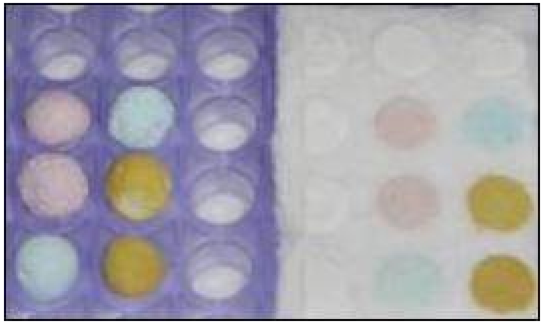
Accelerated Catalyst Discovery

Combinatorial Chemistry Laboratory
Materials Analysis & Chemical Sciences
GE Global Research Center
Jonathan L. Male

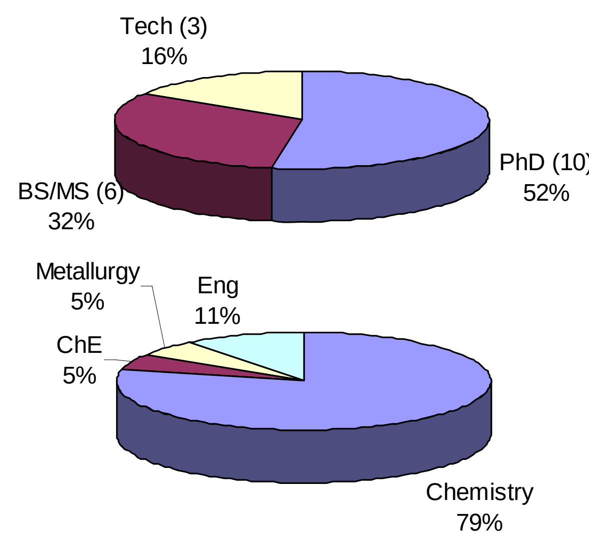
8th DOE Cross-Cut Lean Exhaust Emissions Reduction Simulation Workshop
19th May 2005

imagination at work

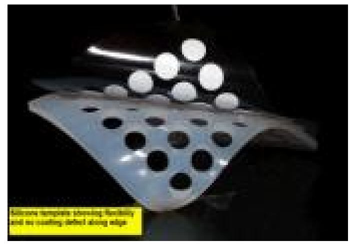
Combinatorial Chemistry Lab

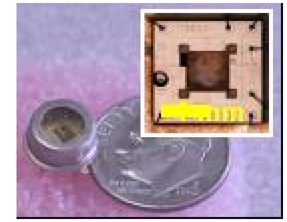
GE Combinatorial Chemistry Lab

- We develop and apply high throughput experimentation – an enabling technology in which materials are created or mixed in arrays or gradients via automation and miniaturization and then rapidly tested for desirable properties
- We work on a diverse portfolio of materials research including catalysis, coatings, phosphors, and many other areas



Evolution of Combinatorial Chemistry at GE





1999

Heterogeneous Catalysis
Polymerization Catalysis
Homogeneous Catalysis

2000

Polymer Composition
Coatings
Heterogeneous Catalysis
Polymerization Catalysis
Homogeneous Catalysis

2001

Polymer Performance
Inorganic Compositions
Polymer Composition
Coatings
Heterogeneous Catalysis
Polymerization Catalysis
Homogeneous Catalysis

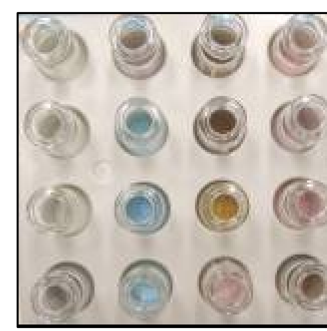
2002 - 2004

Photovoltaics
Phosphors
Sensors
Polymer Performance
Inorganic Compositions
Polymer Composition
Coatings
Heterogeneous Catalysis
Polymerization Catalysis
Homogeneous Catalysis

Steadily expanding capabilities supporting a broad customer base…

Diverse project portfolio in 2005:

Several HTE projects in areas ranging from coatings to catalysis to inorganic materials



imagination at work

Combinatorial Chemistry Lab

High Throughput Catalyst Screening

Multiple Experiments + Miniature Scale + Rapid Characterization = High Throughput Screening of Catalysts

Benefits

- Increased probability and speed of discovery
- Capability to deal with complex systems & synergies
- Cost effective approach to accelerate innovation
- Allows time for testing higher risk catalysts

Variables for NO_x SCR Process

- Catalyst Composition: Active metal + Support + Binders
- Catalyst Fabrication
- Feed composition
- Reductant
- Process Conditions
- Application

Scheidtmann, J.; Weiβ, P. A.; Maier, W. F. *Appl. Catalysis A: General* **2001**, *222*, 79-89.

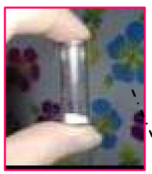
High Throughput Screening Workflow

SCR System

NO + REDUCTANT + O_2 → N_2 + H_2O + CO_2

Reductant

Oxygenates, hydrocarbons



32 tube reactor

Catalyst

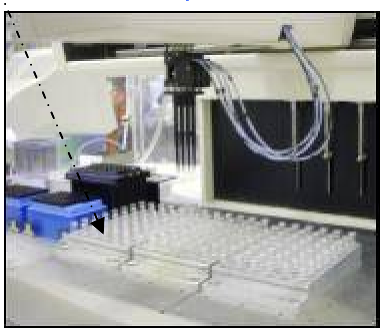
Support

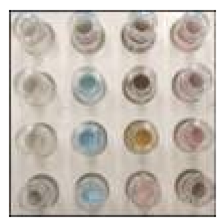
Active Phases

Calcination Conditions

3-T,3-tube furnace

Robotic Liquid Handler





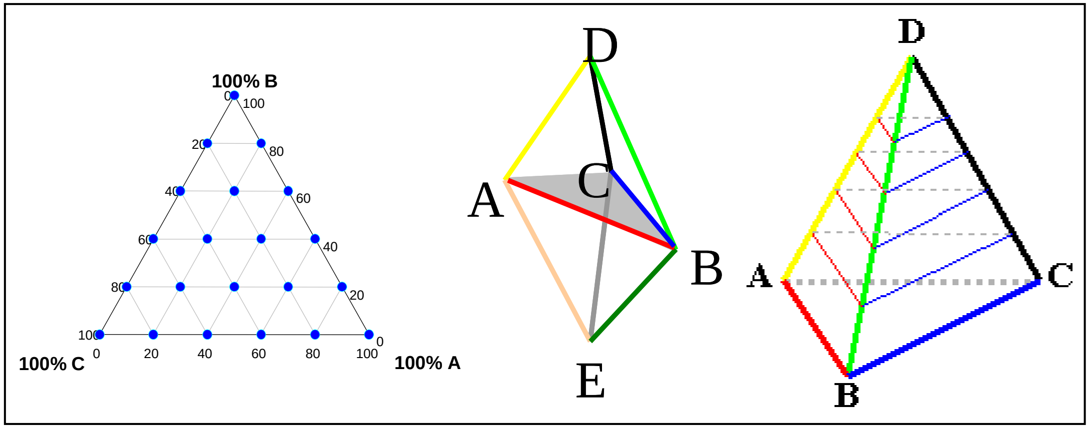
Catalyst Library

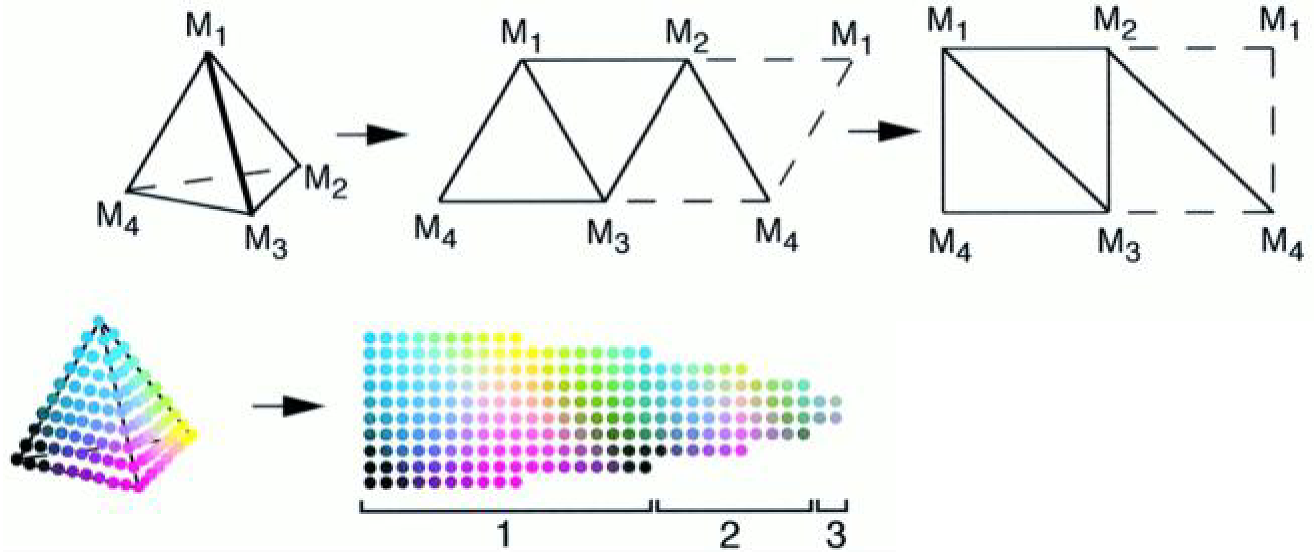
Performance of SCR system = f (composition, processing conditions, reductant)

Efficient Catalyst Screening Designs

Folded 3D Design Space

Overlapping ternary & quaternary multi-component gradient arrays with 20% intervals





Lemmon, J. P.; Wroczynski, R. J. *Polymer Preprints* (ACS, Division of Polymer Chemistry) **2001**, *42* (2) 630-631.

