 2004). Peak at 1599cm⁻¹ is assigned to the asymmetric deformation of $\delta_{as}(\text{NH}_3)$ coordinated to Lewis acid sites. These peaks began to decrease significantly at 300°C and nearly disappeared at 400°C.



Effect of H₂O on NO Conversion

(20 wt% Mn /Hombikat; NH₃ Reductant)



SCR with Ammonia as Reductant

- Good performance with 10 wt% and 20 wt% Mn loaded titania low temperature of 140°C.
- The catalyst performance is mainly coordinated with the ability of the Mn on the support surface to participate in the redox mode and Lewis acidity sites of the titania support (Pena et al., 2004).
- High conversions in presence of H₂O

Summary of Reaction Results with Carbon Monoxide as Reductant

Mn Loading on TiO ₂ (wt%)	NO _x Conversion (%)	T _{rxn} (°C)	Total gas flow rate (sccm)	NO _x (ppm)	CO (ppm)	O ₂ (%)
20	35	175	140	400	400	2
20	28	175	140	400	800	2
20	37	175	140	400	400	3.7

GHSV = 50,000 h⁻¹

SCR with Carbon Monoxide as Reductant

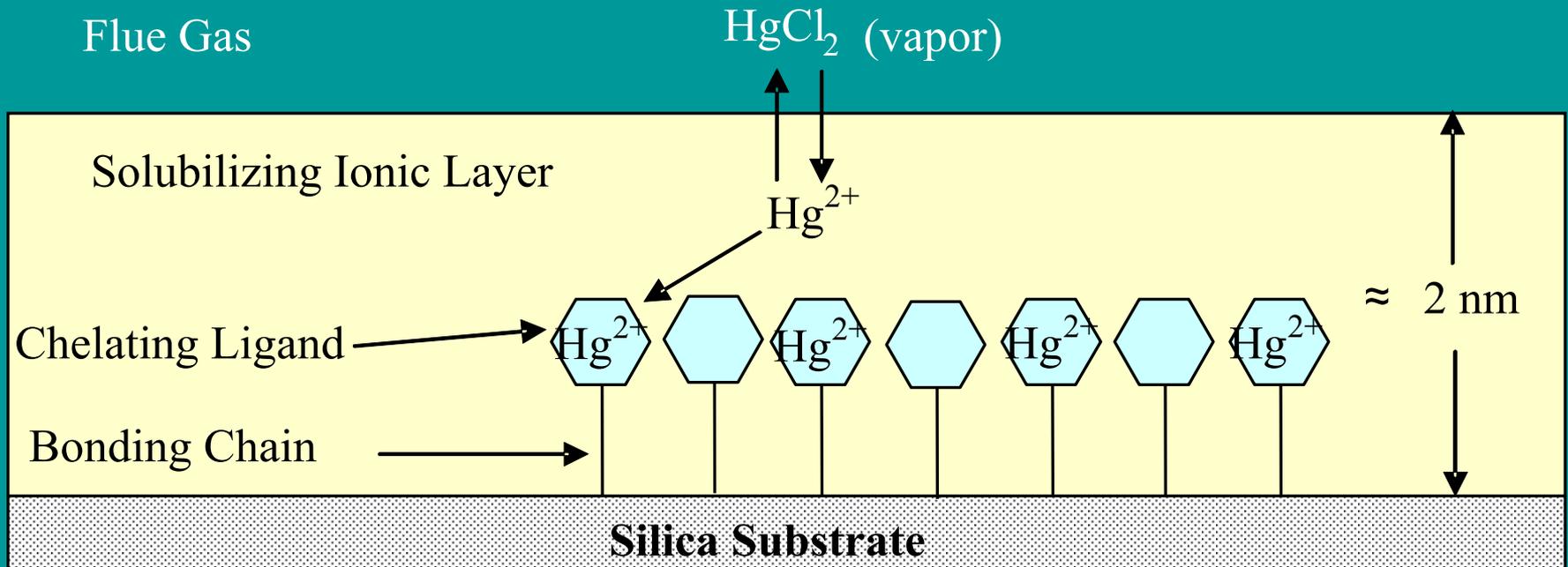
- NO_x conversions >35% were achieved.
- CO can be generated on site in power-plant application
- Change of the O₂ concentration in the range studied does not play a significant role.
- When the CO concentration is doubled from 400ppm to 800ppm the conversion of NO decreased. This is probably due to a coverage of the active sites by the larger concentration of CO.

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

**Adsorption Group
(Neville G. Pinto)**

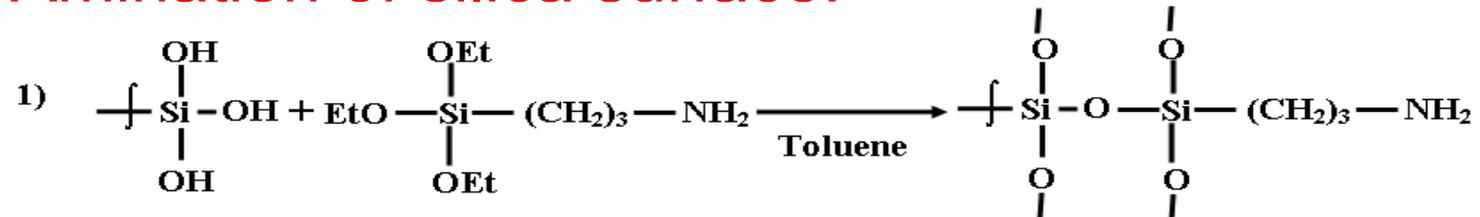
Chelating Adsorbent

Chelating agents: groups containing donor atoms that combine by coordinate bonding with a single metal ion to form a cyclic structure called a chelating complex or a chelate.

