Poisoning/Deactivation Study of V_2O_5/TiO_2 SCR Catalysts

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ACERC Conference

Feb 26, 2008

Provo, UT

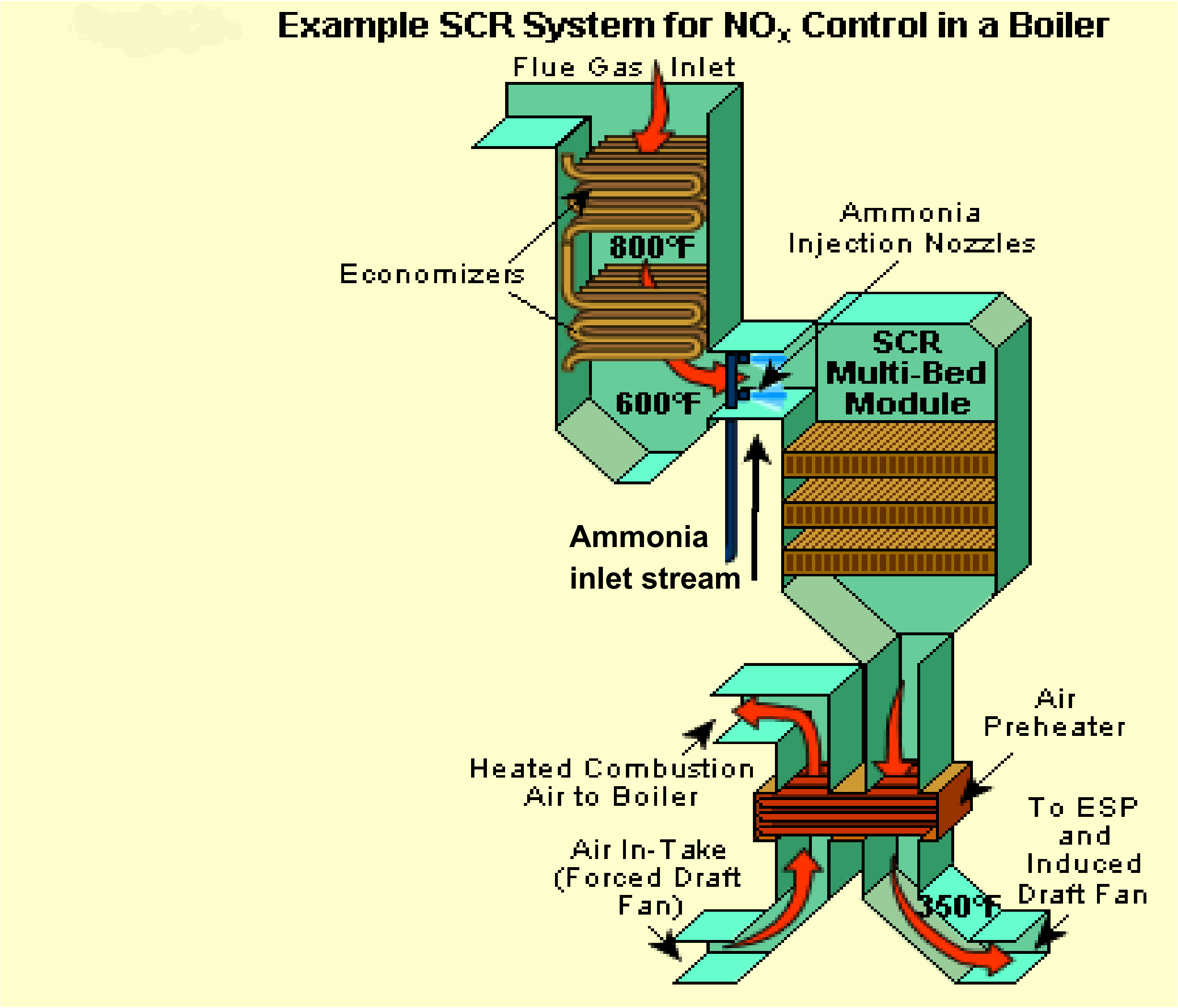
Outline

- Introduction
- Objective and Motivation
- Results and Discussion
- Conclusions
- Acknowledgements

Introduction

- SCR: a high efficient NO_x abatement technique
  - A commercial post-combustion technique
  - Being used on ¼ of the power generated from coal-fired boilers
  - Major problem is catalyst deactivation, especially for low-rank coals and biomass

Example of SCR System



- **Modified from *http://upload.wikimedia.org/wikipedia/en/5/5c/SCR2.GIF***

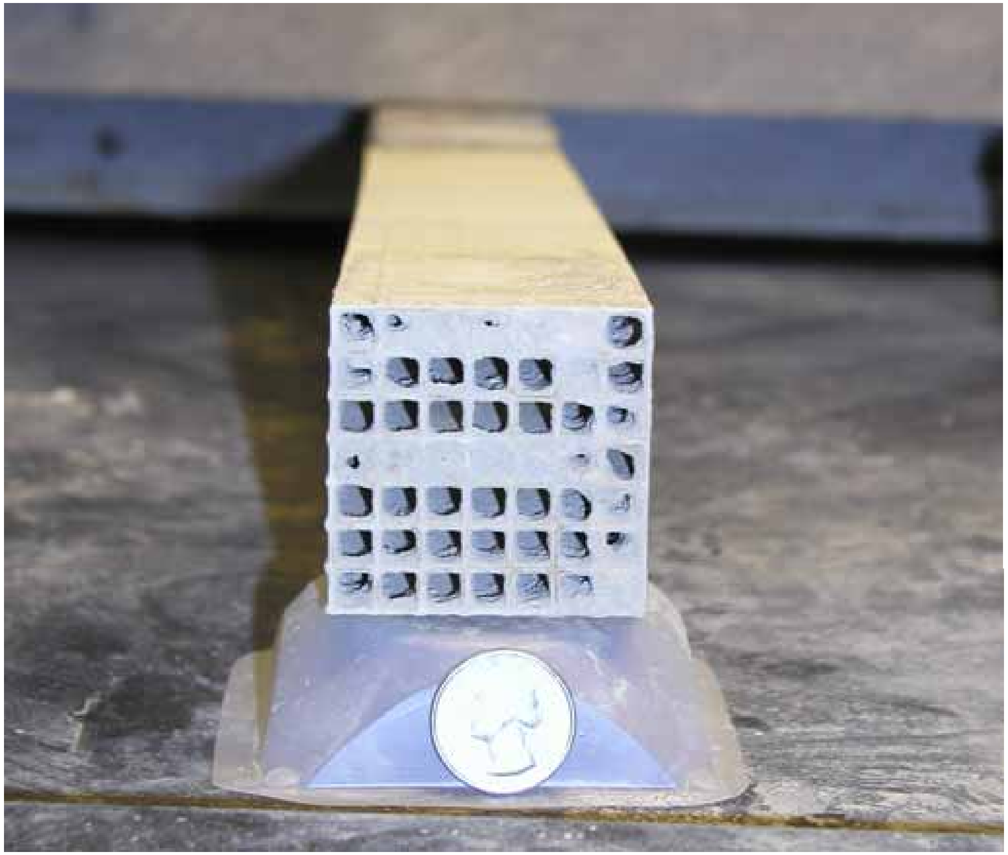
Introduction

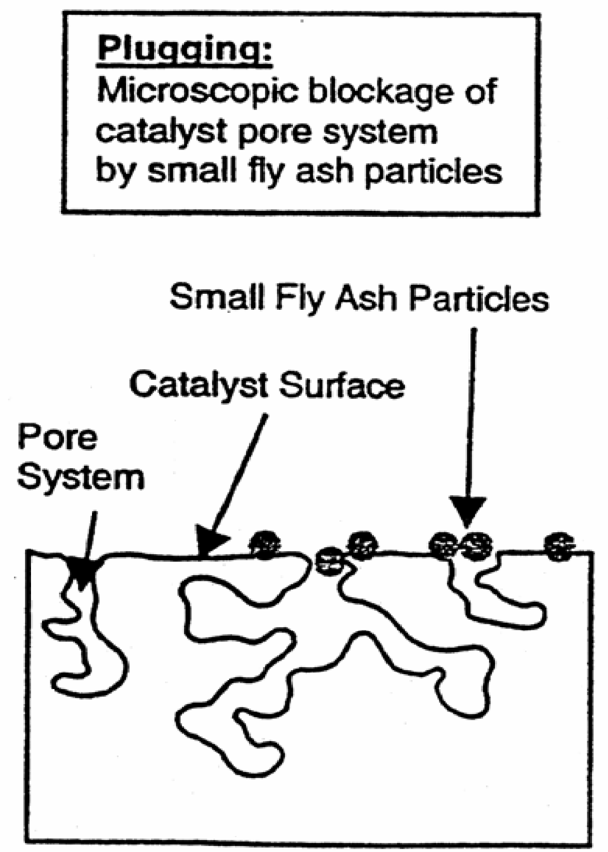
- **SCR: selective catalytic reduction**
  - $4NH_3 + 4NO + O_2 \longrightarrow 4N_2 + 6H_2O$
  - $4NH_3 + 2NO_2 + O_2 \longrightarrow 3N_2 + 6H_2O$
- **SCR catalyst**
  - **Supported vanadia catalyst: $1\%V_2O_5$-$9\%WO_3/TiO_2$**
  - **Currently, in monolith or flat plate structure.**
- **SCR kinetics: $r_{NO} \approx k\ C_{NO}$**