Optimization Using Genetic Algorithms

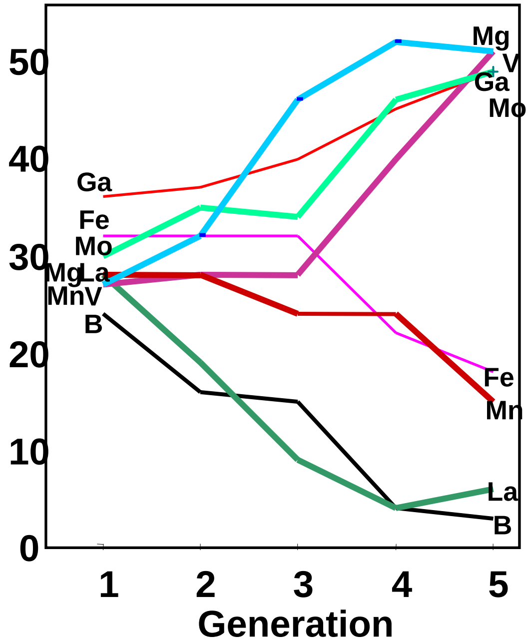
Formulations are encoded as genetic type structures

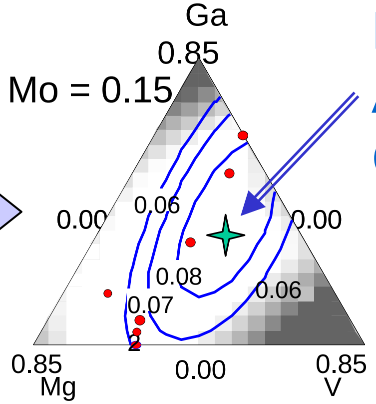
An initial population is generated and evaluated

Successive populations are generated by genetic operations (mutation and crossover) from "fitter" antecedents

Results: Effective search of > 20,000 run space in 286 runs

Representation of element in the population





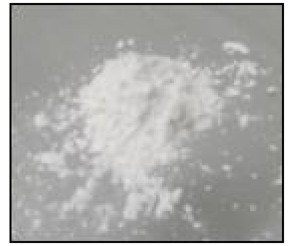
Highly Active Catalyst

Cawse, Baerns Wolf, Holena, *Journal of Chemical Information and Computer Science* 2003, *44*, 143-146.

imagination at work

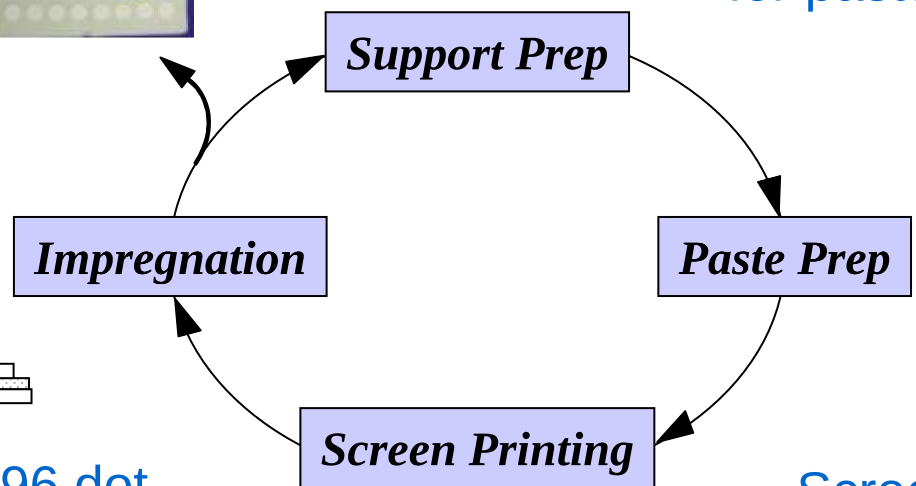
Combinatorial Chemistry Lab

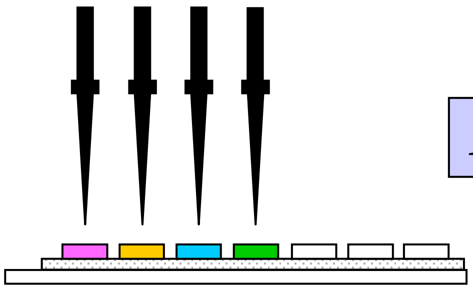
Thick Film Catalyst Synthesis



Al_2O_3 catalyst support milled, calcined, and sieved

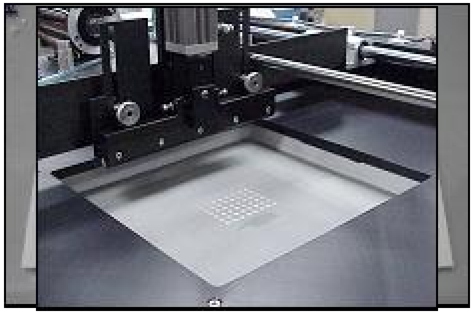
x ≤ 20 μm particles collected for paste preparation





Support printed in 96 dot catalyst array on porous alumina paper

Layering prints to build support thickness



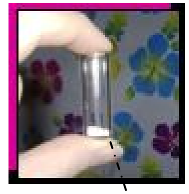
Screen Printing Paste:

- Solids loading
- Vehicle
- Solvent

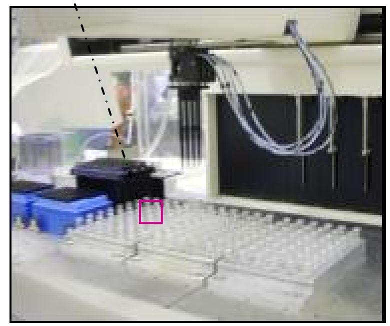
imagination at work

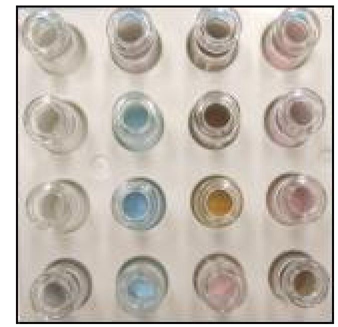
Combinatorial Chemistry Lab

Parallel Catalyst Powder Synthesis



Weighed, sieved
catalyst support





liquid dispensing robot

catalyst library

Incipient wetness impregnation

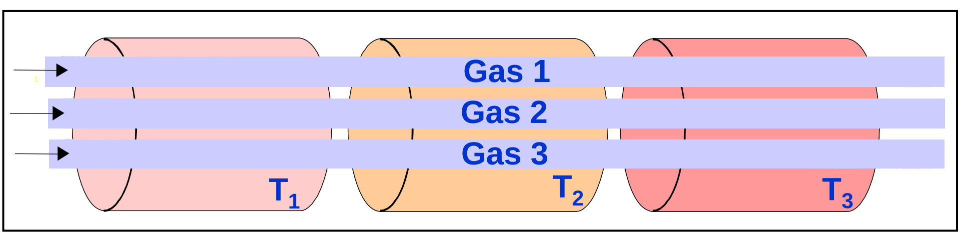
Mixing of catalytic precursors solutions prior to doping yields homogeneous dispersions

Catalyst focus areas:
Mixed multi-metal oxides, spinels and perovskites

High throughput synthesis enables broad compositional space

Catalyst Processing

3 Zone Furnace

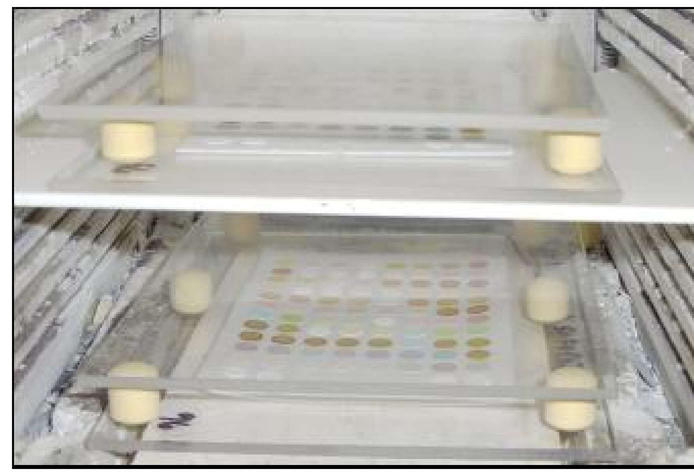


63 formulations
3 tubes
3 heat zones

= 9 conditions
(T < 1450 ˚C)

Catalyst dispersion and final active state influenced by process conditions

1 Zone Furnace



192 formulations
1 atmosphere
1 heat zone

= 1 condition
(T < 800 ˚C)

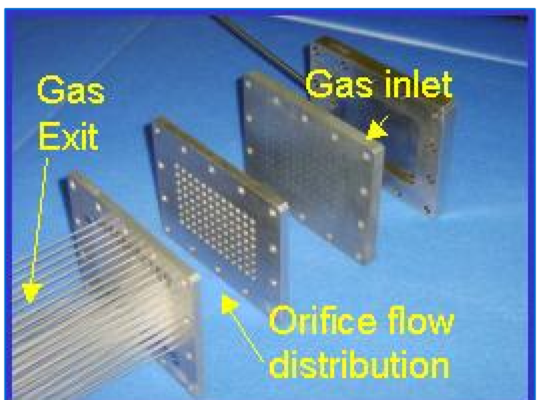
imagination at work

Combinatorial Chemistry Lab

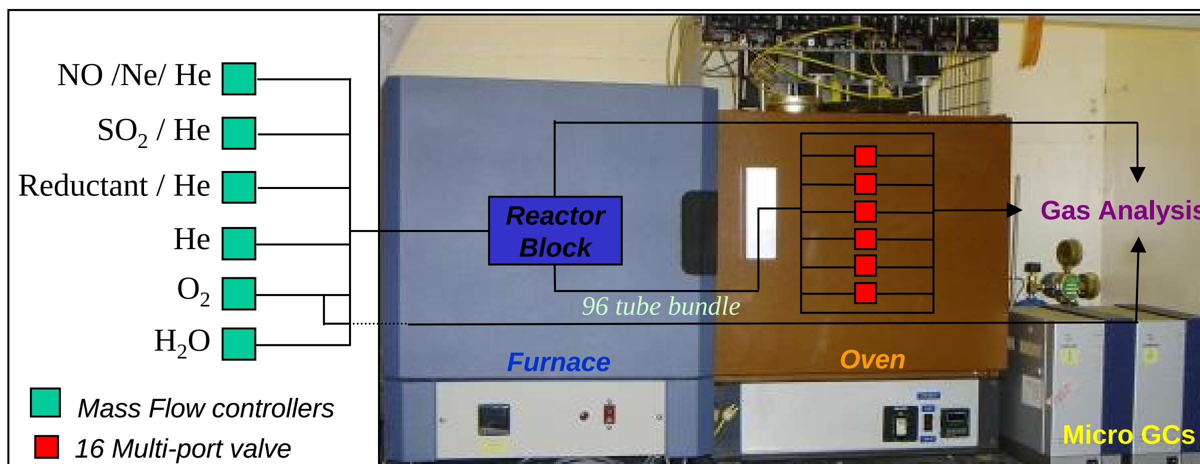
Primary Screening Reactor

- Screen with water, SO_2, hydrocarbon reductants and oxygenated reductants
- Porosity of spots enables high flow rate testing
- Robust Inconel 625 reactor
- Able to detect Ne, N_2, O_2 and CO