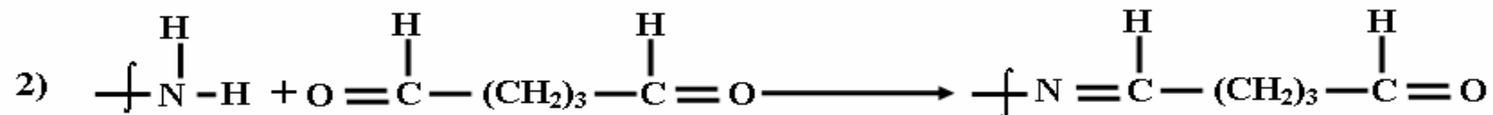


Synthesis of Cysteine Adsorbent

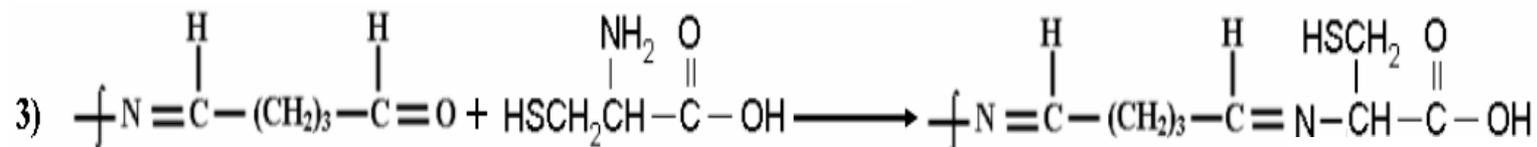
- Amination of silica surface:



- Bonding of Aldehyde Linker:

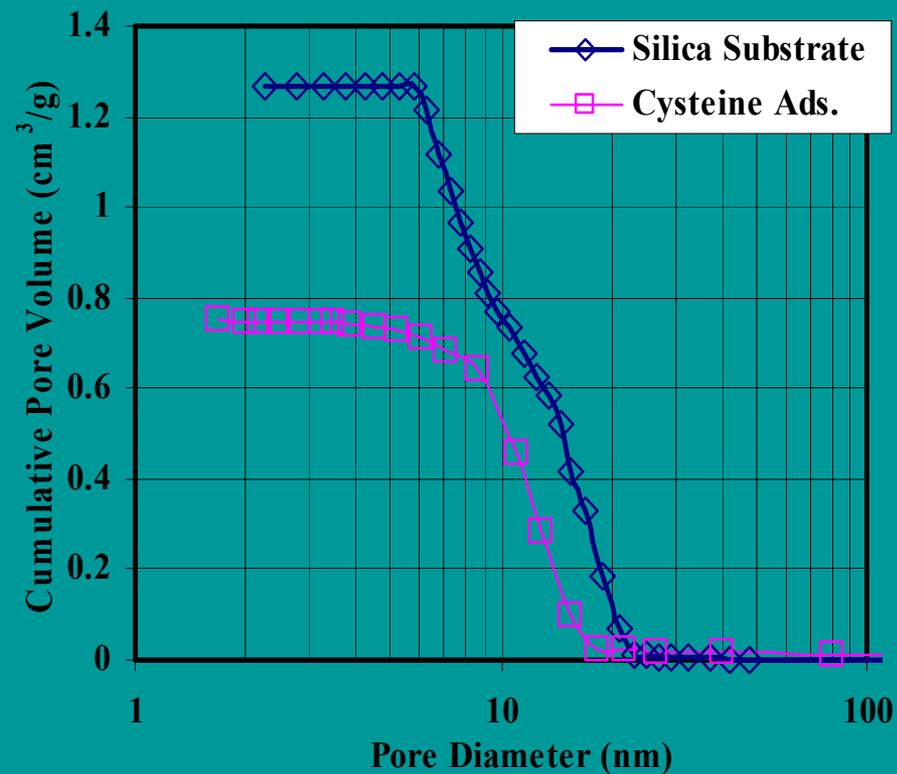
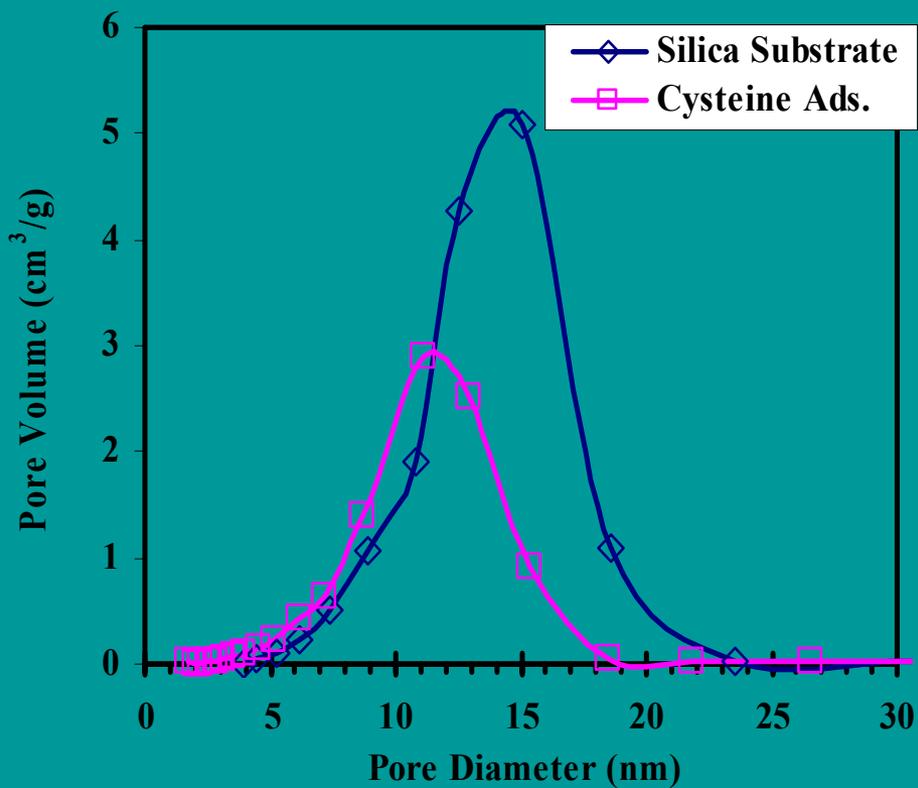


- Bonding Cysteine Residue:

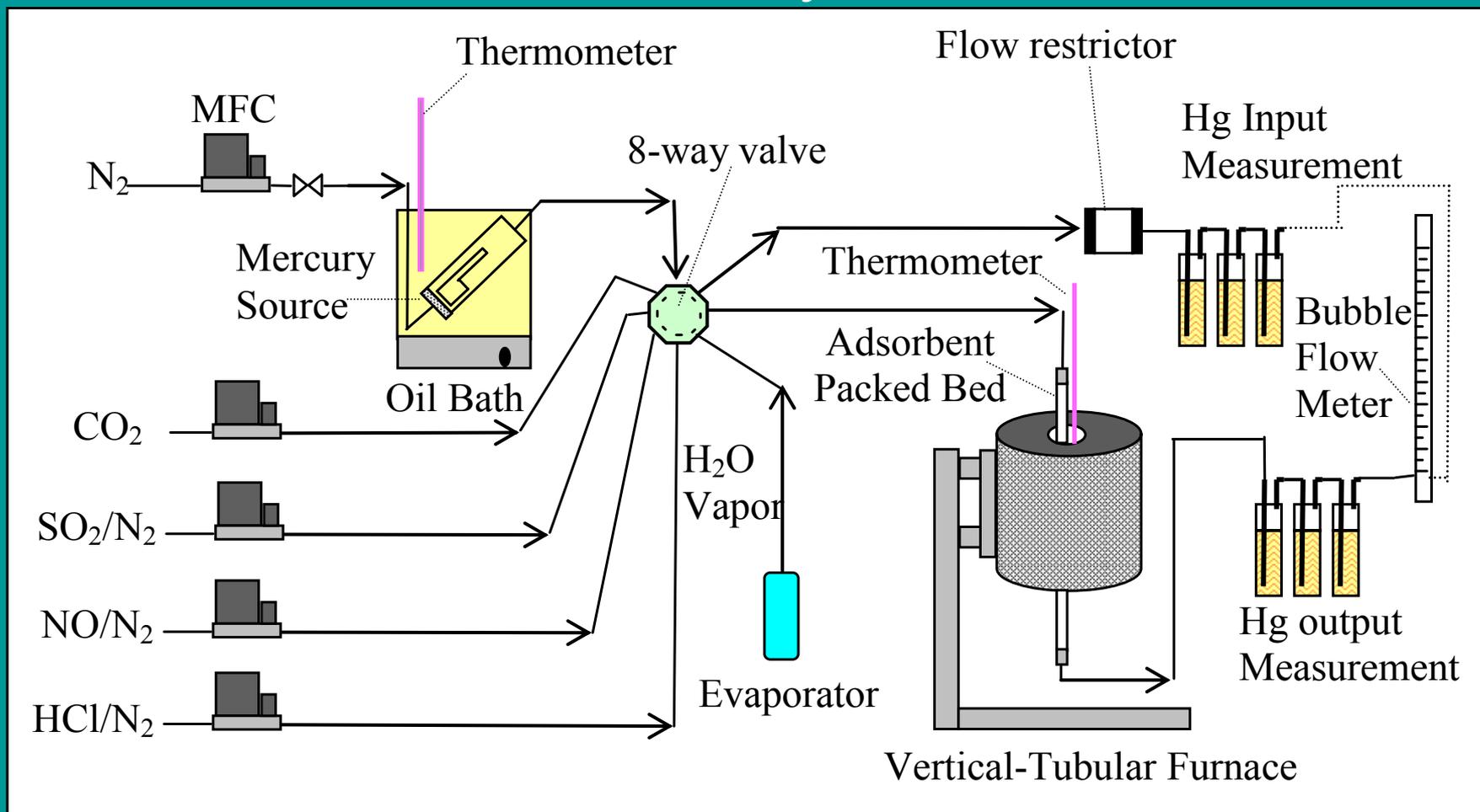


*** Yield 55-60% ***

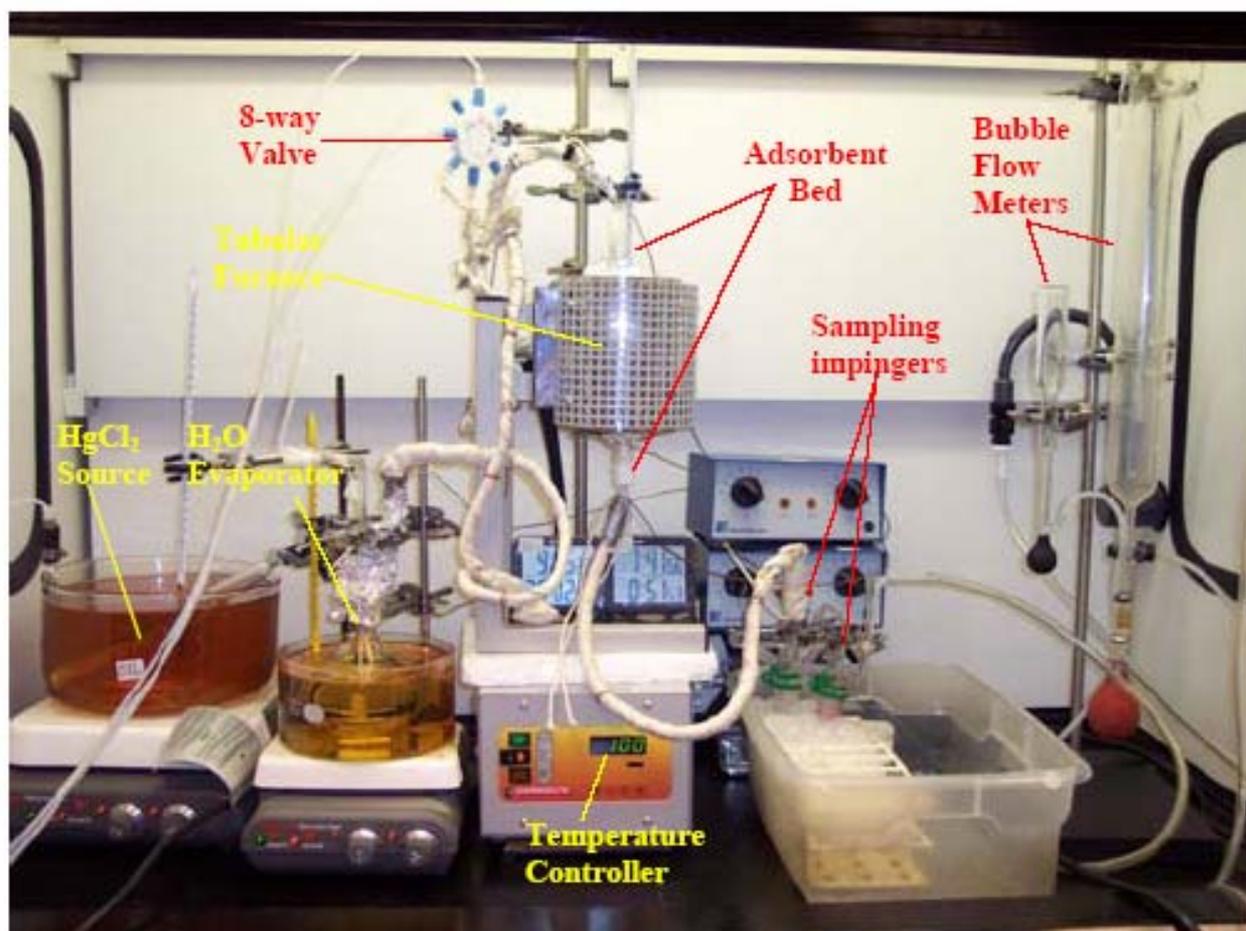
BET Analysis



Schematic of Apparatus for Mercury Adsorption Study