Deactivation Mechanisms

- Plugging
- Fouling/Masking
- Poisoning

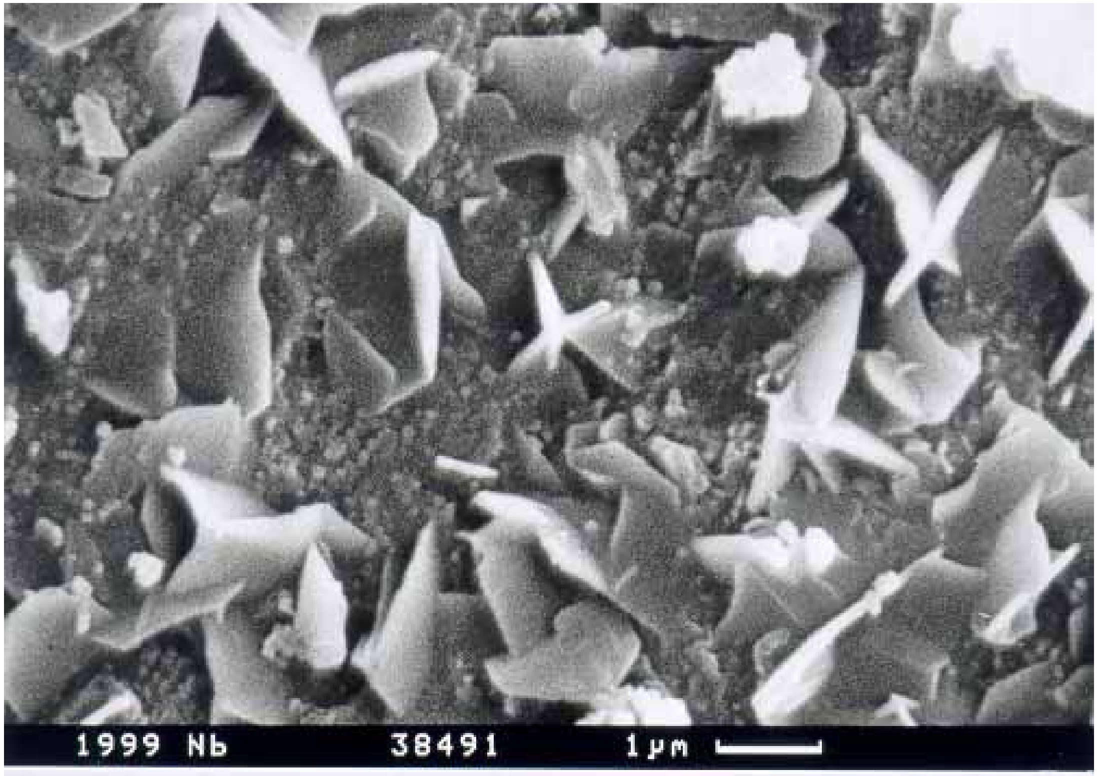
Channel/Pore Plugging

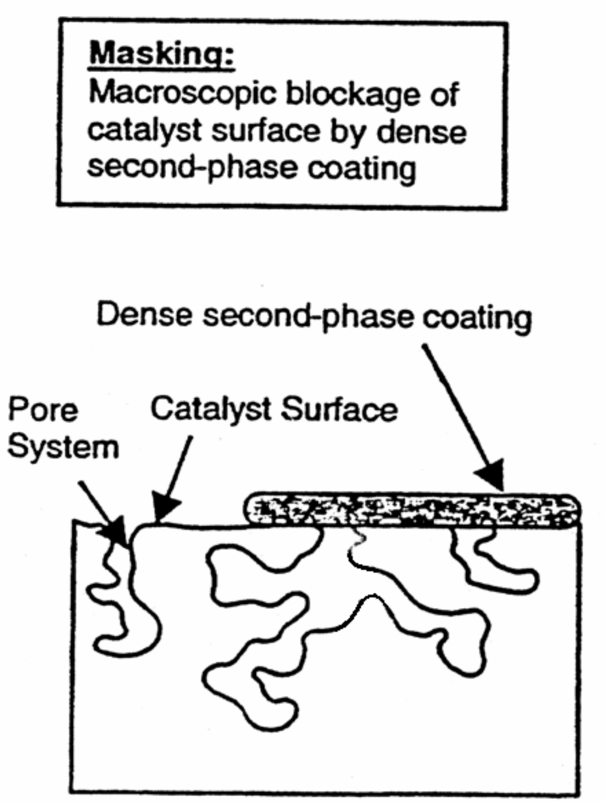




Fouling/Masking

Calcium sulfate coating on catalyst surface

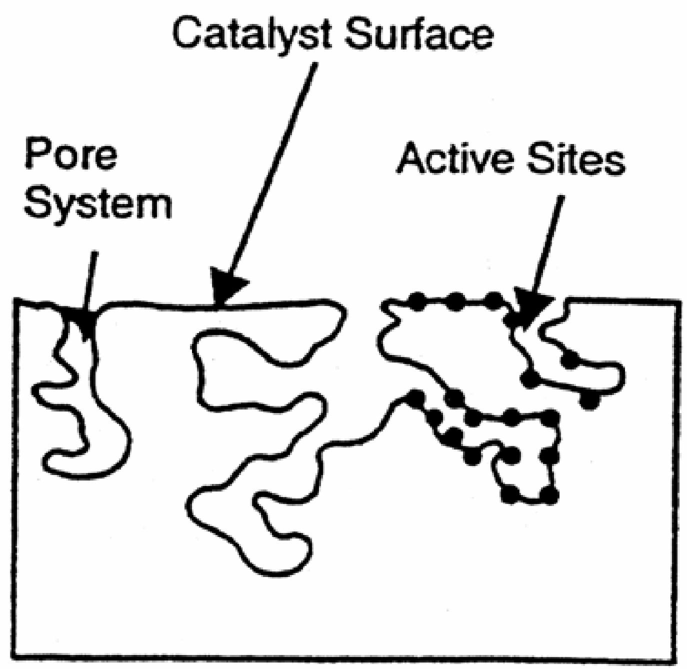




Poisoning

- **Catalytic activity linked to amount/strength of Brønsted acid sites on catalyst surface (Amiridis, Duevel, Wachs, 1999)**
- **Chemical poisoning results from basicity of metal oxide deposits (Chen *et al.*, 1990)**
- **Flyash from coal/biomass contains carbonates, sulfates, and oxides of** Na**,** Ca**,** K**, As, and Mg, which are basic materials**

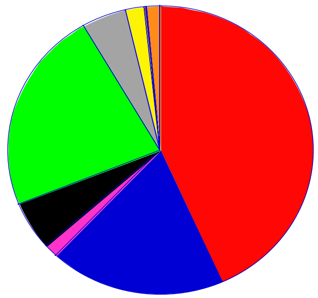
Poisoning:
Deactivation of active catalyst sites by chemical attack



Coal & Biomass Ash Compositions Differ

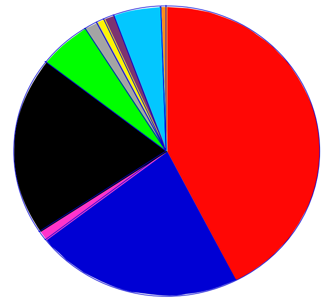
Coal

Black Thunder



7.2% Ash

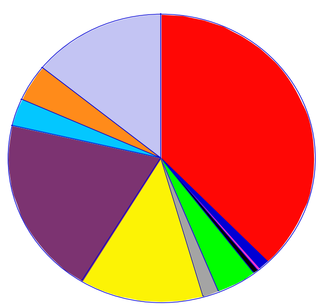
Pittsburgh #8



7.8% Ash

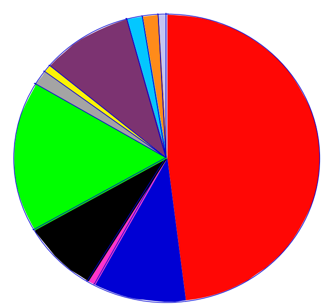
Biomass

Imperial Wheat Straw



15.4% Ash

Red Oak



1.3% Ash

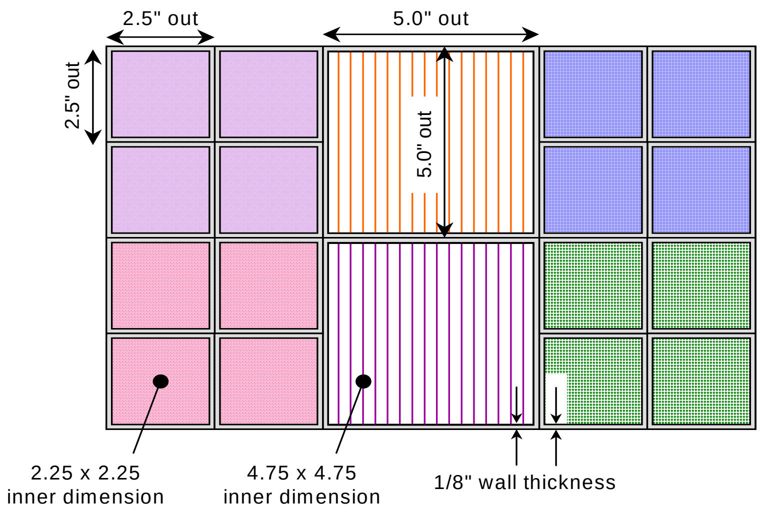
- SiO2
- Al2O3
- TiO2
- Fe2O3
- CaO
- MgO
- Na2O
- K2O
- SO3
- P2O5
- Cl