Flexibility and Capability in a Harsh Environment



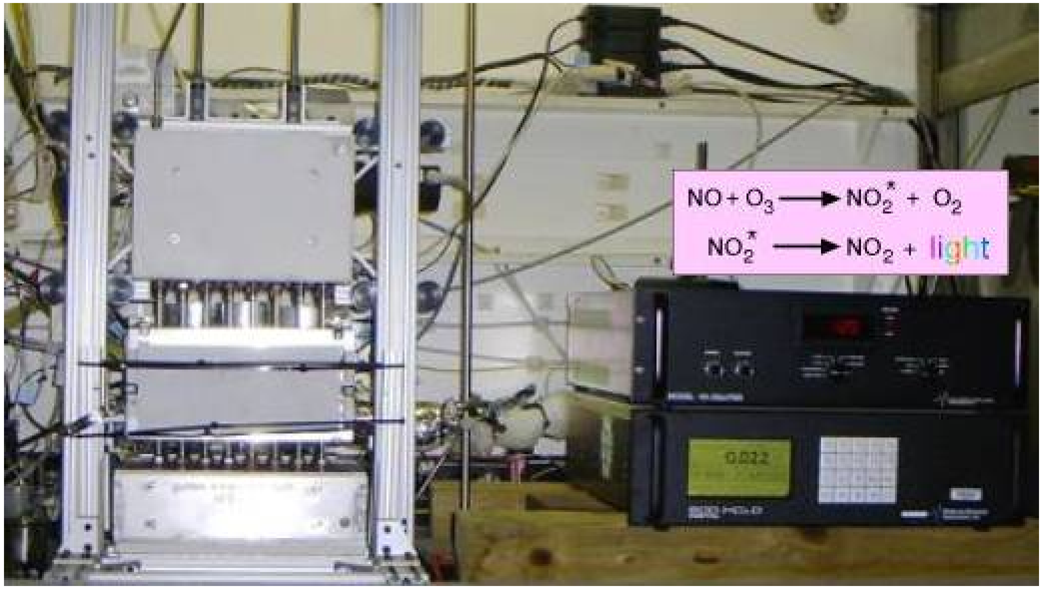
Reactor Block



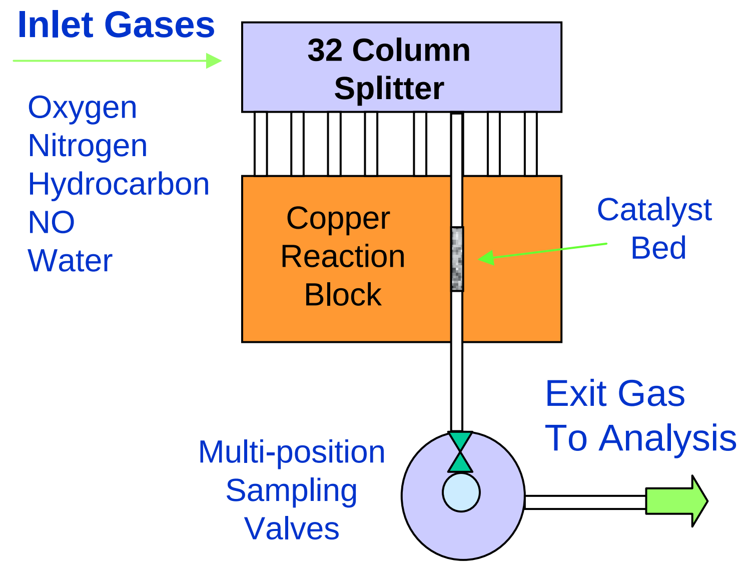
imagination at work

Combinatorial Chemistry Lab

32-Tube Secondary Screening Reactor

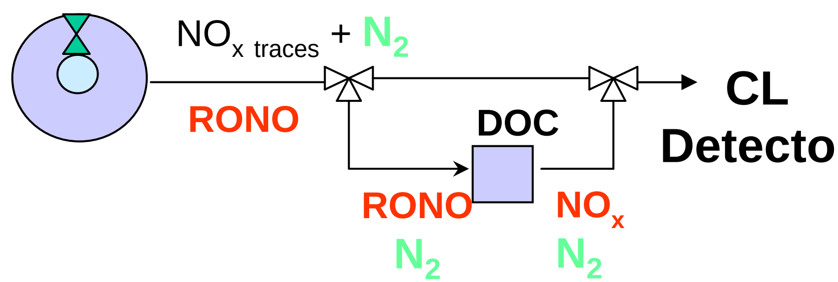


Gas Flow Path



Design Details

- Capable of gaseous and liquid reactant delivery
- Capable of 700 reactions/week
- 20-200 mg catalyst per reaction tube
- Continuous gas/vapor feed
- 5-10% RSD on flow distribution



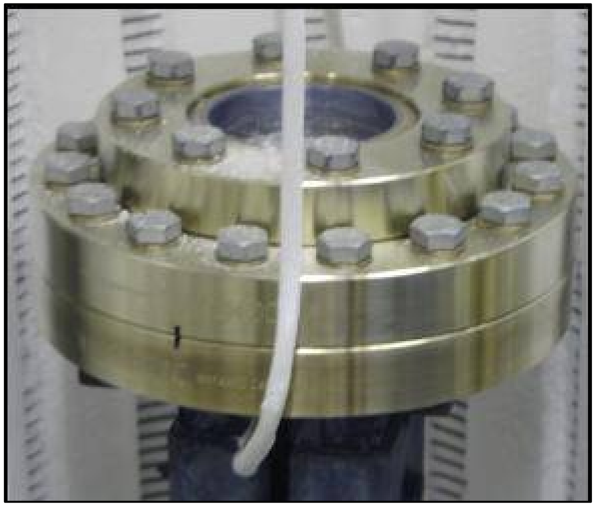
$$RONO + O_2 \xrightarrow{DOC} NO + H_2O$$

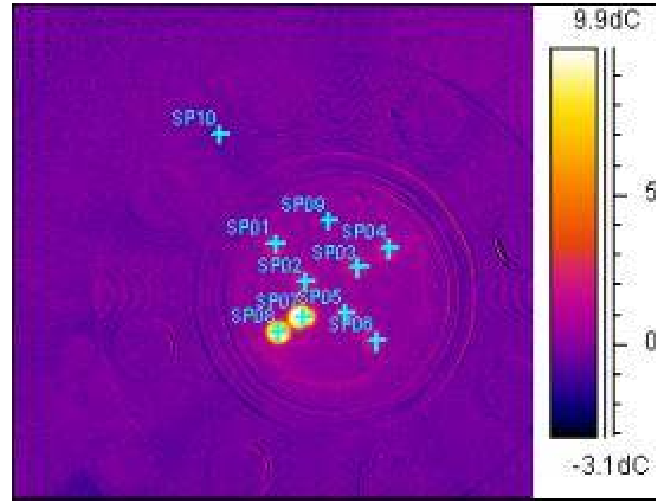
DOC - **D**eep **O**xidation **C**atalyst (Pt/ Al_2O_3 - Johnson Matthey)
RONO – Nitrogen containing Hydrocarbon