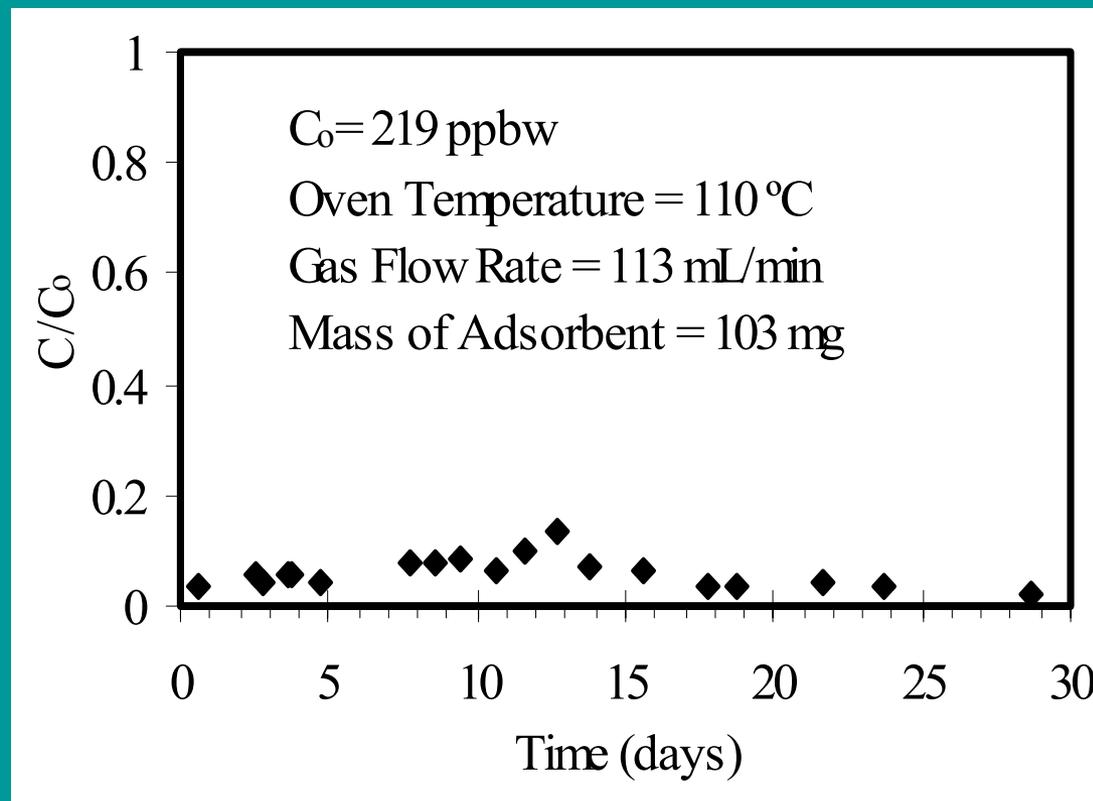
Experimental Setup for HgCl_2 Removal



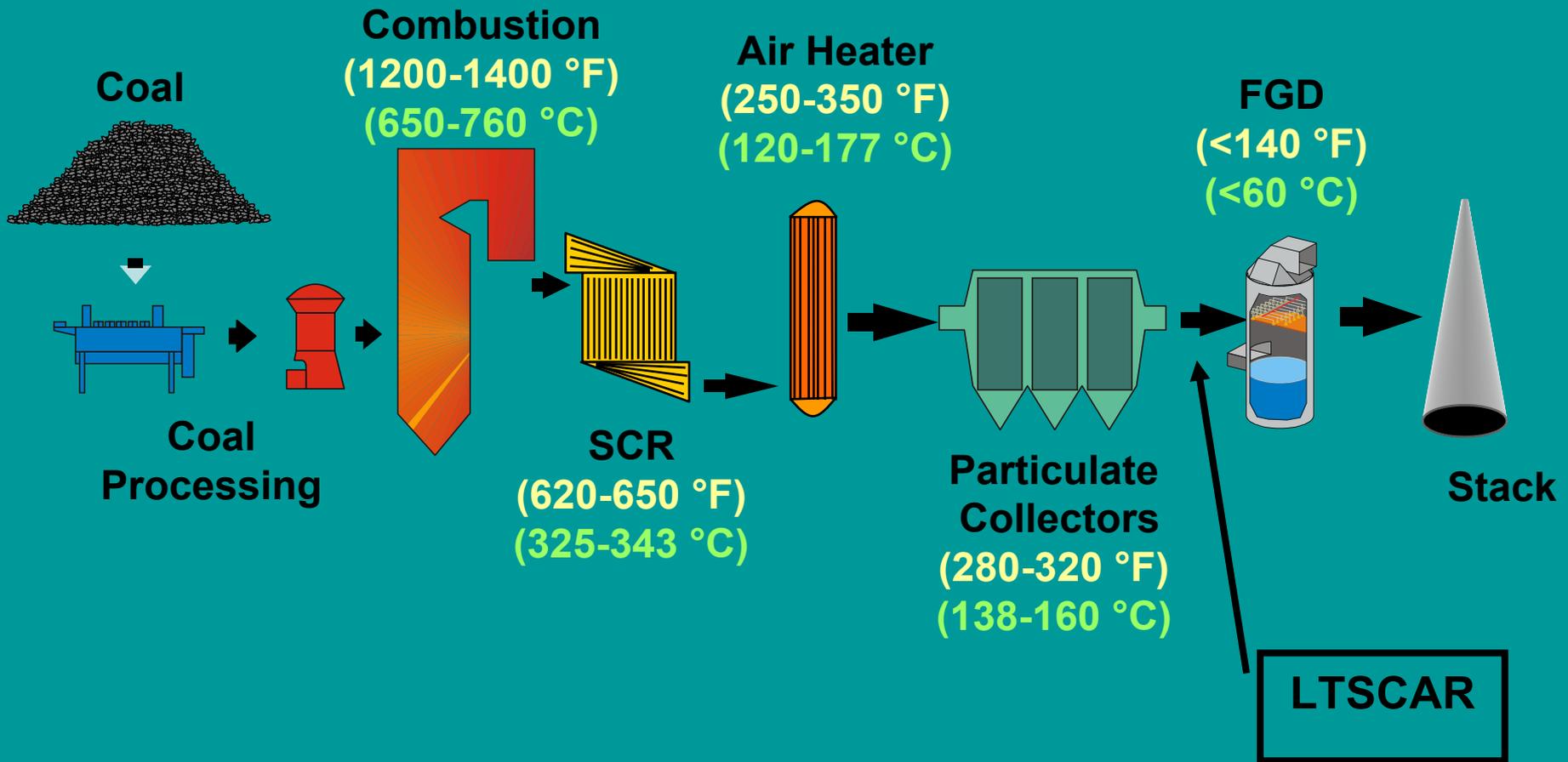
Evaluation of Dynamic Capacity at Flue Gas Conditions