Objective and Motivation

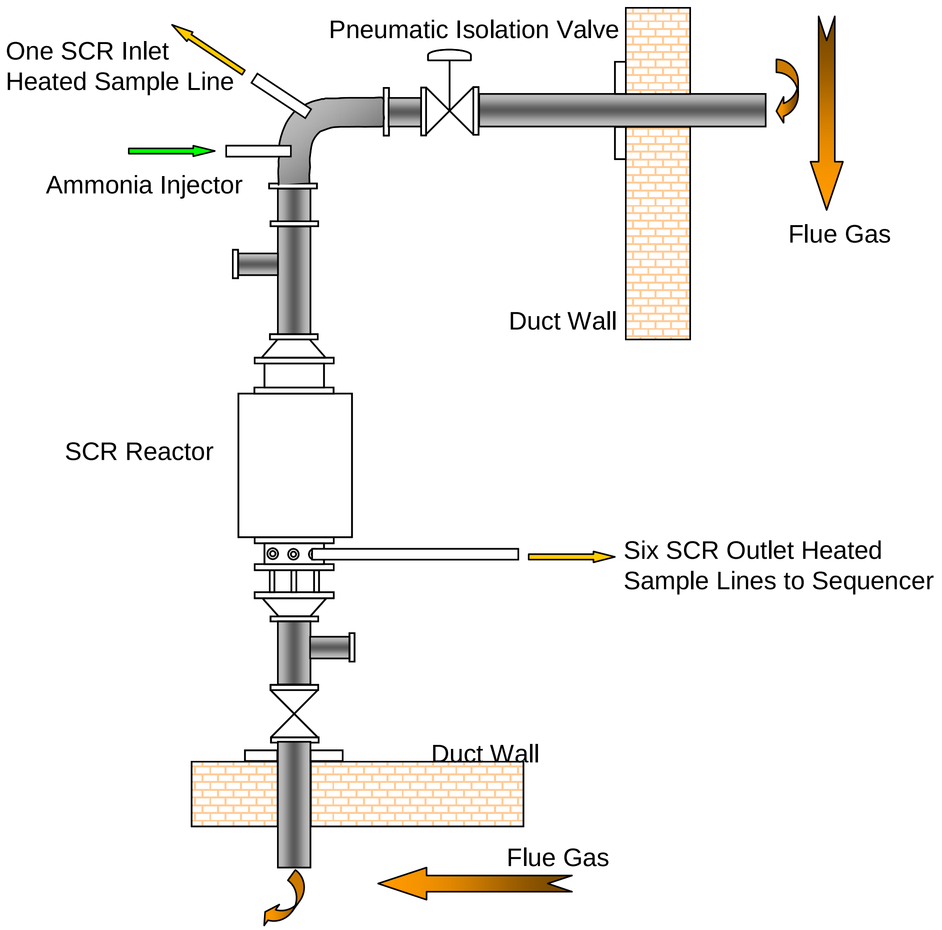
- **Objective**
  - Examine fresh and exposed commercial SCR catalysts and determine the deactivation mechanism
  - Determine the impacts of K, Na, Ca, and SO_2 on vanadia catalyst properties and activities on lab-synthesized catalysts
- **Motivation**
  - Poisoning is a potential mechanism for SCR catalyst deactivation
  - SO_2 is generally present in boiler flue gas
  - Previous studies on non-sulfated catalysts

Slipstream Reactor

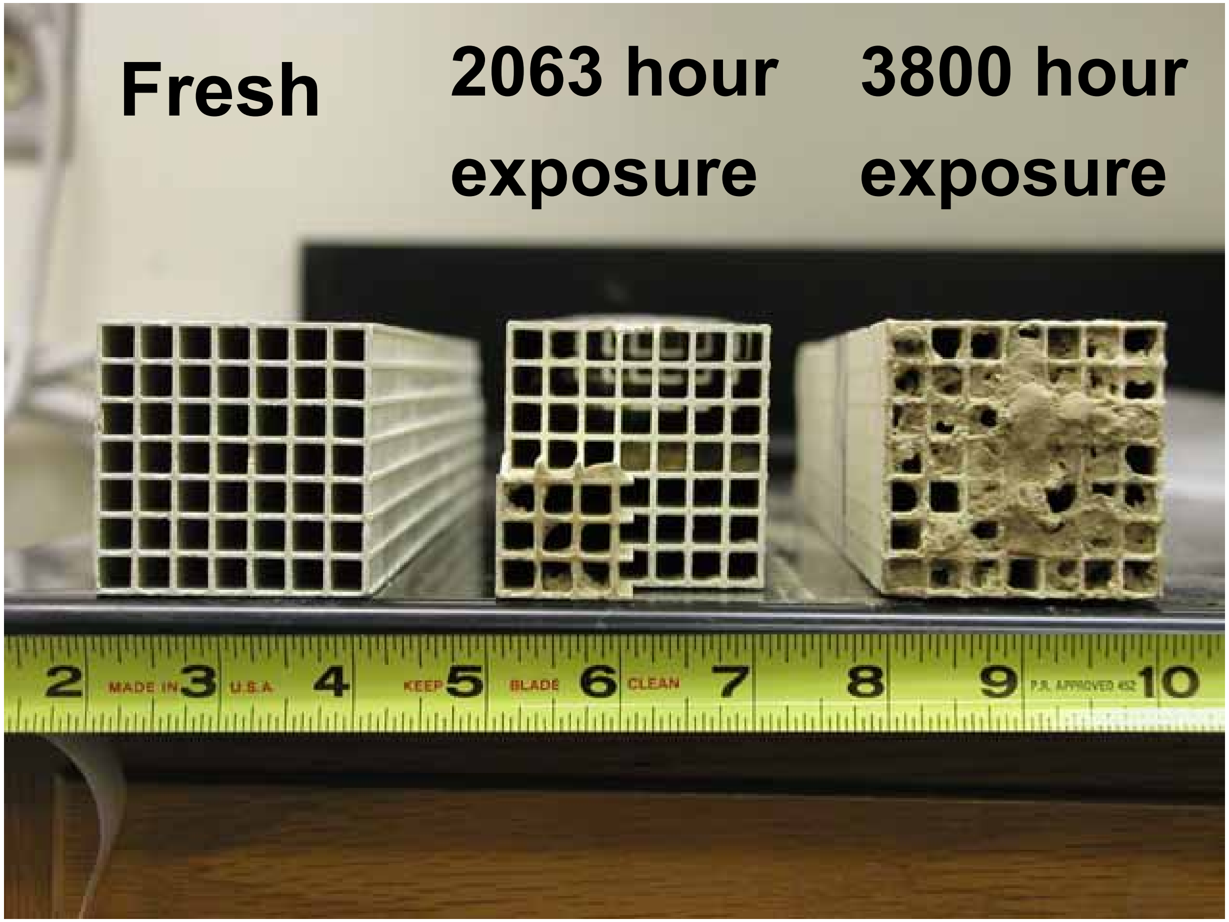
- REI operating slipstream reactor at Rockport, IN
- Reactor contains 6 separate channels for 5 commercial, one BYU -prepared catalyst
- Samples are returned for analysis



Top view of slipstream reactor.
(Schematic courtesy of REI)

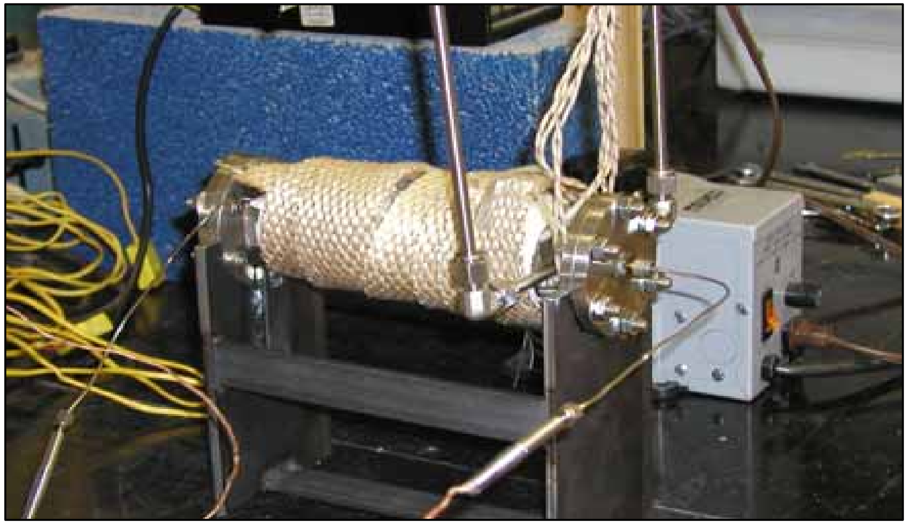


Fresh and Exposed Catalysts Comparison



Catalyst Characterization System

Monolith Test Reactor



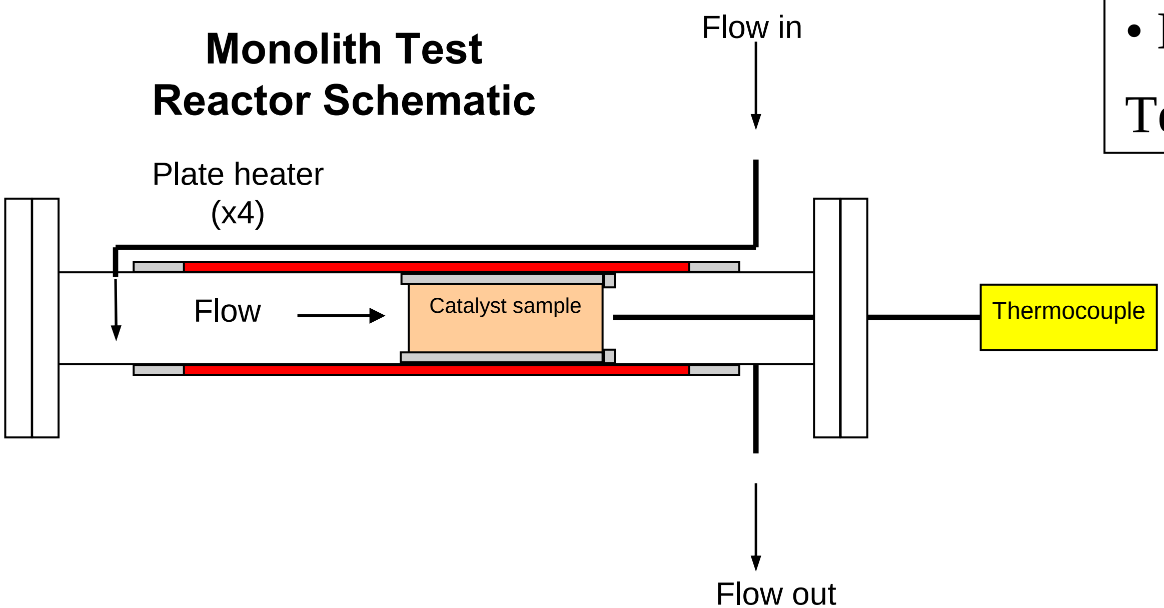
Flow Rate: 1000 sccm

Feed:

- 900 ppm NO
- 900 ppm NH_3
- 2% O_2
- ~10% H_2O
- Balance He

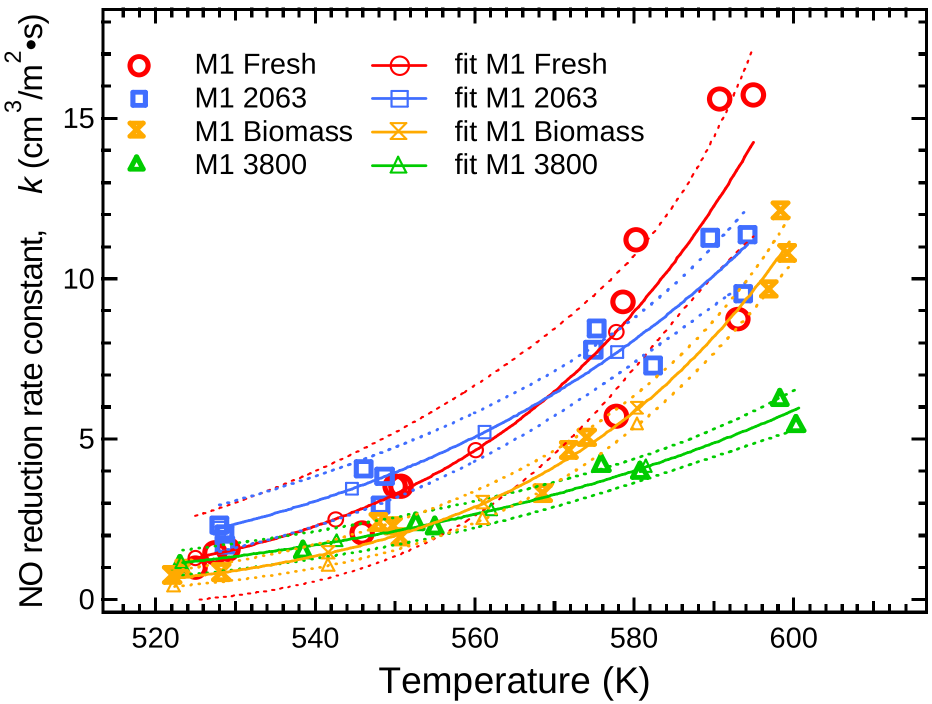
Temperature: 250-325 °C

Monolith Test Reactor Schematic

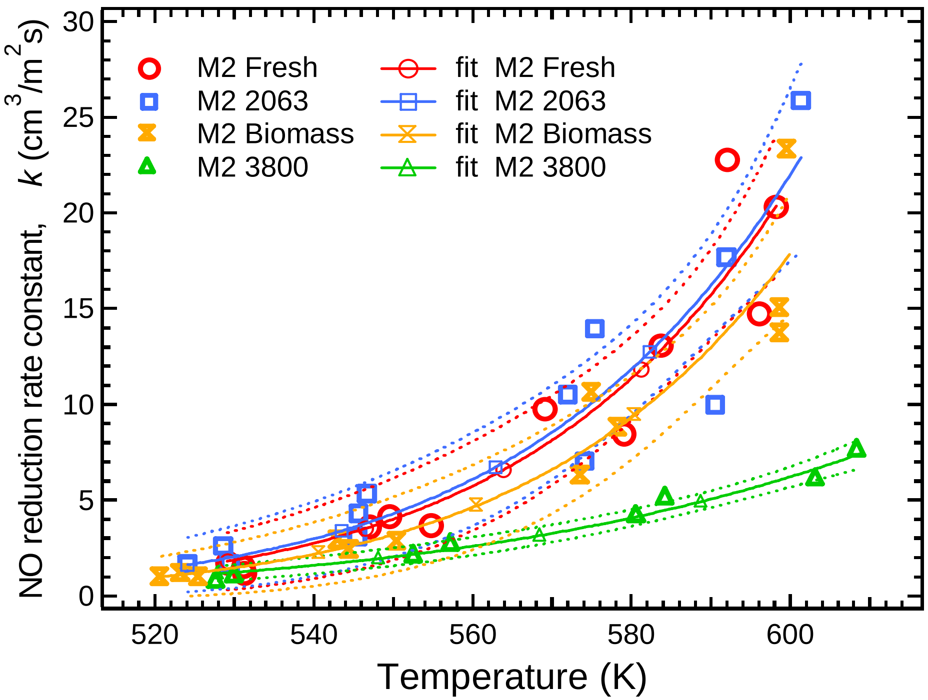


Fresh and Exposed Catalysts Performance

Monolith 1 kinetic data



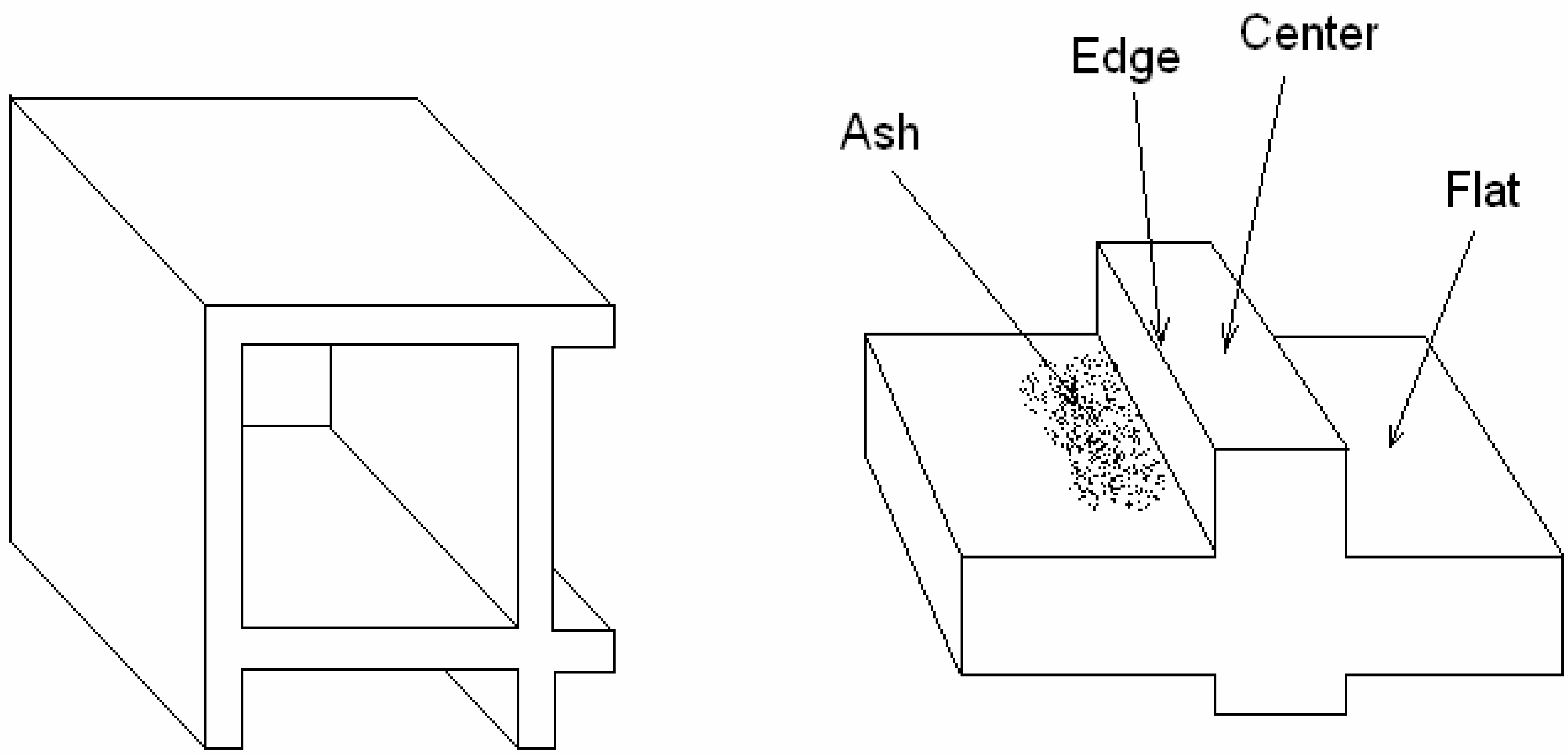
Monolith 2 kinetic data



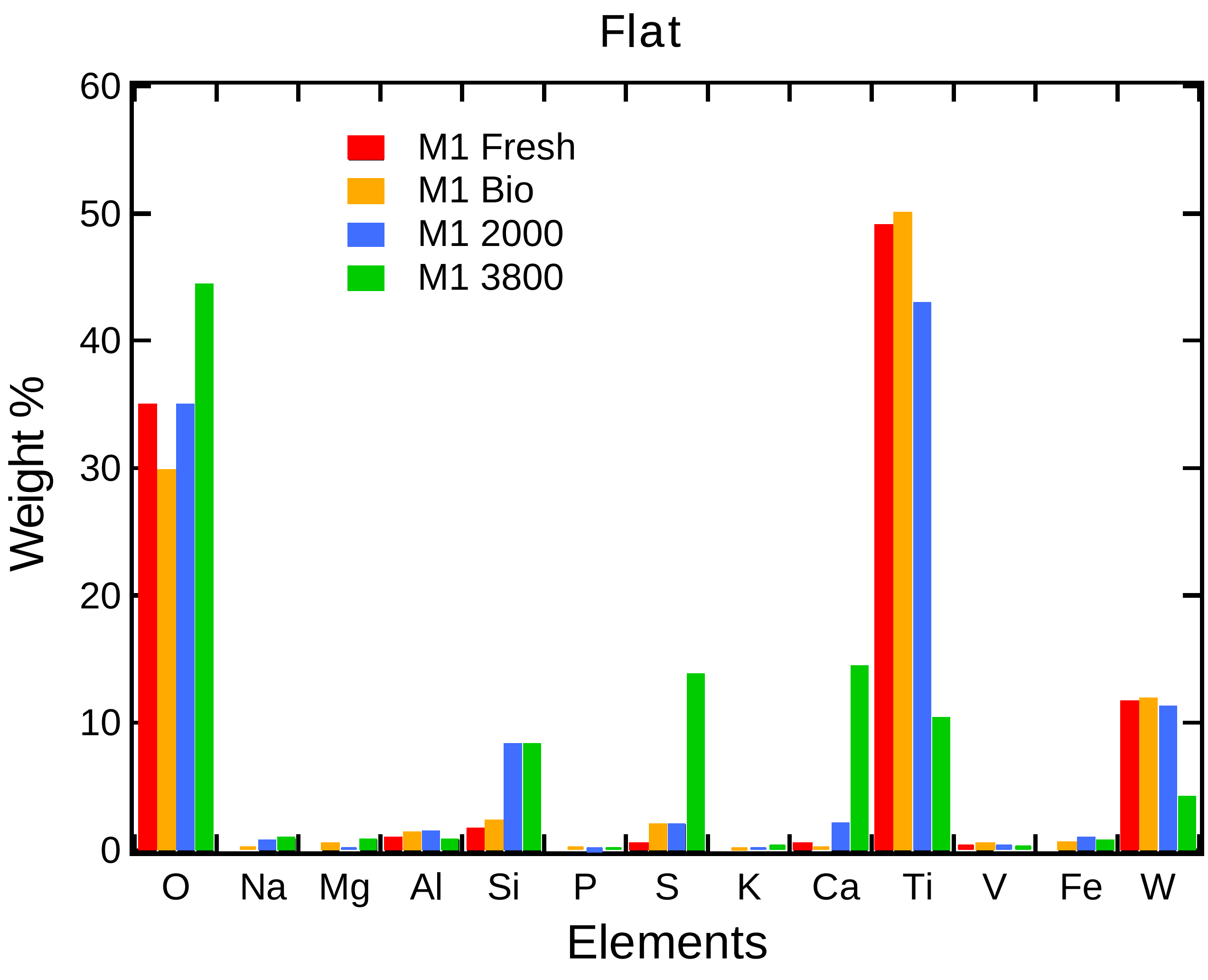
BET Results

Sample	M1		M2	
	BET surface area, m^2/g	Average pore diameter, nm	BET surface area, m^2/g	Average pore diameter, nm
Fresh	61.5	16.4	56.6	13.3
2063	53.5	17.5	54.5	13.6
3800	55.6	17.7	50.0	17.7