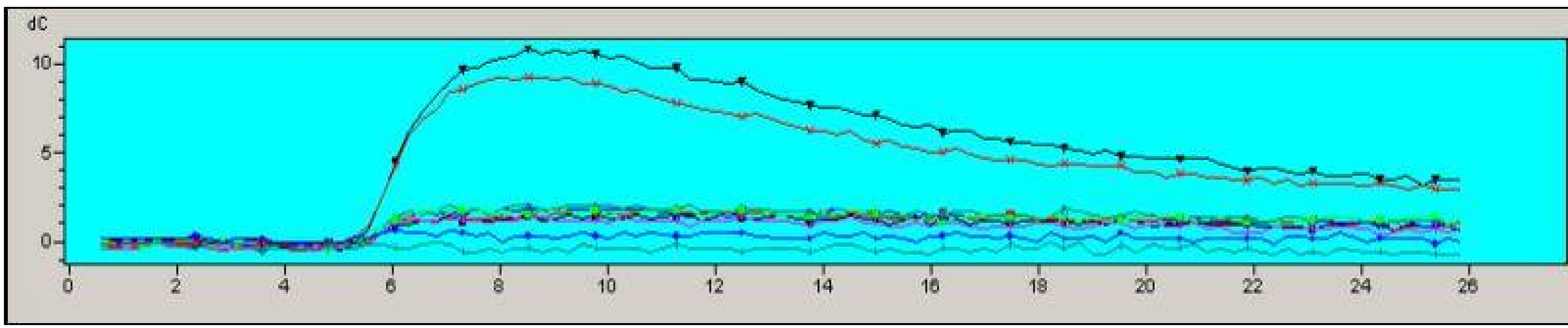
imagination at work

Combinatorial Chemistry Lab

Infrared Thermography Reactor





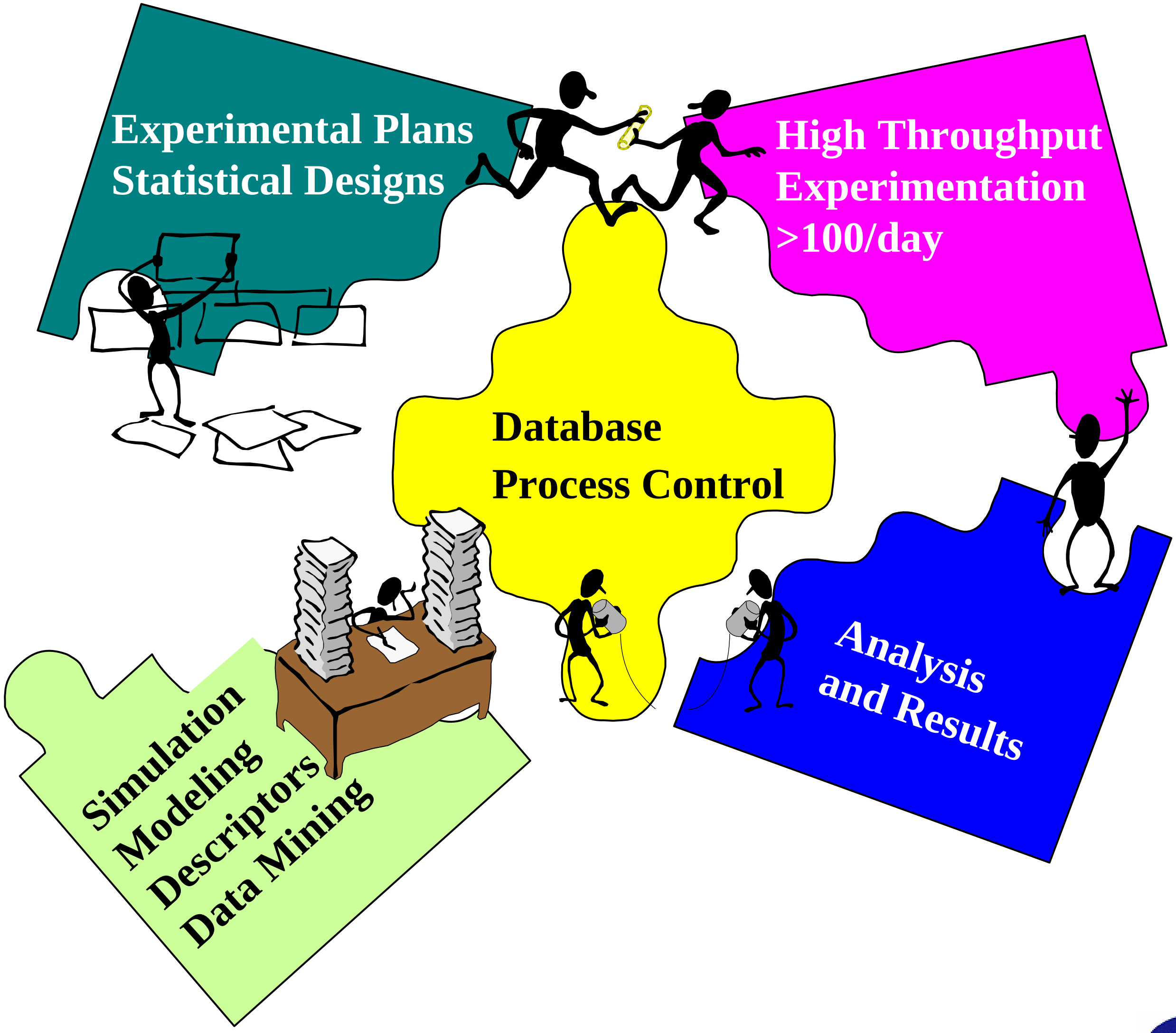


2000 ppm NO, 13% O_2 in helium 300 °C

Rapidly down select catalysts leads qualitatively

Obtains additional mechanistic information

Informatics

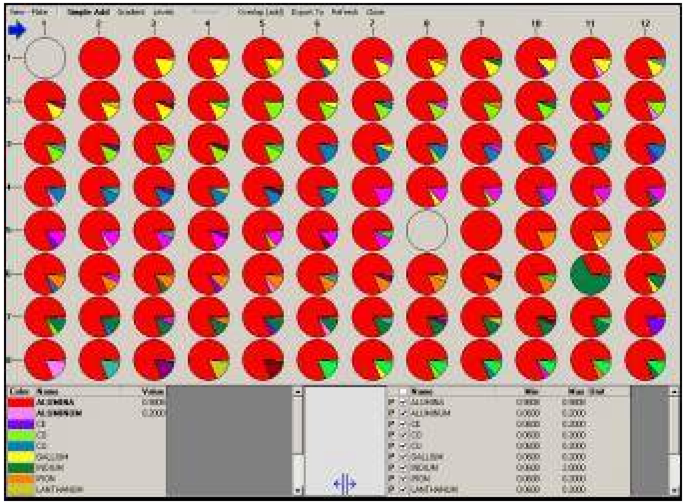


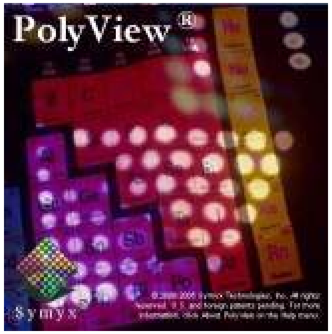
imagination at work

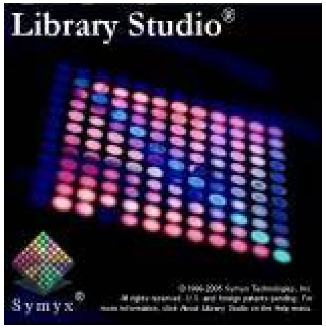
Combinatorial
Chemistry Lab

Data Management

Catalyst Designs







Catalyst Results

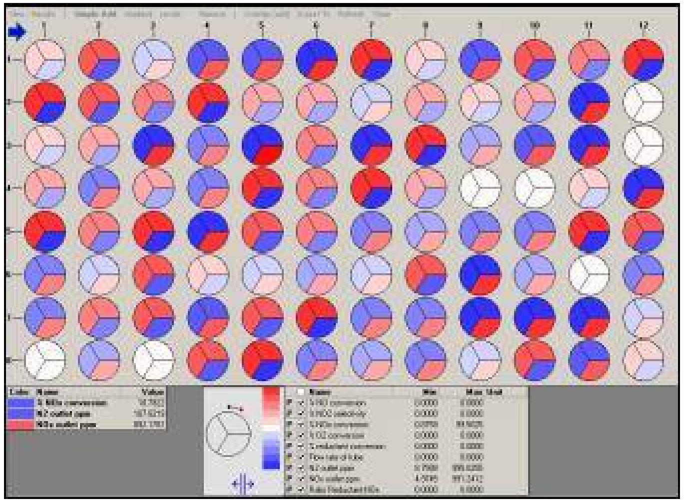


Plate Designer facilitates automated sample preparation and experimental design

eBrowser solves organizational and accessibility issues of vast data arrays

Enables data mining & visualization

Scalability and Reliability Issues

Key Points

- Understand high-level deliverables
- Flow down to screenable project-level CTQs*
- Validate rank order correlations: HTE vs. lab scale
- Characterize subsystem variances
- Flow up to determine system level variance
  - ✓Use propagation of error techniques
- Establish 95% confidence detection intervals
- Establish pass / fail criteria

*CTQ = Critical-to-Quality parameter
(typically refers to the key property that is being measured)

Statistics Based Quality Tools

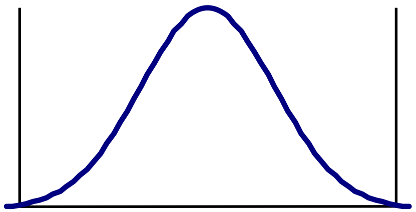
Little y's:

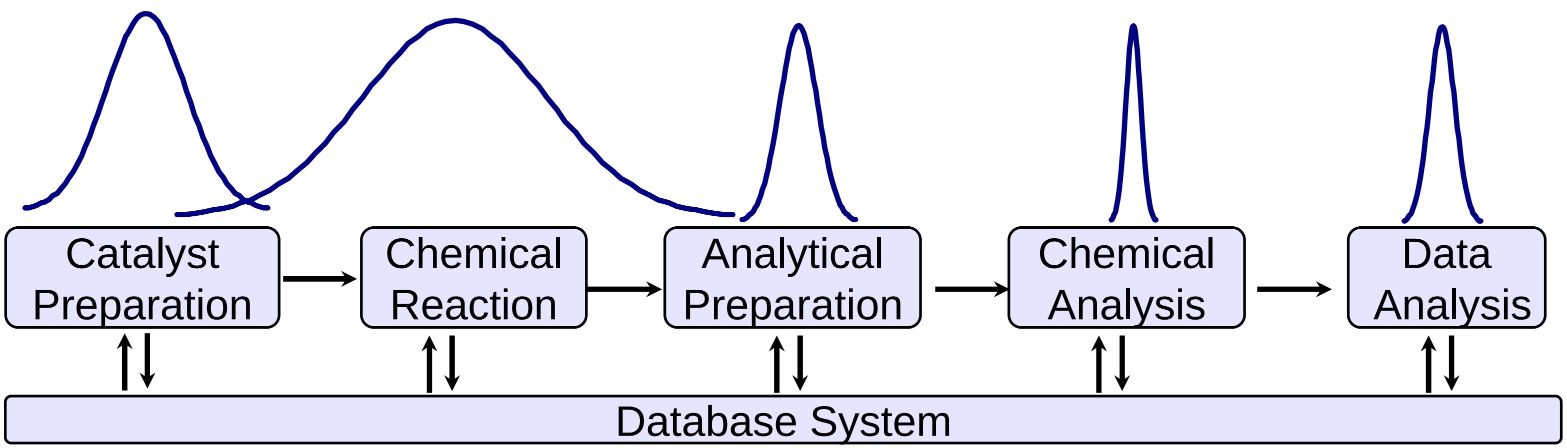
Accurate Lead Identification
Rapid Lead Identification
Catalyst Conversion/Activity

= **f**(subsystem variability)

Specification:

95% probability of detecting 25% improvement in Critical Customer Parameter

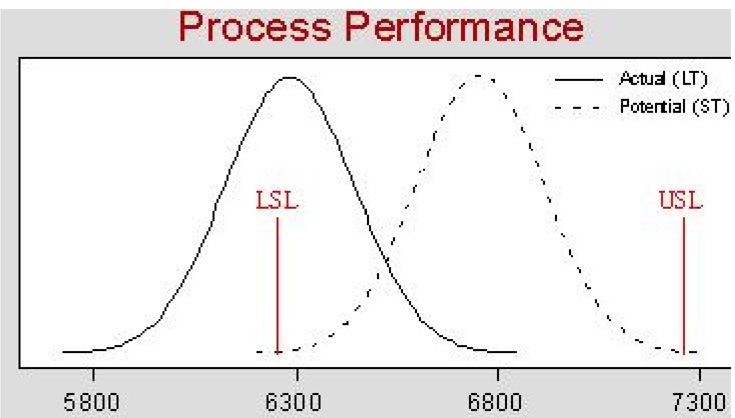


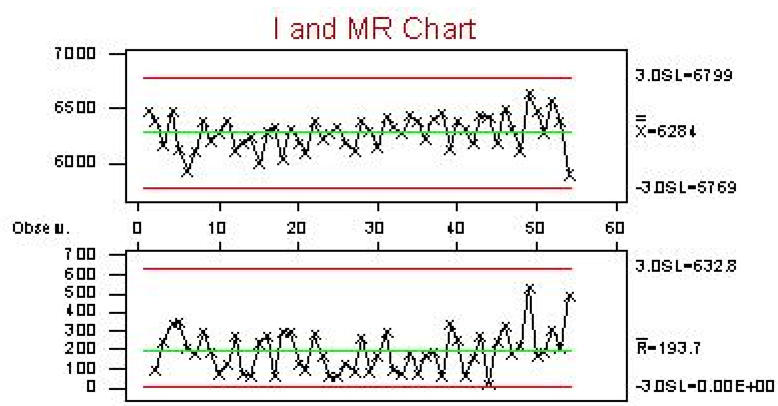


GE's Six Sigma Quality Initiative Provides Unique Advantage When Applied to Combinatorial Chemistry

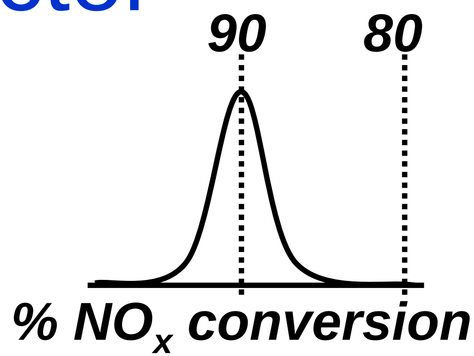
Screen Printing Catalysts for 96-well Reactor

- Spot average diameter target 6.76 ± 0.50 mm
  - Avg. 6.28 mm Std. Dev. 0.16 mm Z_{ST} 2.94 (Z_{LT} 0.17)
- Demonstrated a stable process for spot production
- Re-optimizing diameter to compensate for shrinkage
- Impregnation of colored metals demonstrated
- Porosity of spots enables high flow rate testing

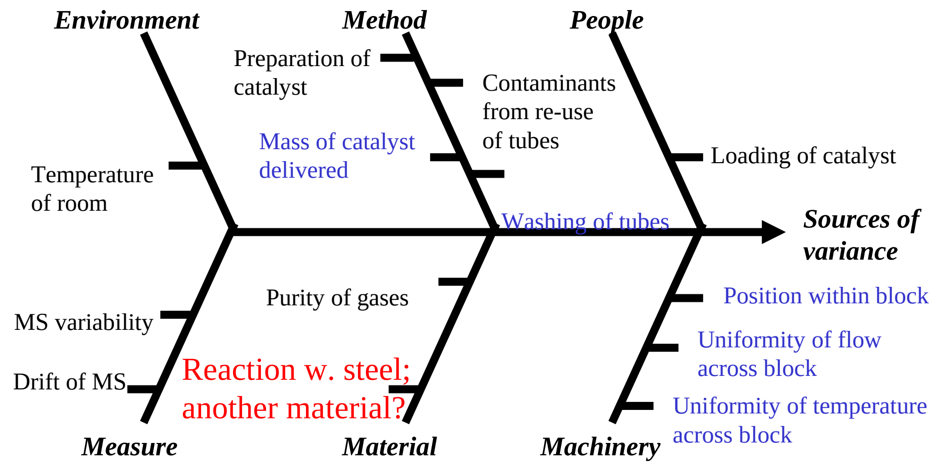


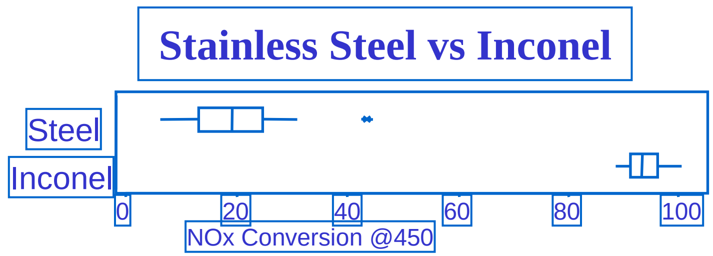


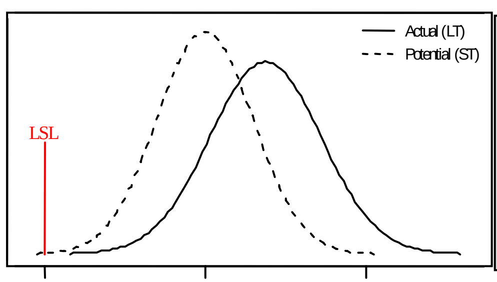
Variabilibilty for NO_x Catalysis in 32 tube Reactor