Species	Concentration (by volume)
CO ₂	15-16%
HCl	100-150 ppm
SO ₂	1500 ppm
NO	500 ppm
H ₂ O	5-7%
N ₂	balance

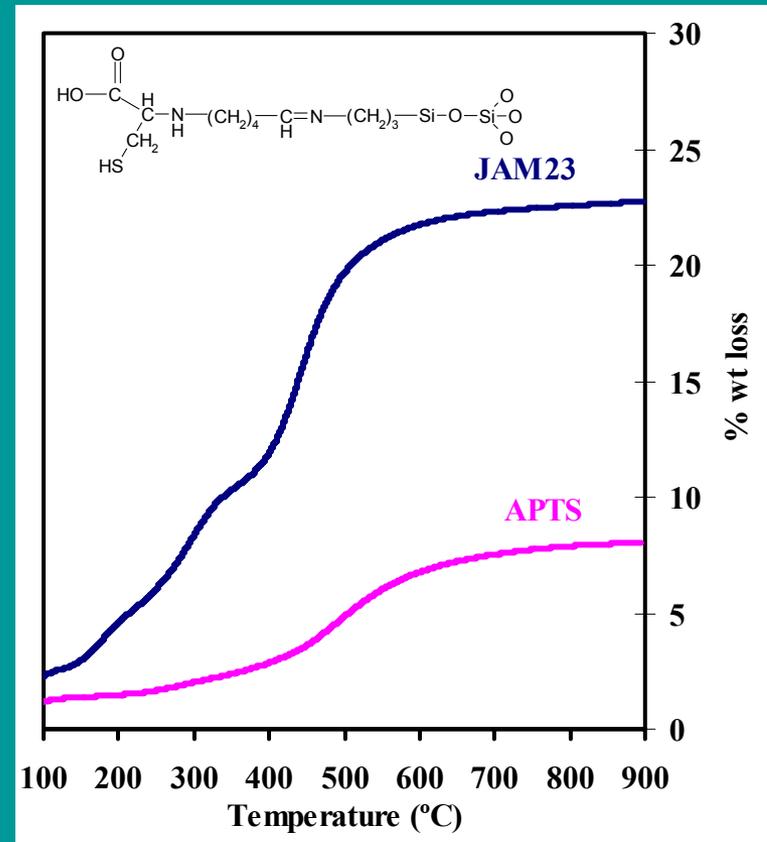
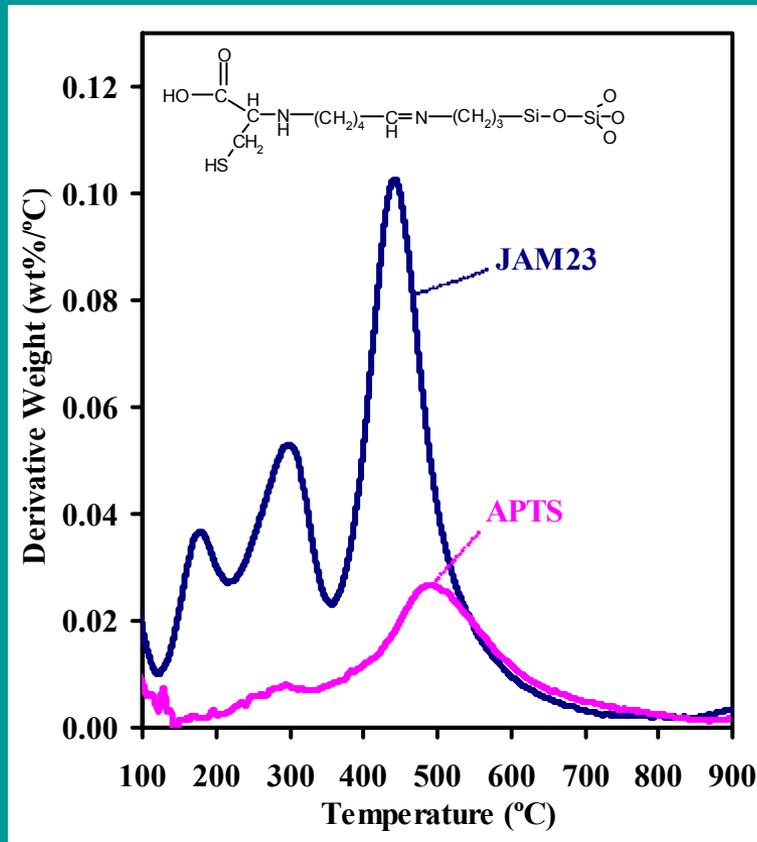
Typical Effluent Concentration History for HgCl_2 from Cysteine Activated Adsorbent Bed



Location of Low Temperature Selective Catalytic and Adsorptive Reactor (LTSCAR)