Biomass	48.2	19.9	43.9	20.0

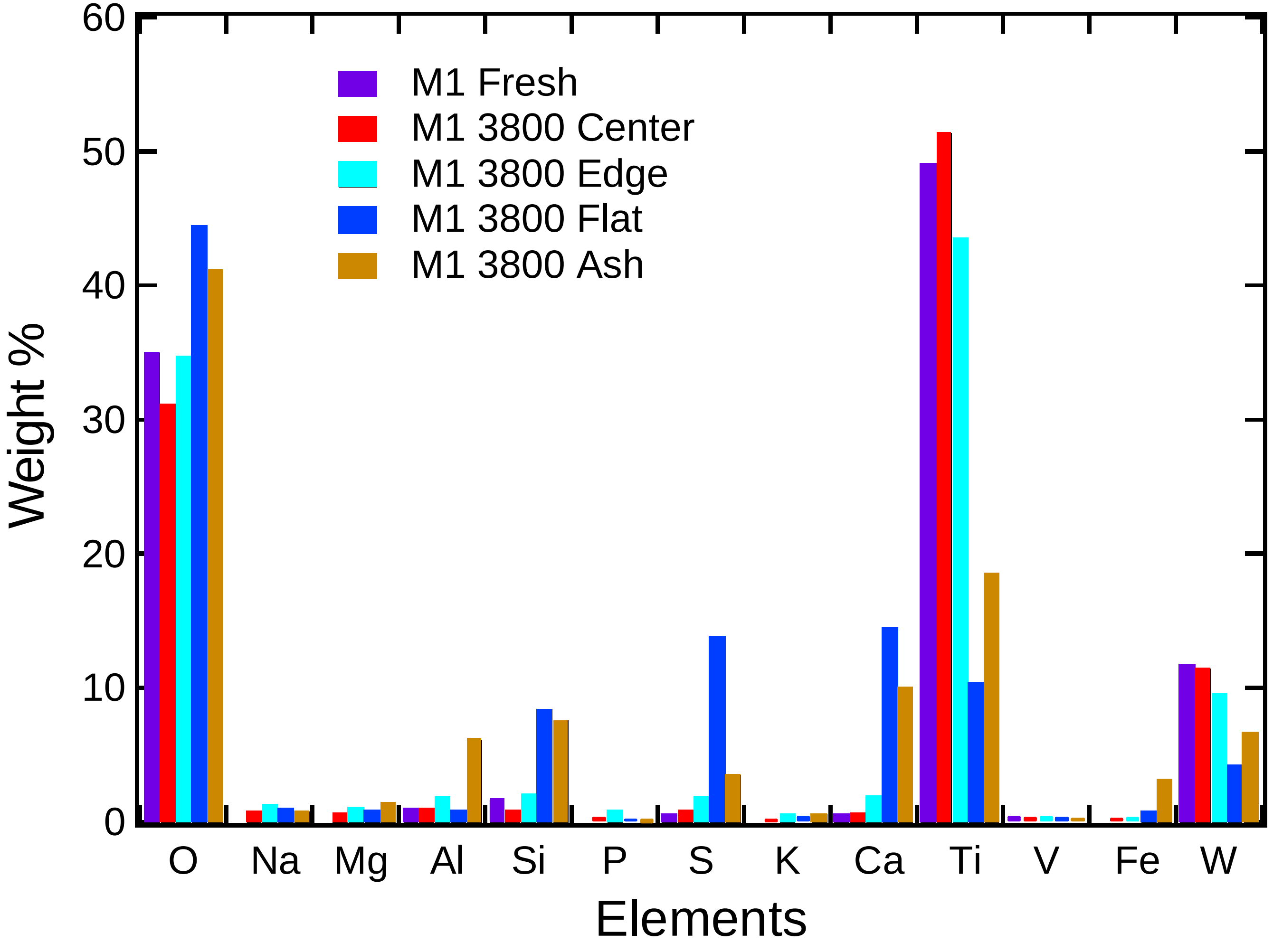
Locations of ESEM Analysis



Elemental Composition vs. Exposure



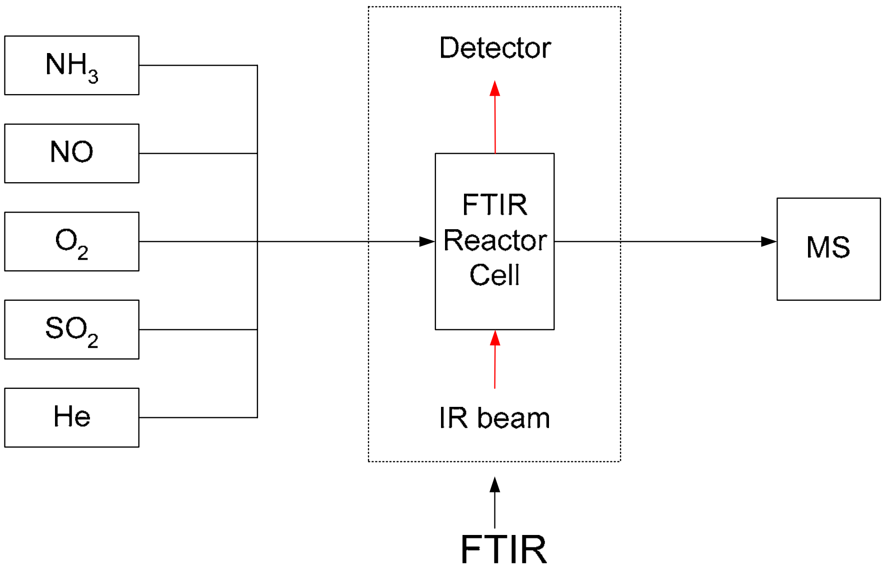
Elemental Composition vs. Position



Indications from Slipstream Samples

- Short exposure indicates a slight increase in activity
- Pore plugging and Fouling appear to be more significant initially with poisoning occurring later
- ESEM results indicate poisons deposit more on the outside edge than on the inside or center of the monolith catalyst
- ESEM results show sulfate accumulates on the catalyst outside surface