CTQ: measure the difference in catalysts that are 5% different in NO_x conversion







Process Benchmarks

	Actual (LT)	Potential (ST)
Sigma (Z.Bench)	3.95	3.3
PPM	38.8	448

imagination at work

Combinatorial Chemistry Lab

Fuel Based Aftertreatment

Approach

Use high-throughput screening to discover leads in high risk NO_x catalyst aftertreatment for diesel engines

Critical Requirements for Mobile Engine SCR

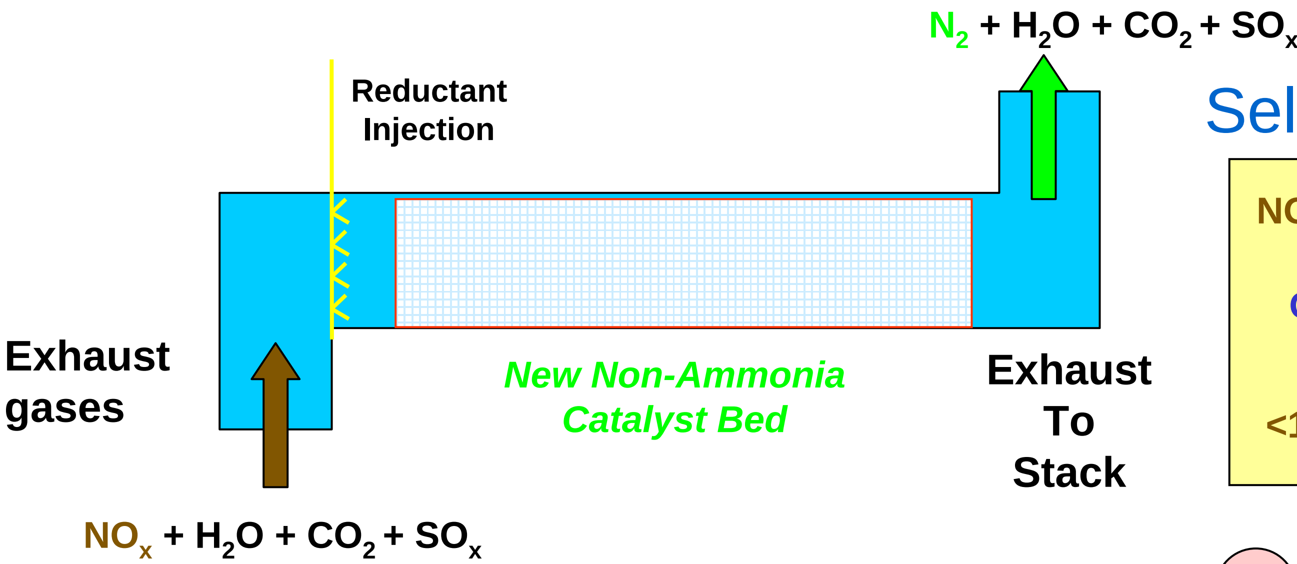
- Diesel fuel based reductant
- > 70% conversion at 15-50 ppm Sulfur
- Some S tolerance to 500 ppm
- Minimal reductant emissions

Advantages

- No ammonia/ urea infrastructure
- No sulfur removal & storage
- Pathway for meeting NO_x emissions with increased fuel efficiency

Fuel Based Aftertreatment a High Risk, High Payoff Solution

Challenges For NO_x HC-SCR



Selective Hydrocarbon

NO_x + HC → N_2 + H_2O + CO_2

New catalyst

O_2 + HC → H_2O + CO_2

Competing reaction

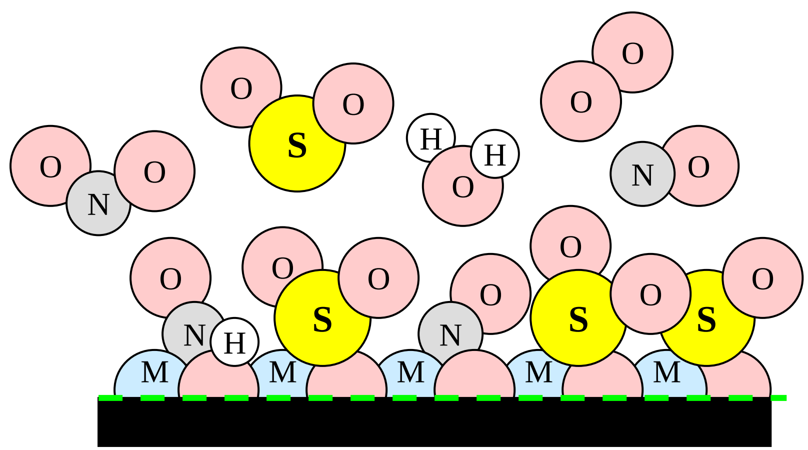
<1000 ppm NO_x vs >10% O_2

Challenging catalyst environment

Poisons: oxygen, water, sulfur

High velocity gas at exhaust temperatures

Limited space between exhaust source and stack



Poisons blocks active catalyst sites

High Risk and Complex Synergies

imagination at work

Combinatorial Chemistry Lab

Case Study: Supported Silver

A. Objective

Performance of Ag SCR catalyst = f (Processing conditions, Reductant, pretreatments, % Ag) and correlate with Ag distribution on the support

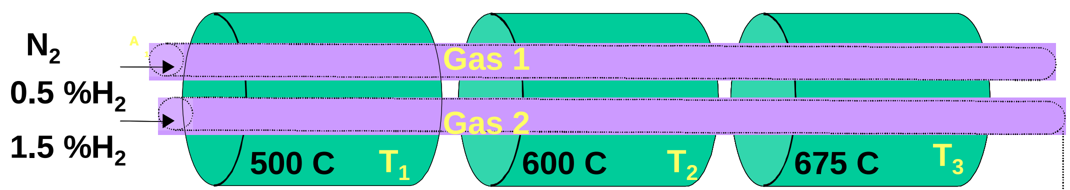
B. Catalyst Library

Compositional space:

Sample	Support	Ag mol. %
1	Al2O3	1
2	Al2O3	2
3	Al2O3	9
4	Support2	1
5	Support2	2
6	Support2	4
7	Support2	9

Al_2O_3:
0.8 g / cm³, 240 m² / g, 0.4-1 mm
Support 2:
0.4 g / cm³, 5 m² / g, 0.4-1 mm

Processing space:



63 compositions = 7 samples x 9 processing conditions

C. Experimental Plan

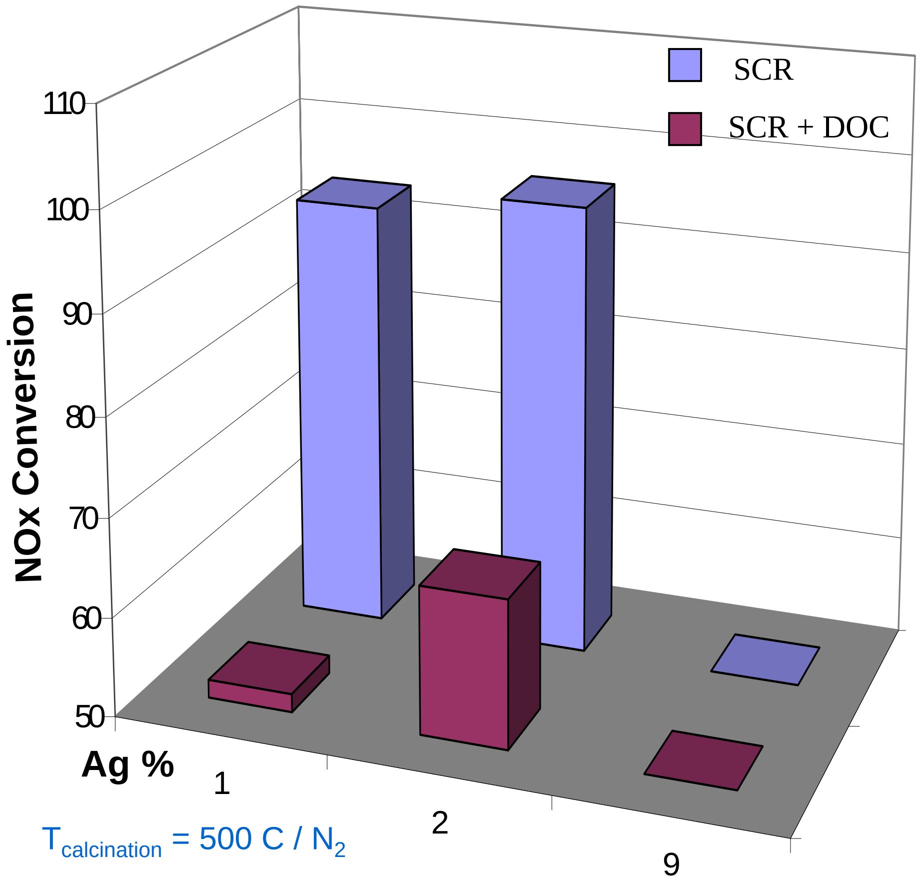
No SO_2: **Hydrocarbons, Oxygenates** → 12 hrs 5ppm SO_2 treatment → Post SO_2 treatment: **Hydrocarbons, Oxygenates** → 5 ppm SO_2: **Hydrocarbons, Oxygenates**

200 ppm NO, 7 % H_2O, 12 % O_2, 9 C_1 : NO, T = 350 - 450 C, with and without DOC

imagination at work

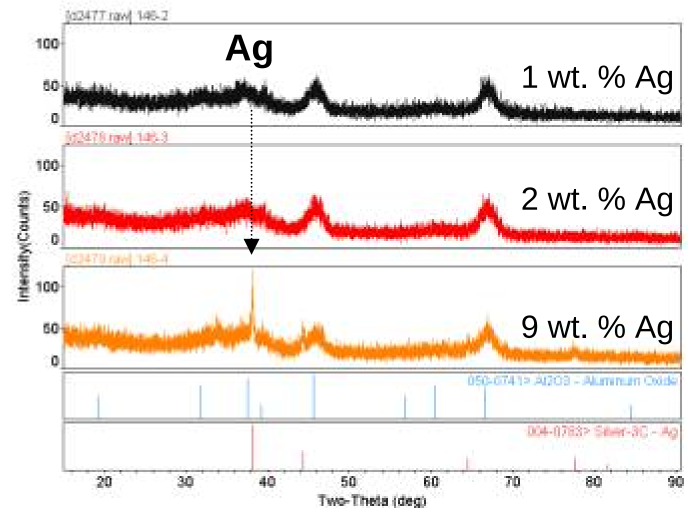
Combinatorial Chemistry Lab

Silver Loading

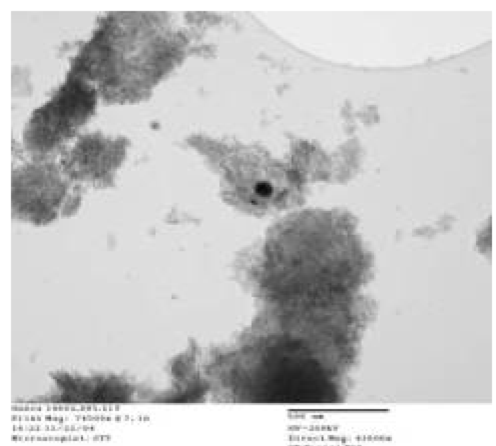


$T_{calcination}$ = 500 C / N_2

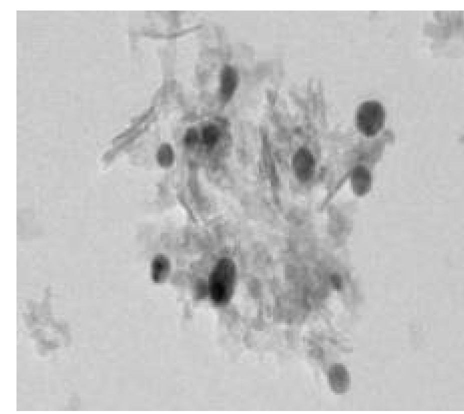
200 ppm NO, 7 % H_2O, 12 % O_2, 900 ppm EtOH, 400 C, 16,000 hr^{-1}