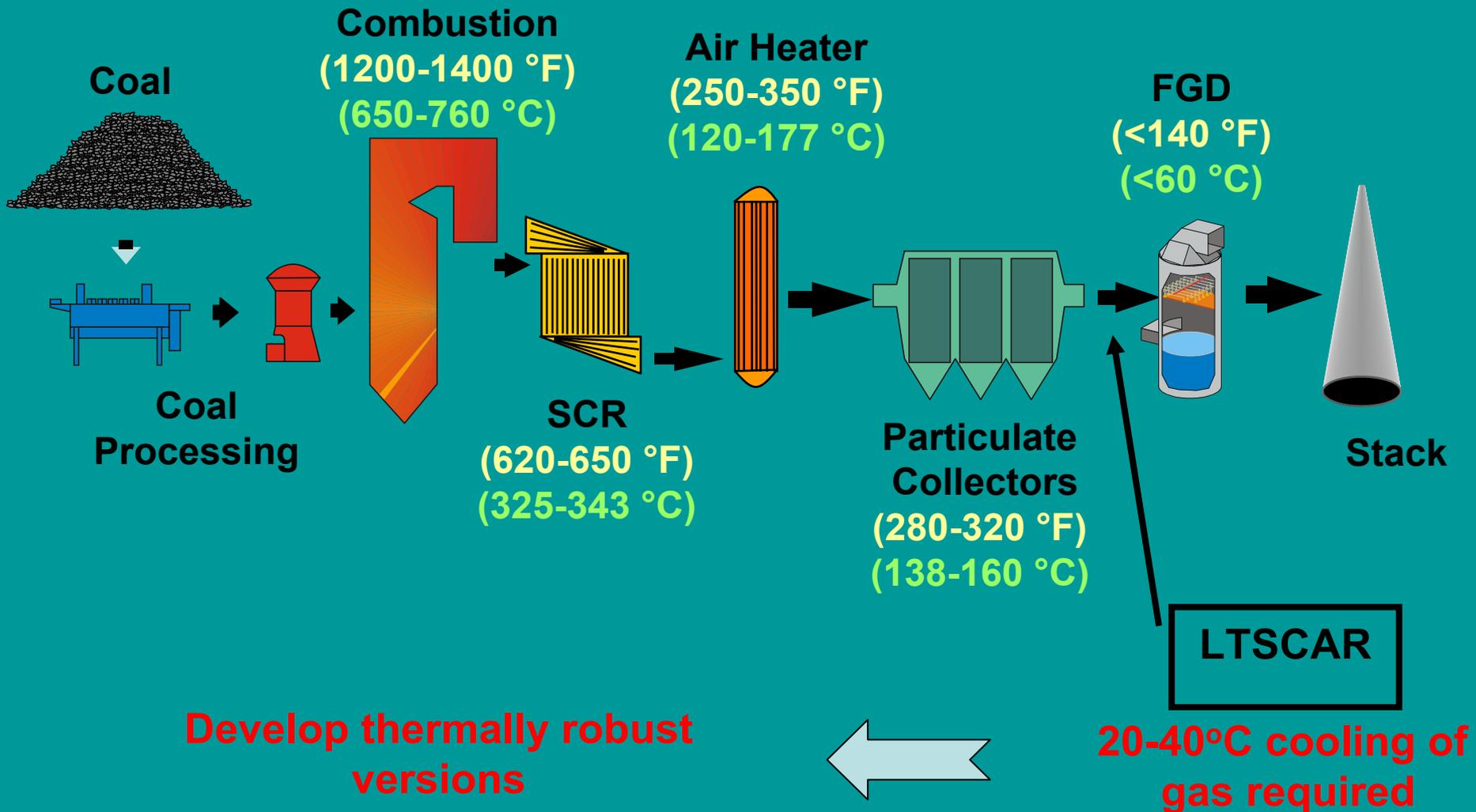
Chelating Bond Thermal Stability



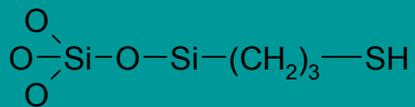
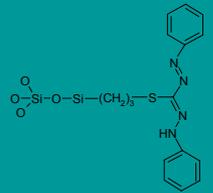
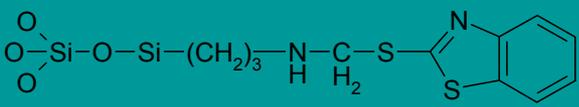
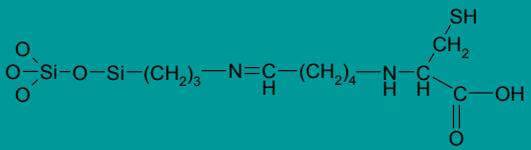
Density of Active Sites

Sample	Element wt%		APTS coverage ($\mu\text{mol}/\text{m}^2$)	Cysteine coverage ($\mu\text{mol}/\text{m}^2$)	Hg capacity (mg/g)
	N	S			
Cys-1	1.35	1.04	2.32	1.18	33
Cys-2	1.54	1.07	2.77	1.21	34
Cys-135°C	1.44	0.85	2.76	0.96	27 (20% loss)
Cys-160°C	1.28	0.61	2.62	0.69	19 (43% loss)

Location of Low Temperature Selective Catalytic and Adsorptive Reactor (LTSCAR)

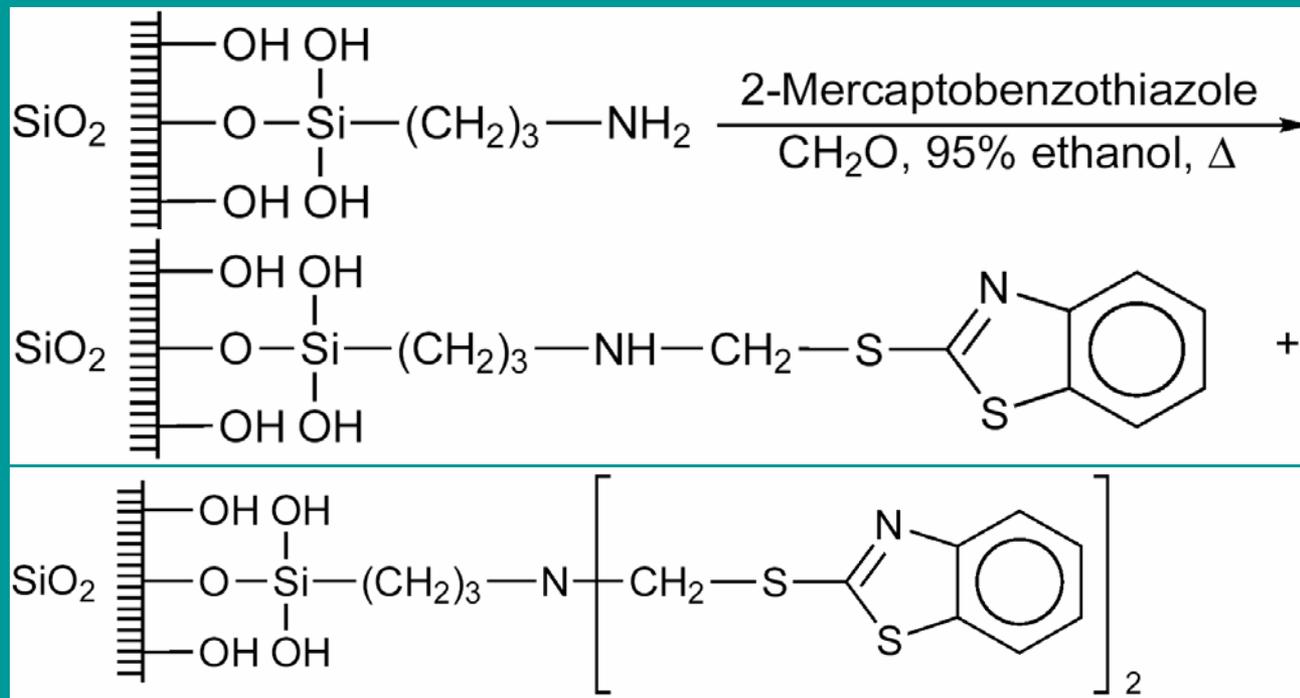


Thermally Stable Adsorbents Characteristic Properties

chelating ligand	chemical structure	surface coverage	BET area	Hg capacity	T _{up}
		mmol/g	m ² /g	(mg/g)	°C
Pure Silica		-	291	-	-
MPTS		0.58	259	117 (1:1)	200
CPTS-DZ		0.17	215	17 (2:1)	180
APTS-MBT		0.22	245	22 (2:1)	190
Cysteine		0.33	235	33 (2:1)	135