In situ FTIR - MS Reactor



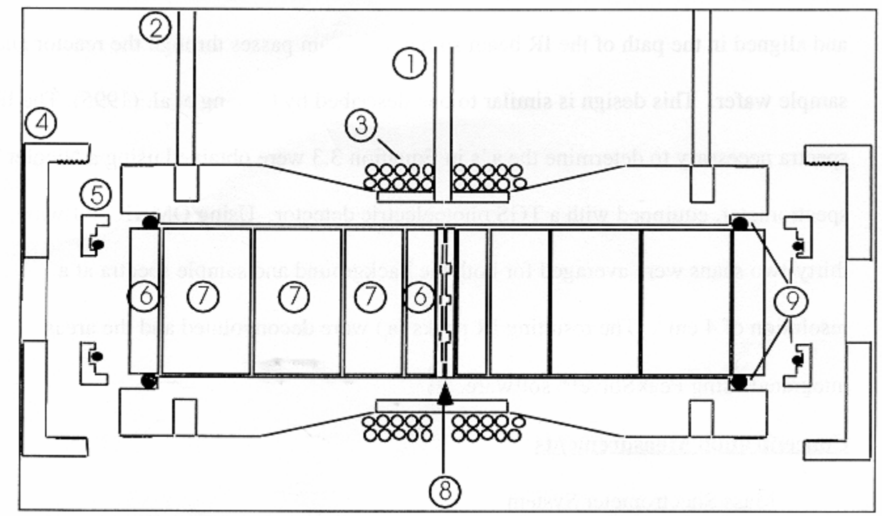
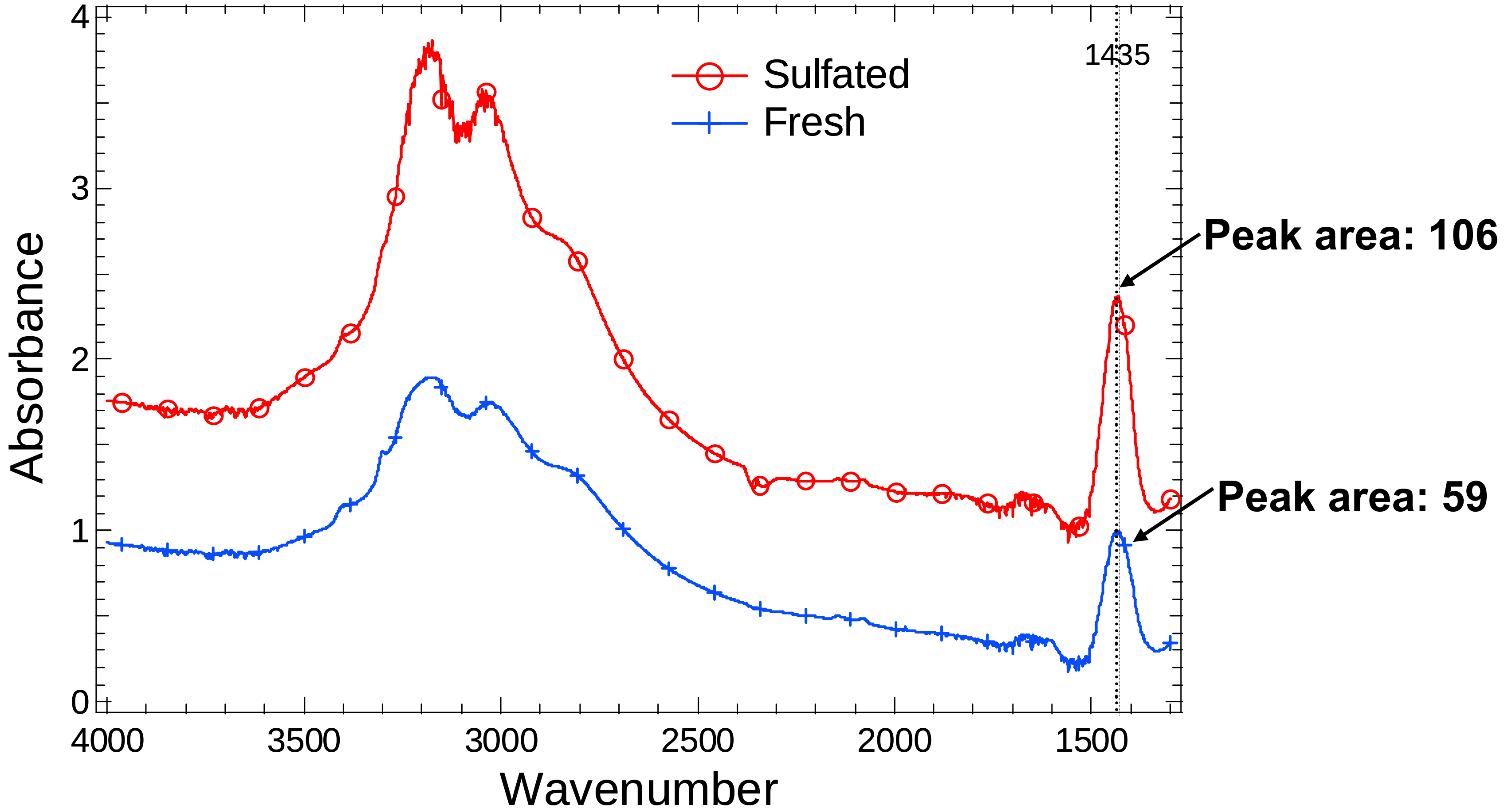


Figure 3.1. Schematic of FTIR reactor cell. 1) Thermocouple port, 2) water cooling ports, 3) Thermocoax heating cable, 4) end caps, 5) teflon window holders, 6) CaF_2 windows, 7) KCl windows, 8) aluminum wafer holder, 9) nitrile (large) and Kalrez (small) O-rings. Not shown are the gas inlet and outlet ports, located on either side of the reactor near (6) coming out of the page. (Drawn to scale.)

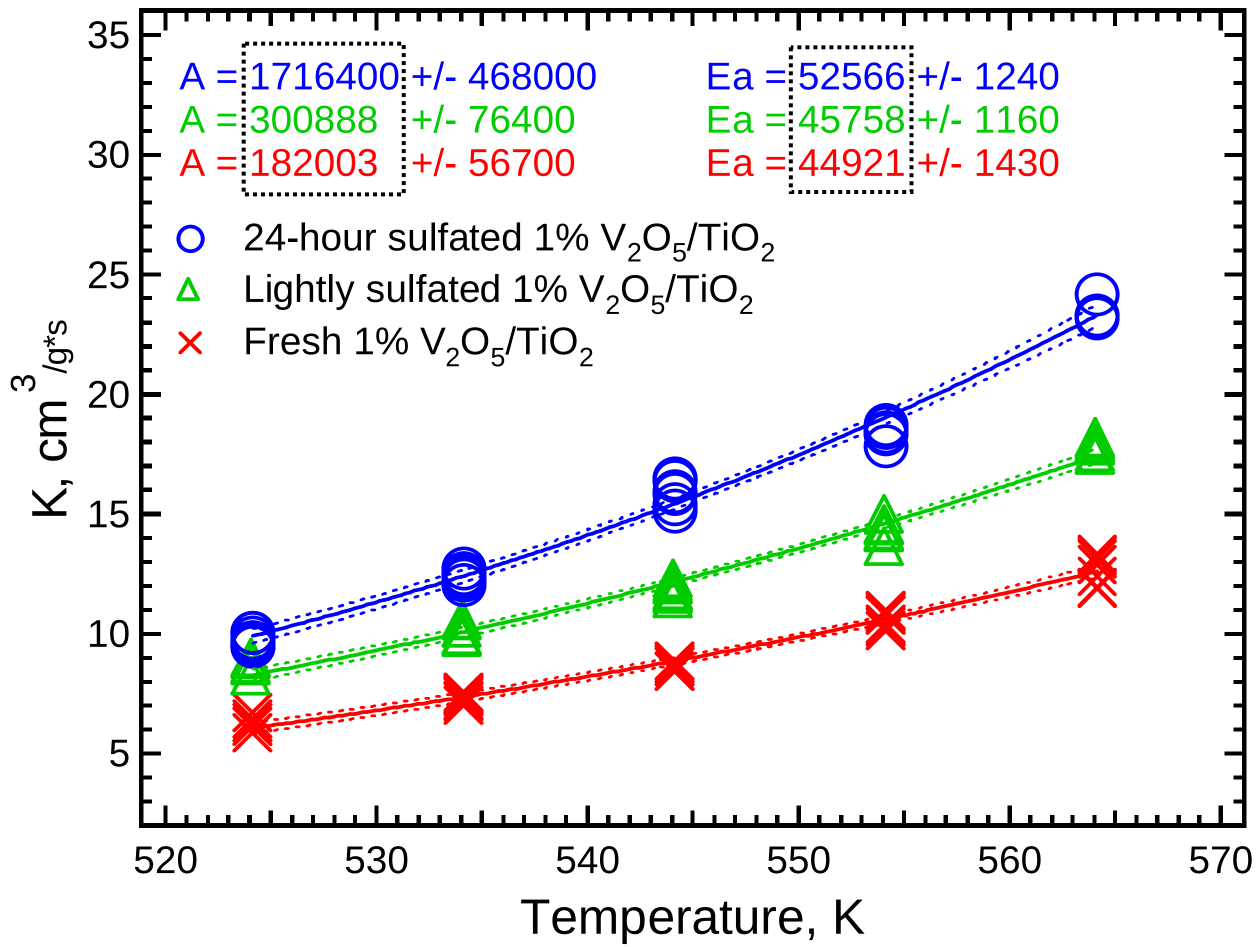
Sulfates Enhance NH_3 Adsorption

Sulfation increases the amount of Brønsted acid sites on the vanadia catalysts surface