2 wt. % Ag / Al_2O_3



9 wt. % Ag / Al_2O_3



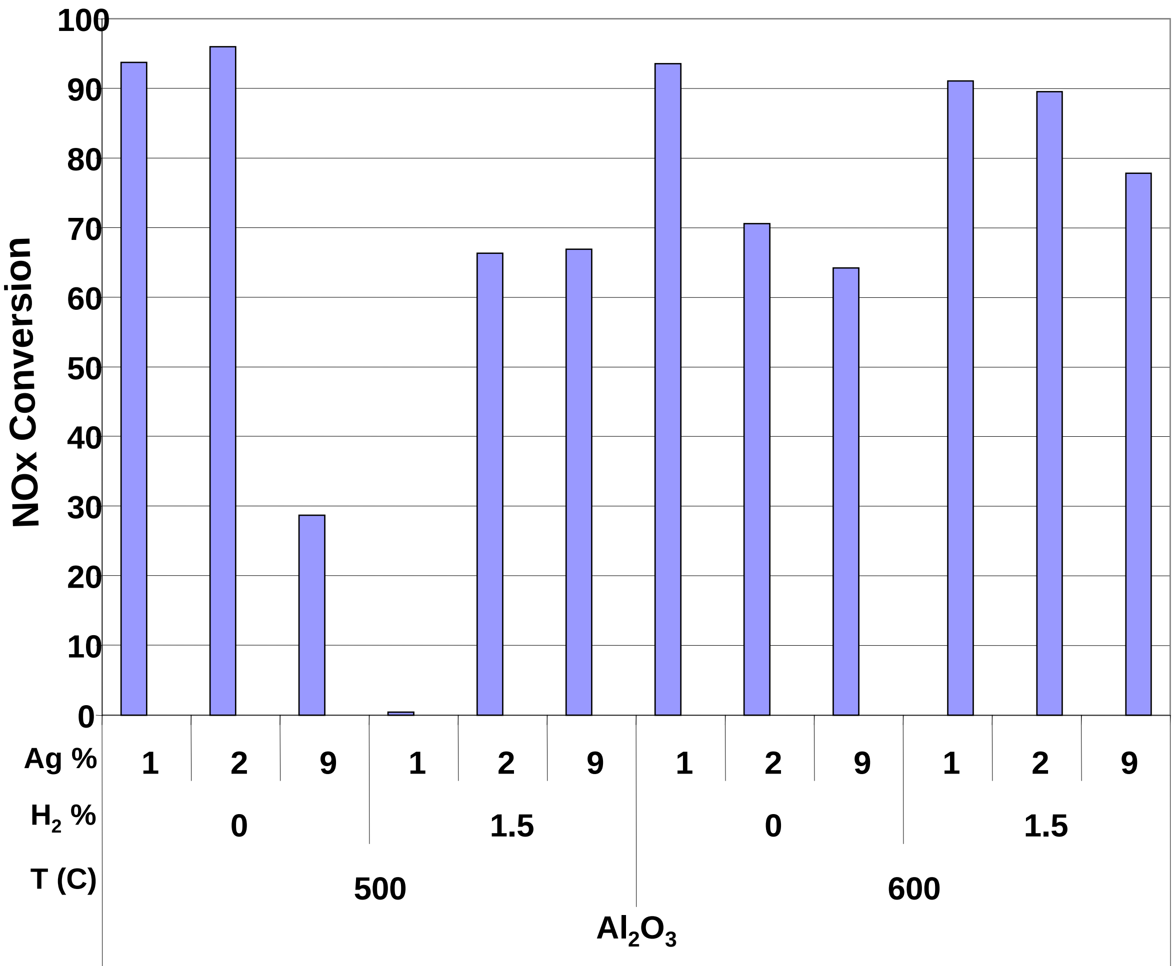
NO to N_2 Conversion reaches a maximum at 2 wt. % Ag /Al_2O_3

Burch, R.; Breen, J. P.; Meunier, F. C. *Appl. Catalysis B: Environmental* **2002**, *39*, 283-303.

imagination at work

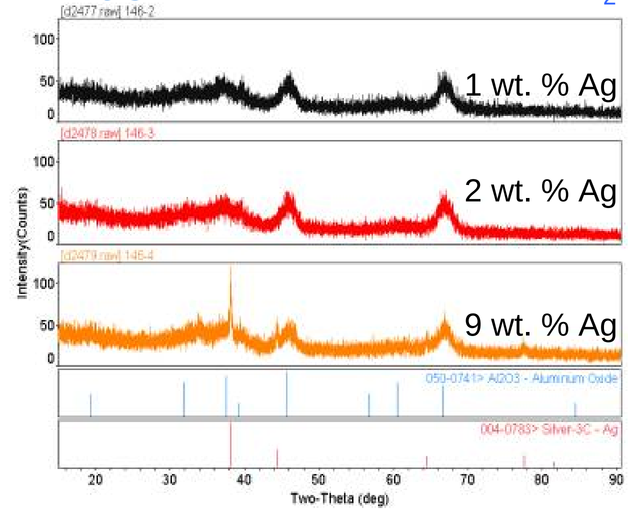
Combinatorial Chemistry Lab

Catalyst Pretreatment

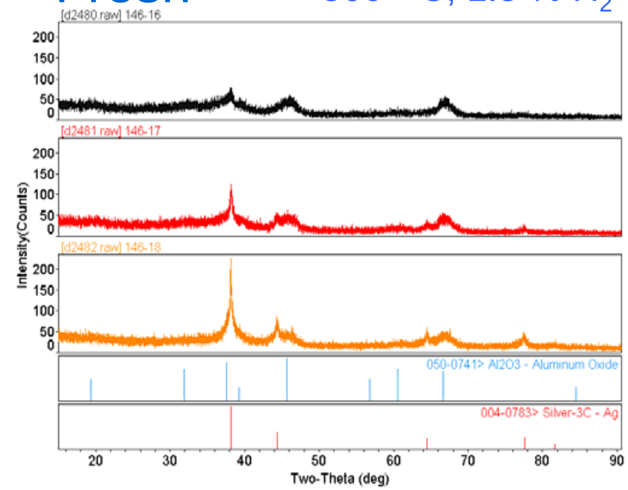


200 ppm NO, 7 % H_2O, 12 % O_2, 900 ppm EtOH, 400 C, 16,000 hr^{-1}, no DOC

Fresh 500 °C, N_2



Fresh 500 ° C, 1.5 % H_2

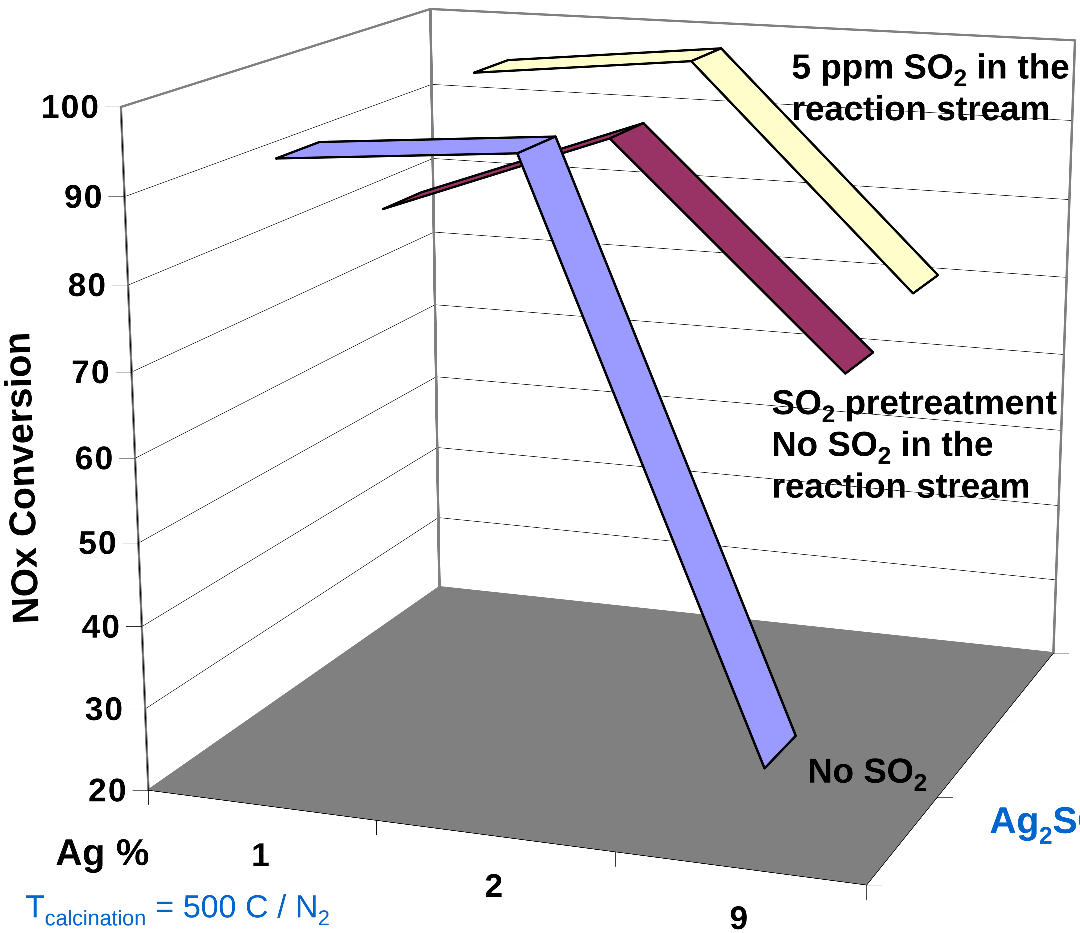


Higher pretreatment temperatures improve robustness of Ag/Al_2O_3

imagination at work

Combinatorial Chemistry Lab

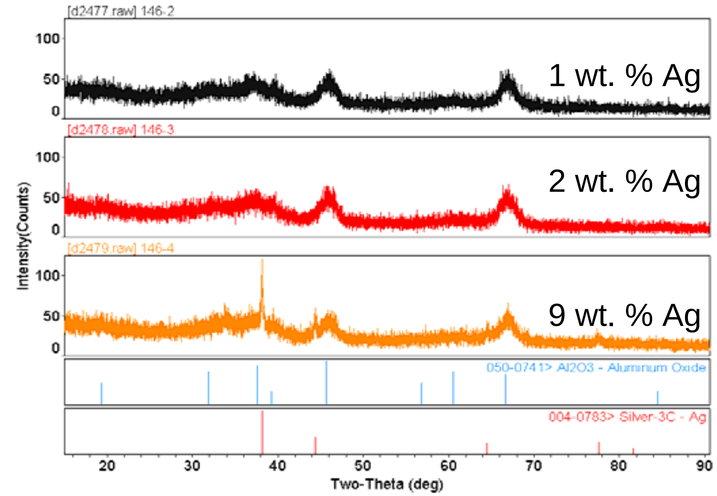
Sulfur Dioxide Effect



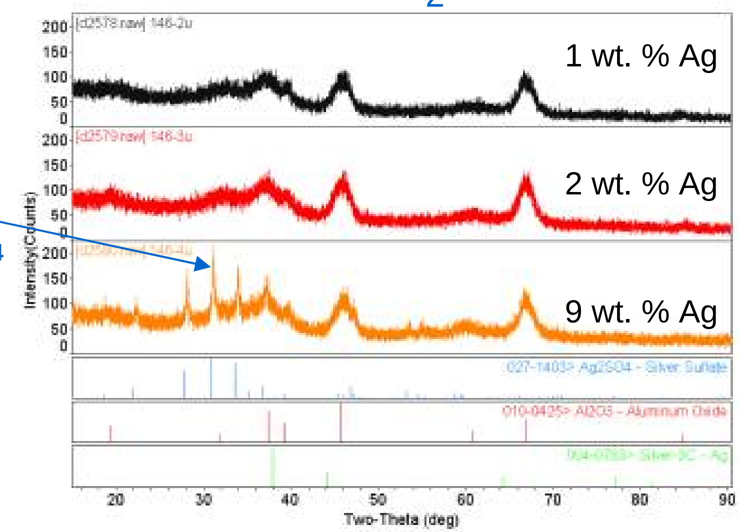
$T_{calcination}$ = 500 C / N_2

200 ppm NO, 7 % H_2O, 12 % O_2, 900 ppm EtOH, 400 C, 16,000 hr^{-1}

Fresh



SO_2-Pretreated



SO_2-pretreatment improves performance at higher Ag loadings

imagination at work

Angelidis, T. N.; Christoforrou, S.; Bongiovanni, A. Kruse, N. *Appl. Catalysis B: Environmental* **2002**, *39*, 197-204.