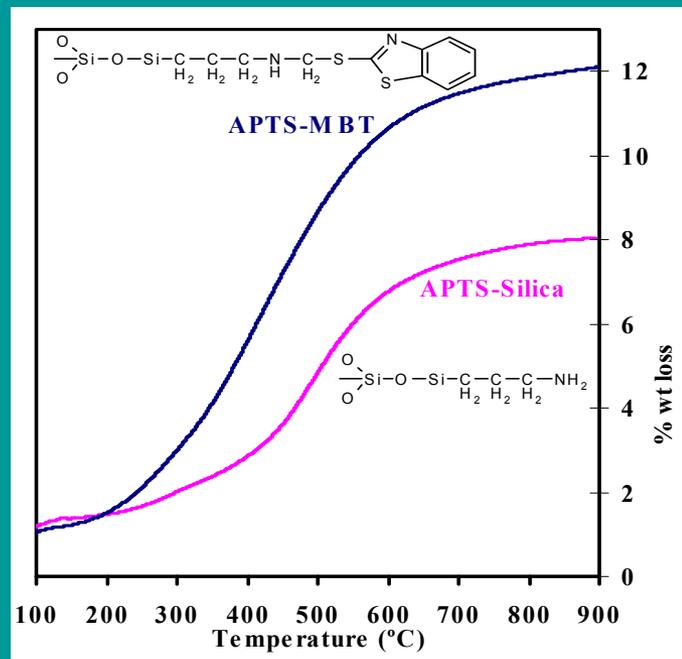
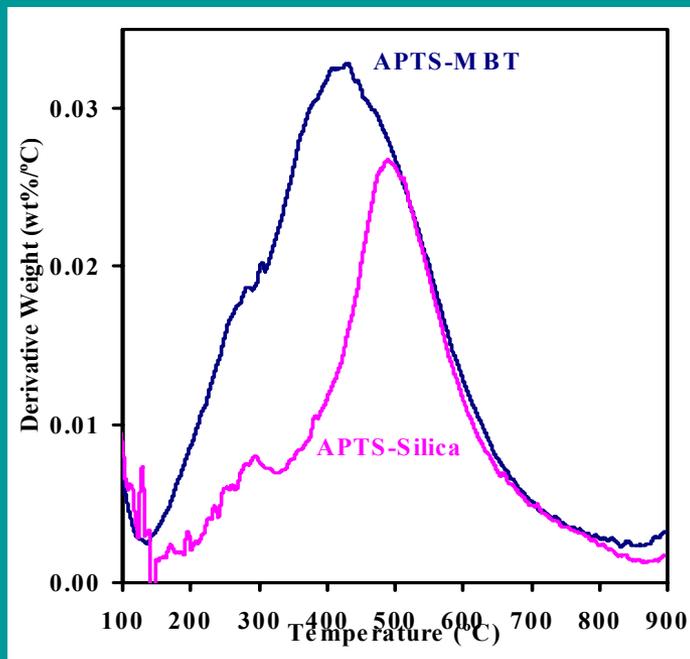
2-Mercaptobenzothiazole (APTS-MBT)

React MBT with 3-aminopropyltriethoxysilane (APTS) modified silica gel.



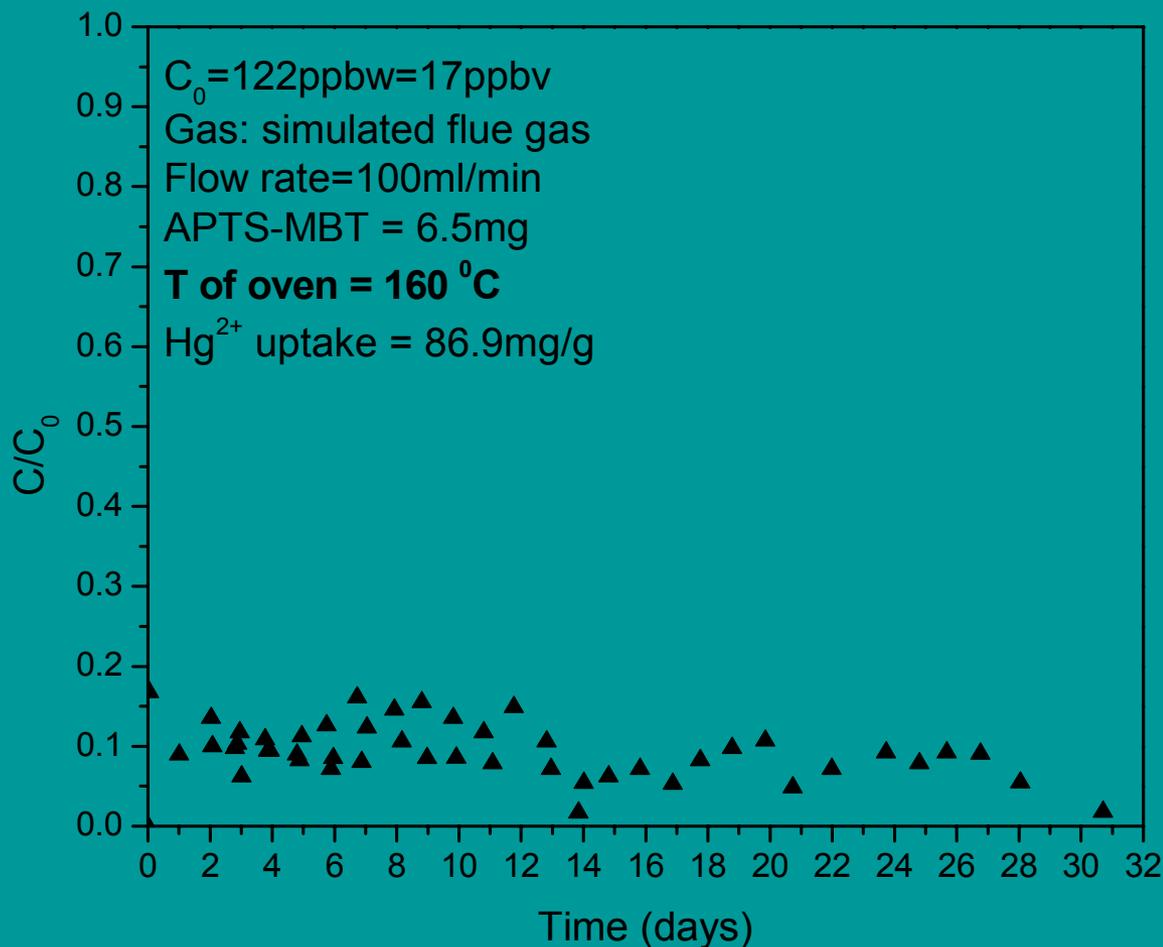
Pu et al., *J. Anal. At. Spectrom.*, **13**, 1998.