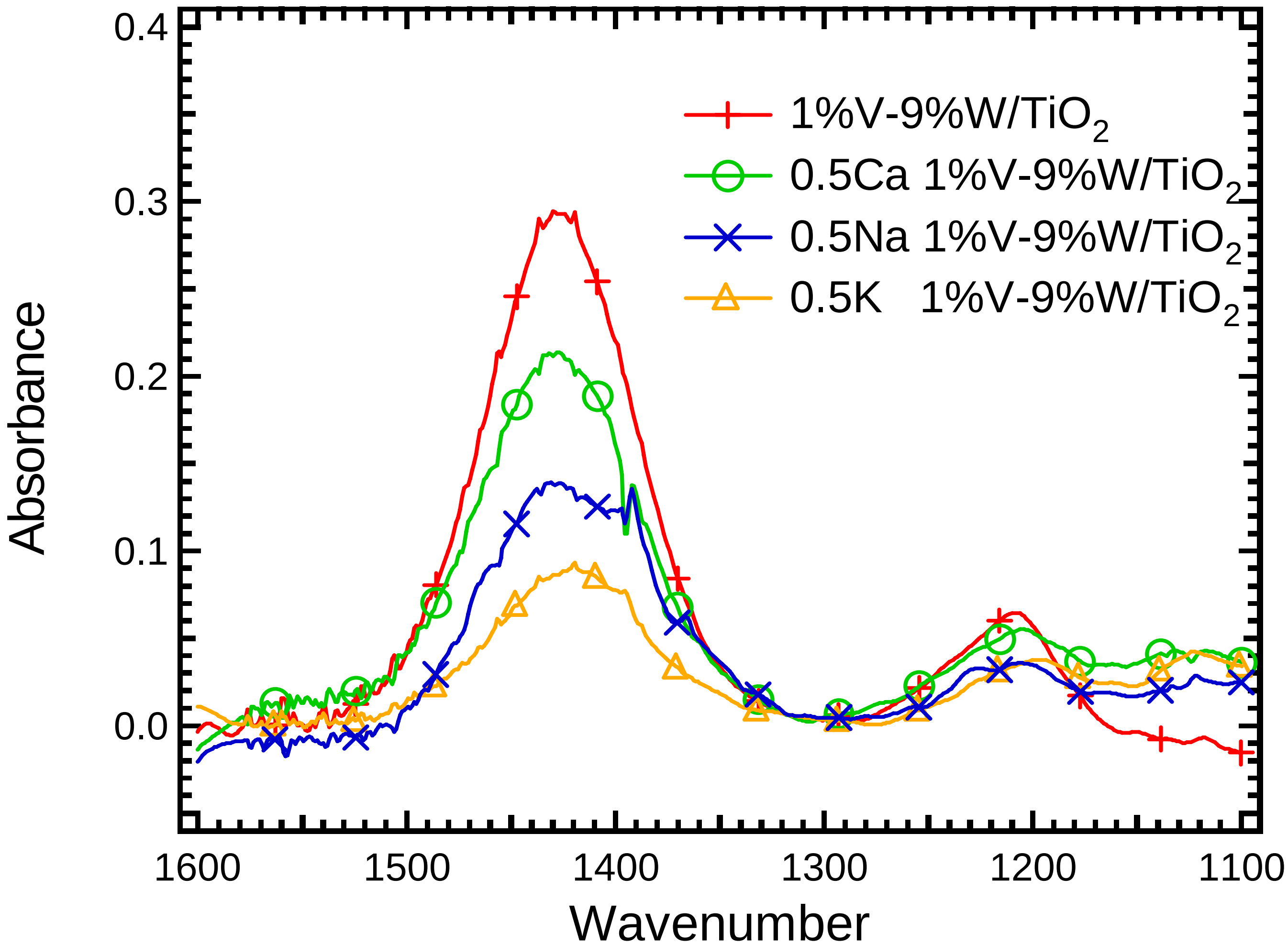
Sulfates Enhance NO Reduction Reactivity

Sulfation enhances NO reduction activity by increasing A, while E_a remains approximately constant before and after sulfation