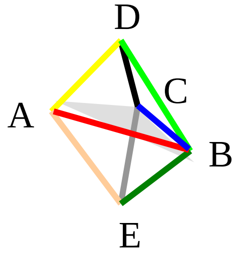
Combinatorial Chemistry Lab

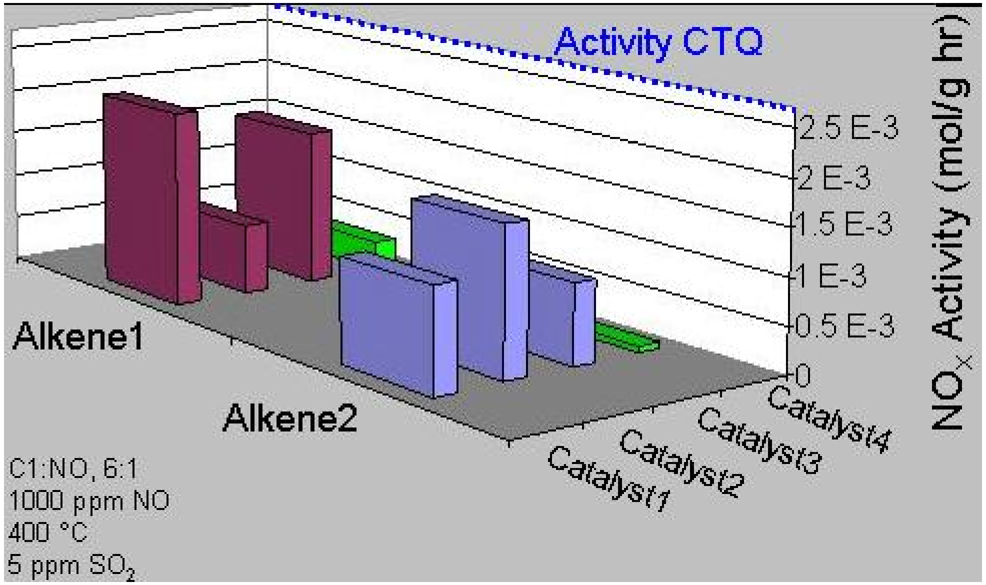
Screening NO_x Catalysts Spots

Catalysts with Alkenes

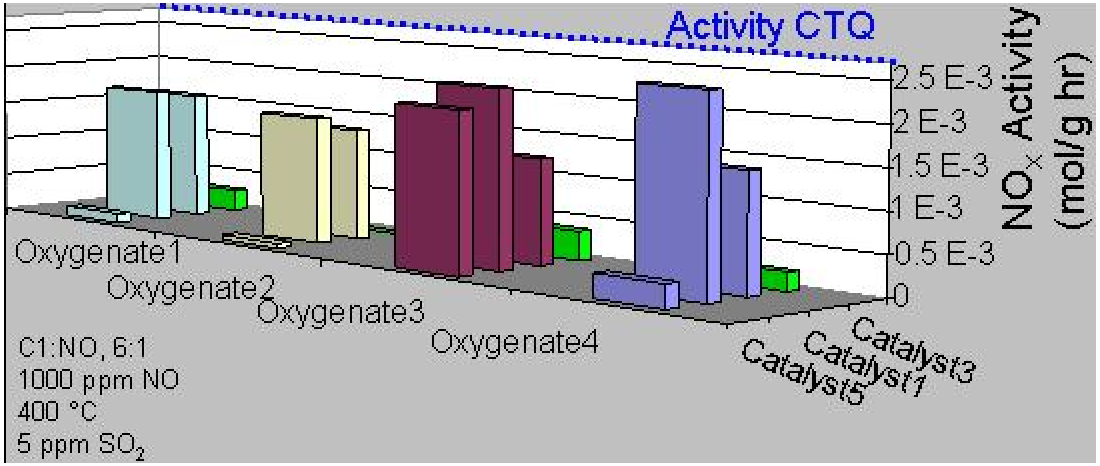
Demonstrated that several alkenes contribute to activity

Promising new leads





Catalysts with Oxygenates



New leads with oxygenates

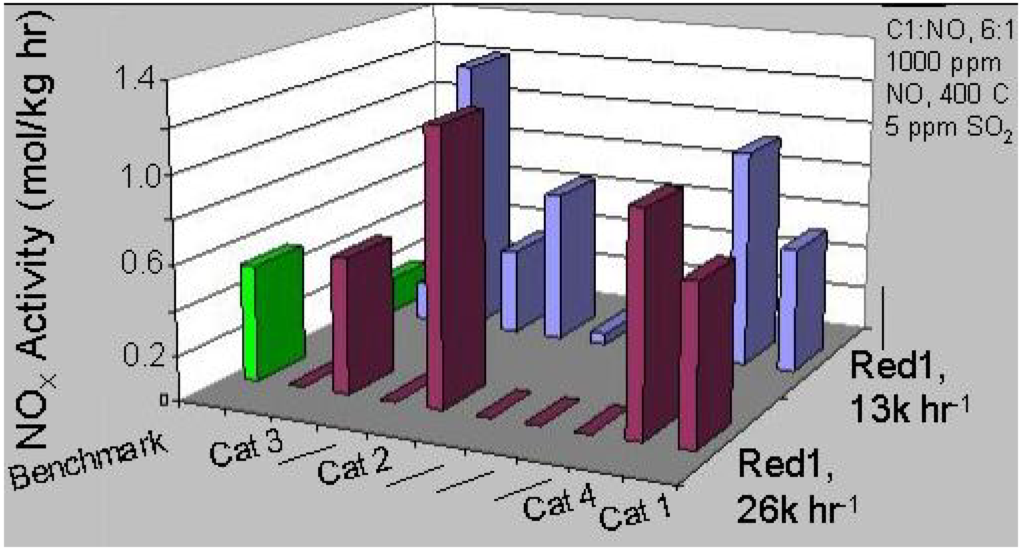
Sulfur tolerance in limited test times

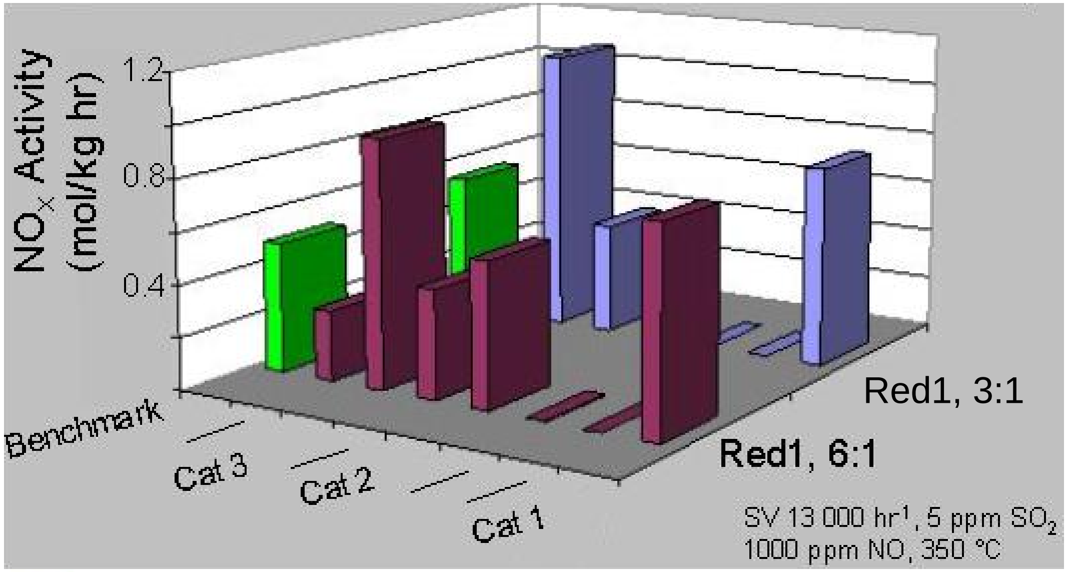
All catalysts with 4 mmoles metals/g alumina metals/g, 13 000 hr^{-1} SV

Capturing Complex Synergies

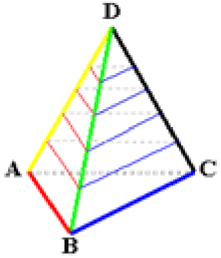
Catalysts with Oxygenates

- Promising catalyst leads with improved activity and increased flow rates
- New metals and quaternaries in screening





- Demonstrated feasibility at lower reductant usage
- New leads with lower total metal loading