Thermal Stability of APTS-MBT

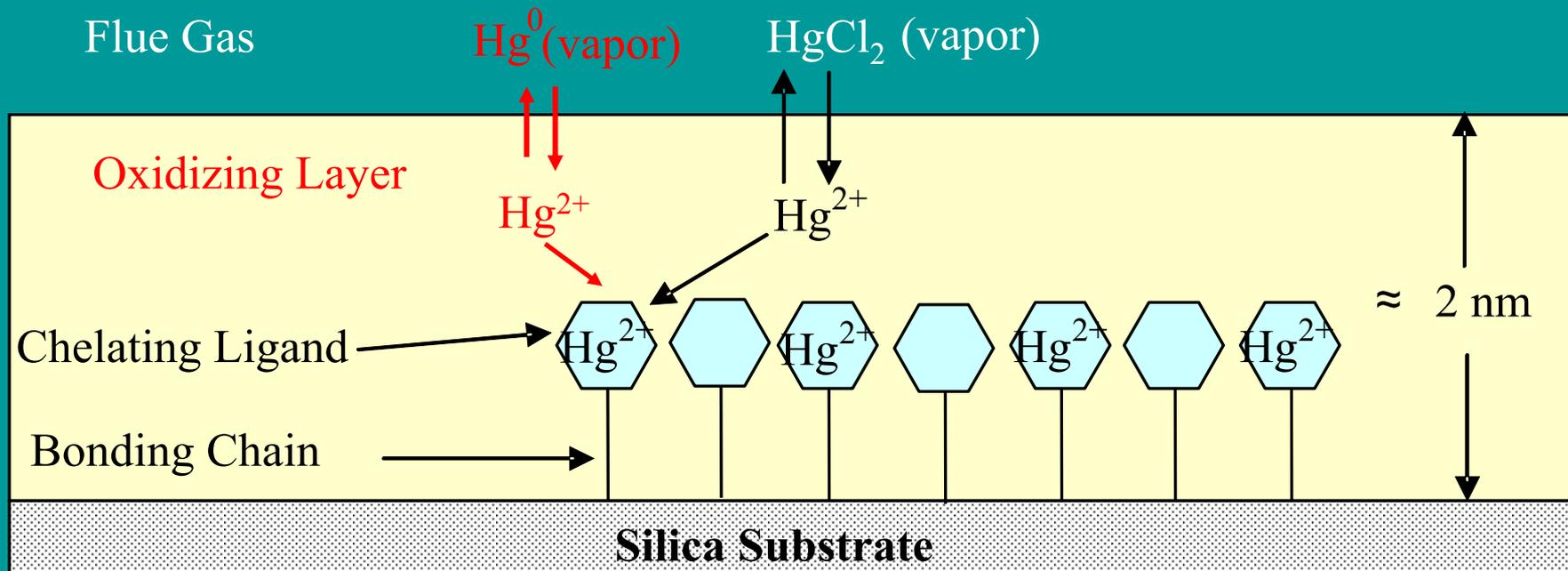


Sample	S wt%	Surface Coverage (mmol/g)
APTS-MBT	1.39	0.22
APTS-MBT-190°C	1.2	0.19 (14% loss)

Effluent Concentration History for HgCl_2 Using APTS-MBT Adsorbent at 160°C



Simultaneous Removal of Elemental and Oxidized Mercury



Hg⁰ Oxidation Using Novel Oxidizing Layers

Experiment	Hg ⁰ in feed (μg) 1 hr collection	Hg ⁰ in effluent (μg) 1 hr collection	Hg ²⁺ in effluent (μg) 1 hr collection
Control (N ₂ carrier gas)	1.06	1.06	0
Control (N ₂ carrier gas +227 ppm HCl)	1.06	1.06	0
Layer A + N ₂ carrier gas	1.06	0.42	0
Layer A + N ₂ carrier gas +227 ppm HCl	1.06	0.42	0.63
Layer B + N ₂ carrier gas	1.06	0	0

Effect of Oxidizing Layers A and B on Surface Area and Porosity of Silica

Oxidizing layer	wt %	BET surface area(m ² /g)	Mean pore diameter (nm)	Cumulative pore volume (cm ³ /g)	Coating layer thickness (nm)
Coating Layer A	0	283	16.3	1.18	0
	5	245	16.1	1.05	0.1
	10	217	16.1	0.99	0.2
	15	195	16.3	0.89	0.4
	20	166	16.4	0.81	0.6
	25	144	16.0	0.73	0.8
	30	130	16.1	0.61	1.0
Coating Layer B	25	150	16.1	0.69	0.8

Summary

NO_x Removal

- Hombikat titania loaded with 10wt% and 20wt% Mn showed very good performance even at low temperature of 140°C with NH₃ as reductant.
- When carbon monoxide was used as the reductant, NO_x conversions of more than 35% were achieved at the low temperature of 175°C

Mercury Capture

- Thermally stable, high capacity chelating adsorbents for capture of Hg²⁺ have been developed. These are suitable for flue-gas contacting at temperatures in the range 160-190°C.
- Novel oxidizing layers for the *in situ* oxidation of Hg⁰ on the chelating adsorbent surface with subsequent capture as Hg²⁺ are being investigated. Preliminary results are promising.

Future Work

- Investigation of mechanism of SCR with CO as reductant, at low temperature and in simulated coal combustion flue gas mixture
- Development of Mn-Me (Me=transition metal) bimetallic combinations as potential high activity catalysts for this reaction.
- Synthesis and characterization of oxidation catalysts and oxidants for elemental mercury.
- Very long term experiments to obtain complete effluent concentration histories for Hg adsorption on thermally stable chelating adsorbents.
- Preliminary studies on simultaneous removal of NO_x and Hg.