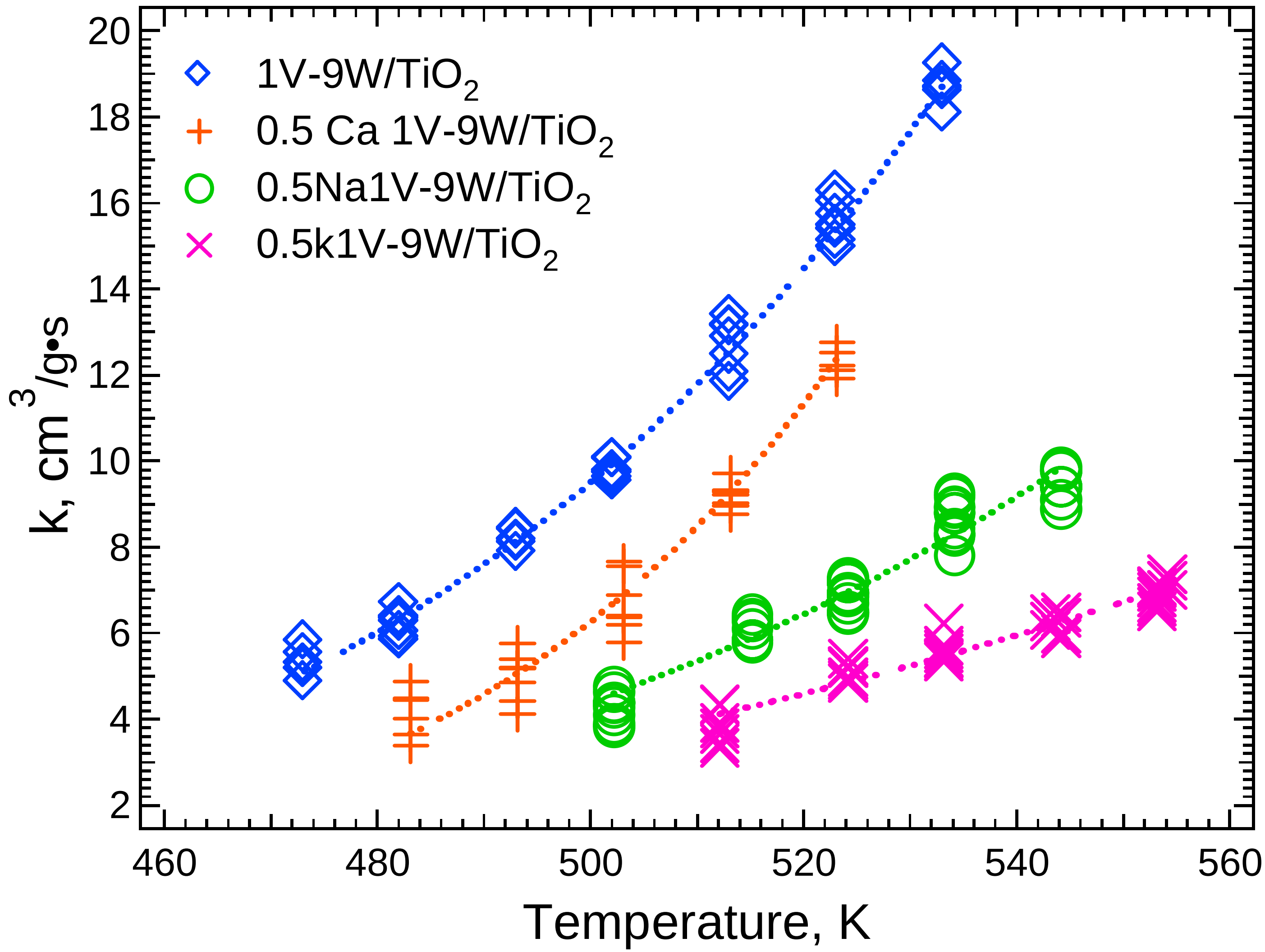


Ca, Na, and K Effects on NH_3 Adsorption

NH_3 adsorption ↓ with ↑ basicity of metals

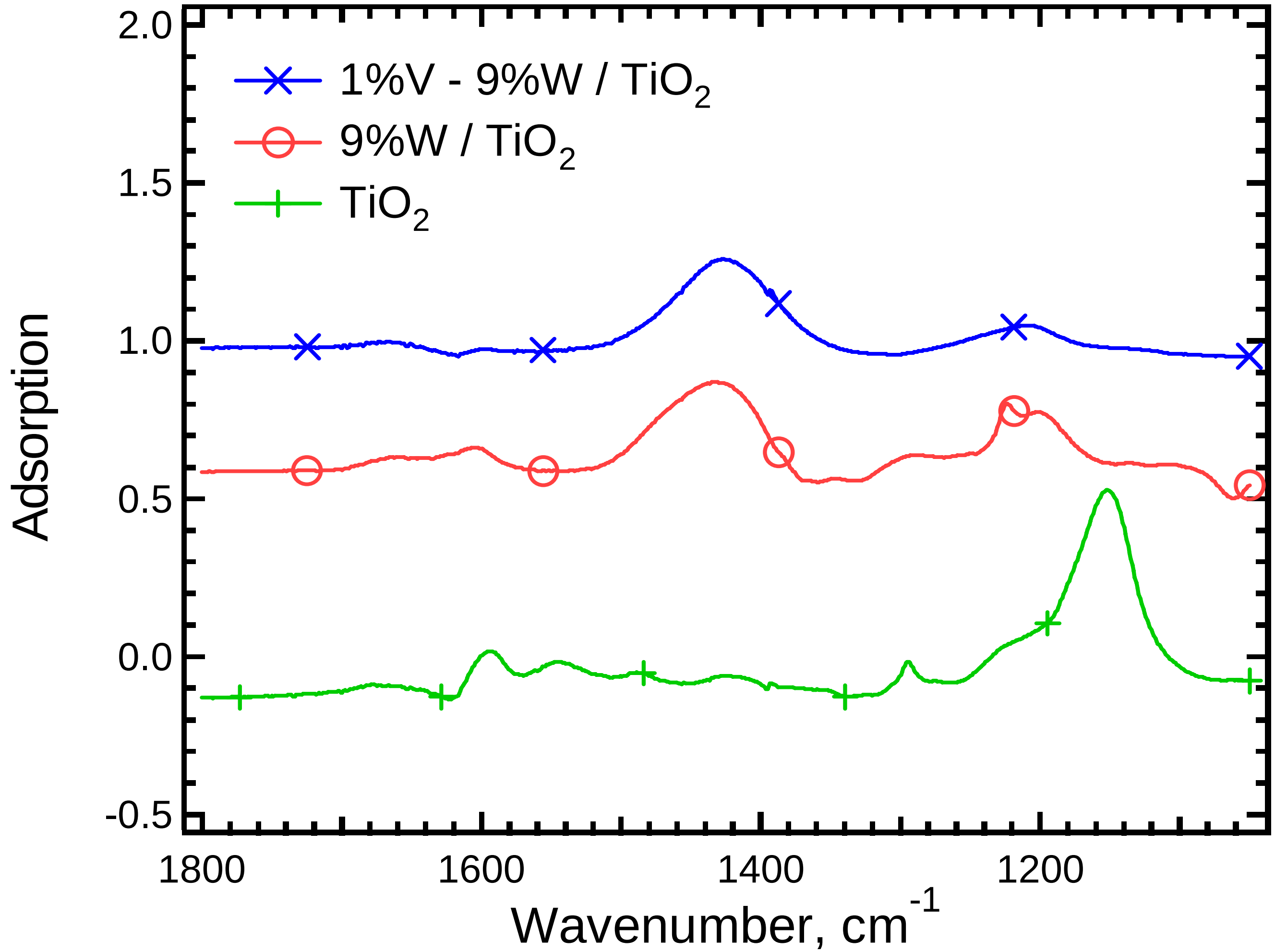


K, Na, and Ca Impacts on SCR Activity

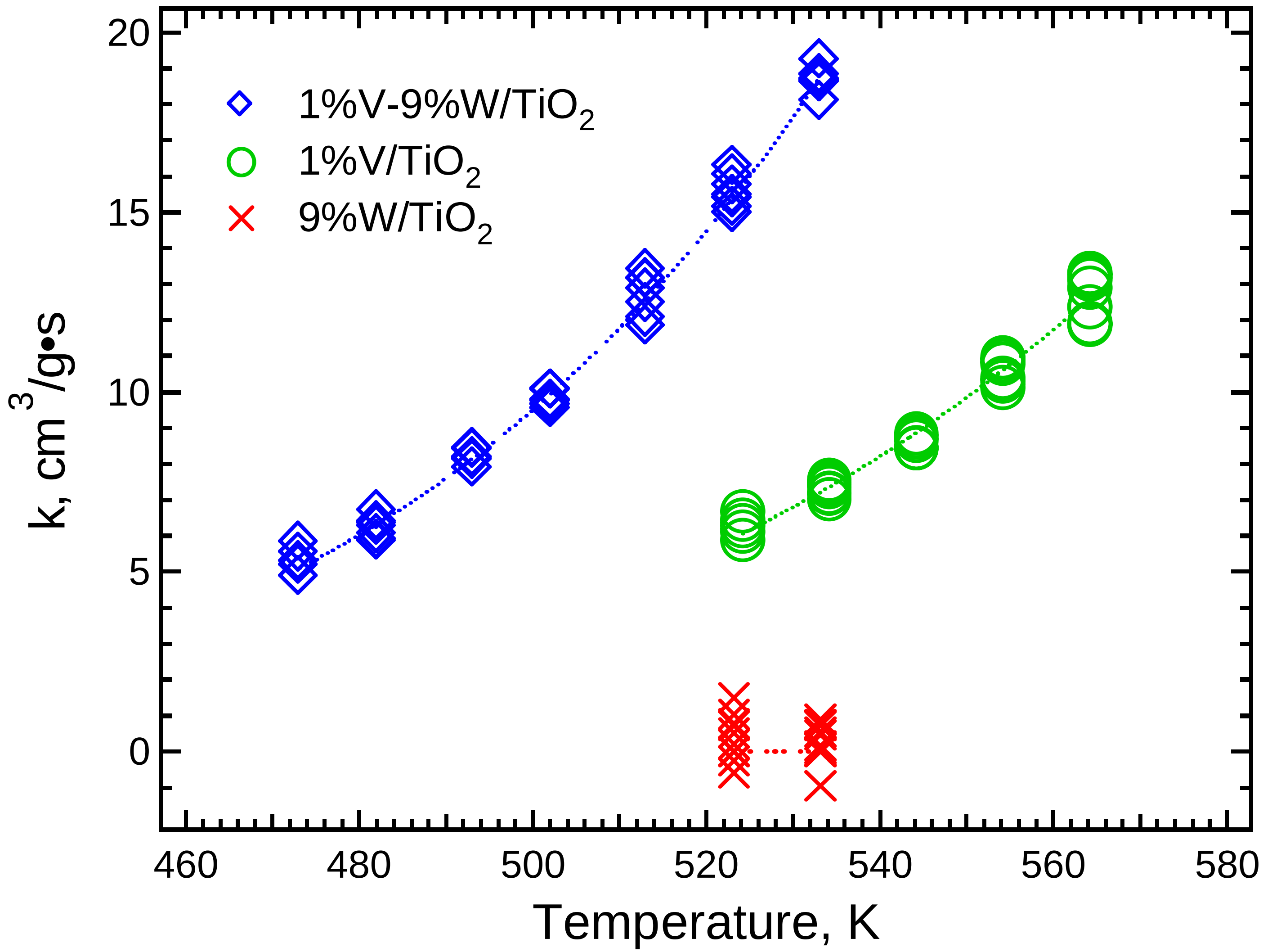


Tungsten Impact on NH_3 Adsorption

1000ppm NH_3 adsorption at 50 ˚C



NO_x Reduction Activity Comparison



Conclusion

- **Major deactivation mechanisms for vanadia catalysts during low-rank coal combustion:**
  - **Plugging by popcorn ash**
  - **Fouling and masking by fly ash**
  - **Chemical poisoning is not important**
- **Impacts of sulfation**
  - **Enhances NO_x reduction activity**
  - **Increases ammonia adsorption**
  - **Influences rate, but not mechanism**

Conclusion cont.

- Impact of K, Na, Ca
  - Significant poisons
  - K>Na>Ca, proportional to basicity
  - Biomass potentially is worse than coal
- Impact of Tungsten
  - Increase the amount of Brønsted acid sites
  - Does not provide activity but assists vanadia species significantly in the NO_x reduction

Current work

- **Affect of SO_2 flowing in reactant gases**
  - **Appears to significantly enhance NO_x reduction activity in preliminary experiment**
  - **More data is needed to validate effect**
- **Problems**
  - **Forms sticky ammonium salts when mixed with NH_3 in stream**
  - **Must heat all lines and MS above 300°C to prevent plugging**

Acknowledgments

- EPRI
- DOE/NETL
- REI
- University of Utah

Statistical Experimental Design

Runs	Composition Factor				Runs	Composition Factor			
	K	Na	Ca	SO_4		K	Na	Ca	SO_4
1	0	0	0	0	9	0	0	0	1
2	0.5	0	0	0	10	0.5	0	0	1
3	0	0.5	0	0	11	0	0.5	0	1
4	0	0	0.5	0	12	0	0	0.5	1
5	0.5	0.5	0	0	13	0.5	0.5	0	1
6	0.5	0	0.5	0	14	0.5	0	0.5	1
7	0	0.5	0.5	0	15	0	0.5	0.5	1
8	0.5	0.5	0.5	0	16	0.5	0.5	0.5	1

Statistical Experimental Design

Runs	Composition Factor				Runs	Composition Factor			
	K	Na	Ca	SO_4		K	Na	Ca	SO_4
1	0	0	0	0	9	0	0	0	1
2	0.5	0	0	0	10	0.5	0	0	1
3	0	0.5	0	0	11	0	0.5	0	1
4	0	0	0.5	0	12	0	0	0.5	1

Empirical rate constant expression

$$k = \exp\left(\begin{array}{l} 2.5 - 1.16\dfrac{K}{V} - 0.76\dfrac{Na}{V} - 0.3\dfrac{Ca}{V} + 0.17\dfrac{S}{S_0} + 0.38\dfrac{K}{V}\dfrac{S}{S_0} + 0.55\dfrac{Na}{V}\dfrac{S}{S_0} \\ + 0.27\left(\dfrac{1}{T} - \dfrac{1}{T_0}\right) - 0.12\dfrac{S}{S_0}\left(\dfrac{1}{T} - \dfrac{1}{T_0}\right) \end{array} \right)$$