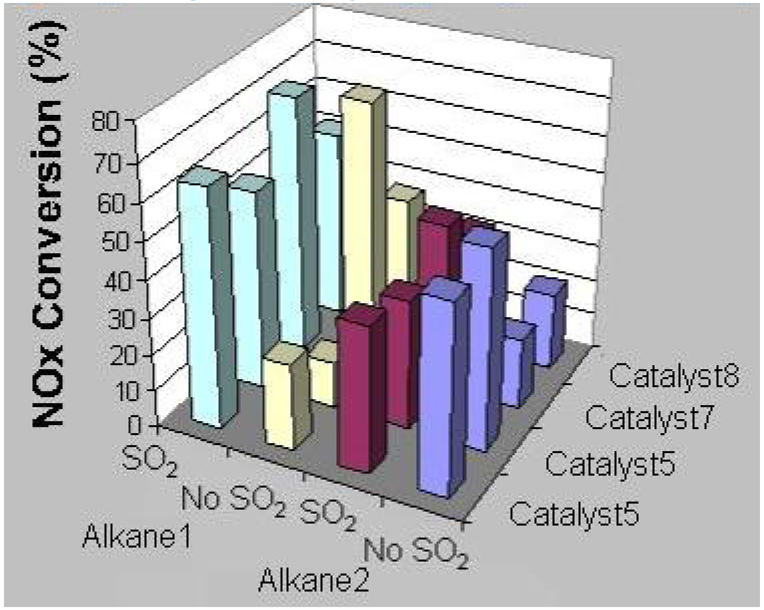


imagination at work

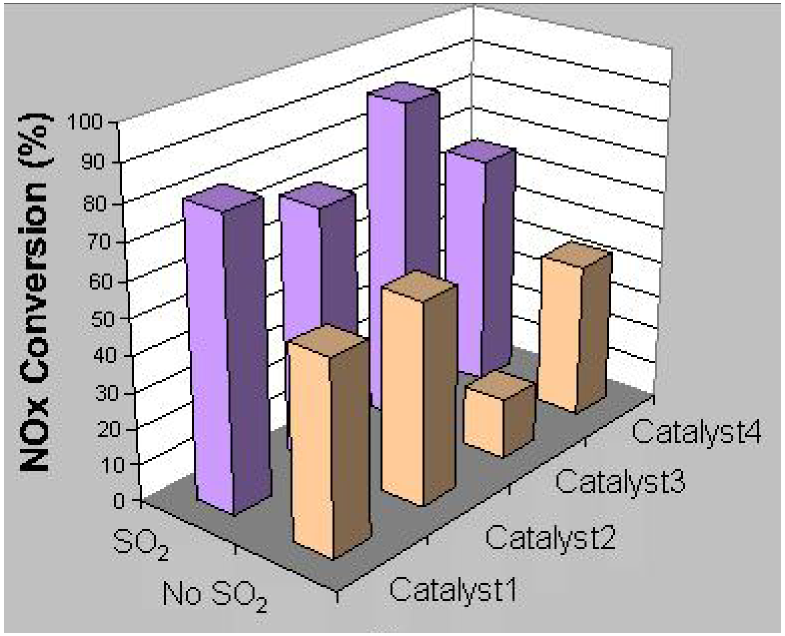
Combinatorial Chemistry Lab

Catalyst Leads with Powders

Leading Catalysts with Alkanes



Leading Catalysts with an Oxygenate

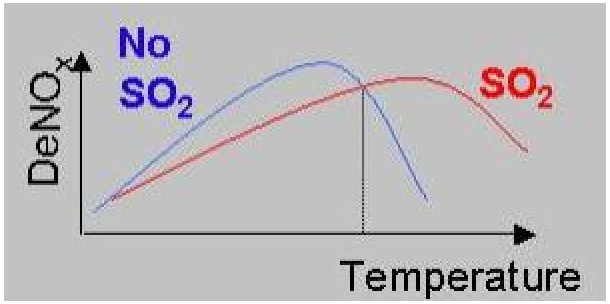


450 C, 200 ppm NO, C1:NO 6:1, 7% H_2O, 12% O_2, SO_2 5 ppm, SV 16 000 hr^{-1}

Promising results with alkanes and oxygenated reductants

Some catalysts robust to broad temperature range

Top catalyst leads demonstrate excellent performance in the presence of SO_2 & water

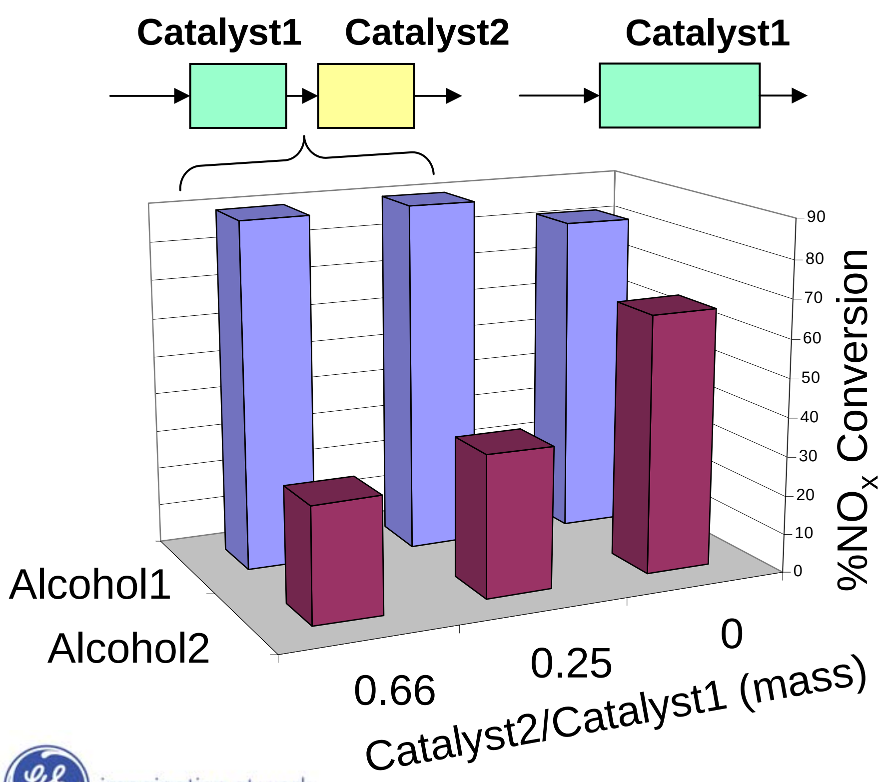


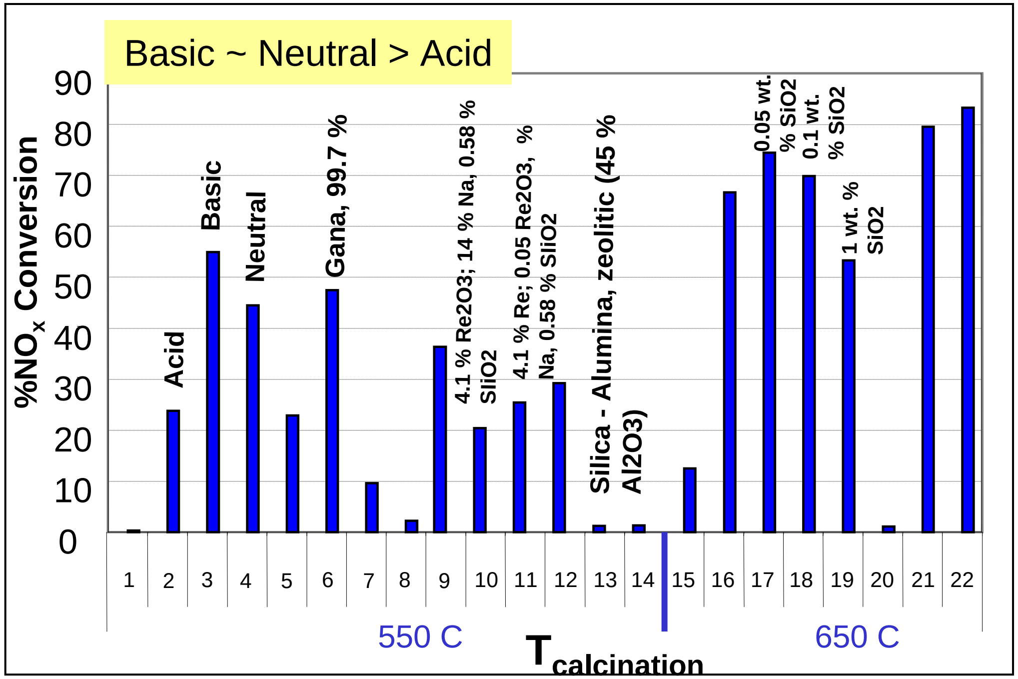
imagination at work

Combinatorial
Chemistry Lab

Facilitating Scale Up

Screening synergies between dual bed catalysts





Screening commercial aluminas to examine effects of additives, stabilizers & binders

imagination at work

Combinatorial Chemistry Lab

High Throughput Screening of Catalysts

With catalyst expertise, HTS greatly accelerates rate of catalyst discovery and optimization

A tool to increase research productivity

- Strategic and efficient search strategies carried out with 6σ rigor
- Allows for traditional experiments plus:
  - Synergistic combinations – binaries, ternaries, quaternaries…
  - Multiple concentrations and process conditions for each catalyst

Silver Alumina HC-SCR Catalyst

- Firing Ag / Al_2O_3 catalyst at 600 °C, or 675 °C in a reducing atmosphere increases the robustness of the catalyst with respect to silver loading
- NO to N_2 conversion reaches a maximum at 2 wt% Ag
- SO_2 pretreatment improves performance at higher silver loadings

Risks and Next Steps

Risks

Transfer of catalysts to ceramic structured support

NO_x catalyst activity and reductant usage

Poisons

Next Steps

Identify selection of possible catalyst suppliers, model and kinetic studies

Improve catalyst activity to enable use with high flow rates and reduced volumes

Optimize and scale up current NO_x catalyst leads

Life testing with sulfur

IR thermography studies to aid in understanding mechanism

Continue to work with PNNL to develop optimal oxygenated reductants from diesel

Acknowledgements

NO_x Emissions Team

Richard Kilmer
Teresa Grocela
Dan Hancu
William Flanagan
Alison Palmatier
Jennifer Redline
Benjamin Wood
Harish Acharya
John Lemmon
John Weistroffer

Pacific Northwest National Lab

Darrell Herling
Chris Aardahl
Kenneth Rappe
George Muntean

imagination at work

GE Global Research Center

Skill Set for HTE Projects

Organic Chemistry
Inorganic Chemistry
Polymer Science
Small-molecule Synthesis
Analytical Chemistry
Computational Chemistry
Statistics
Chemical Engineering
Mechanical Engineering

GE Global Research
Niskayuna, NY
Bangalore, India
Shanghai, China
Munich, Germany

GE Global Research Center, Niskayuna
~ 1200 technical staff
~ 500 Ph.D.'s

Screen Printing Technology

"Ink"

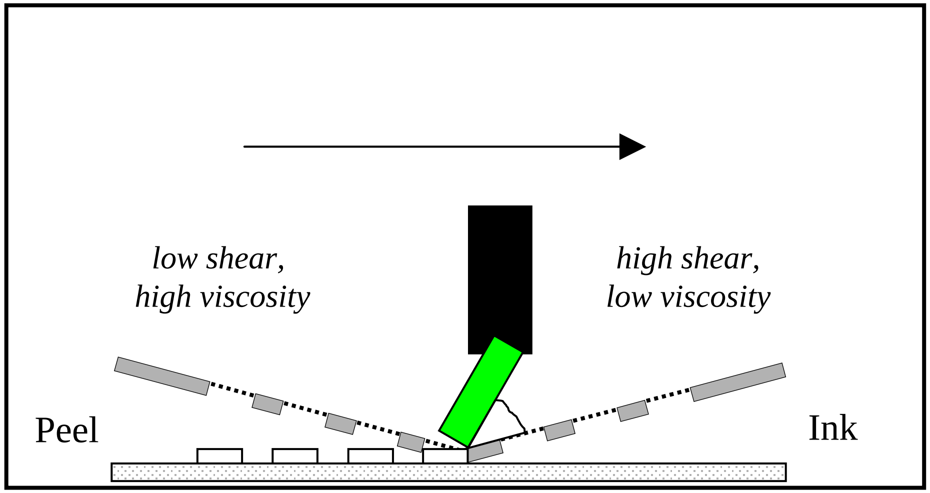
- Dispersion of an inorganic powder in a fluid, organic vehicle
- Pseudoplastic – shear thinning

Screen

- Mesh (count, wire, angle, weave)
- Emulsion
- Tension (wire & mesh)

Printer

- Snap off distance
- Squeegee Downstop
- Squeegee Pressure
- Squeegee Speed
- Squeegee Durometer
- Squeegee Angle



Benefits of the HC-SCR Technology

While locomotives consume only about 1% of the total U.S. energy, they are responsible for nearly 5% of total U.S. NO_x emissions, amounting to the release of over one million tons of NO_x emissions each year.[1]

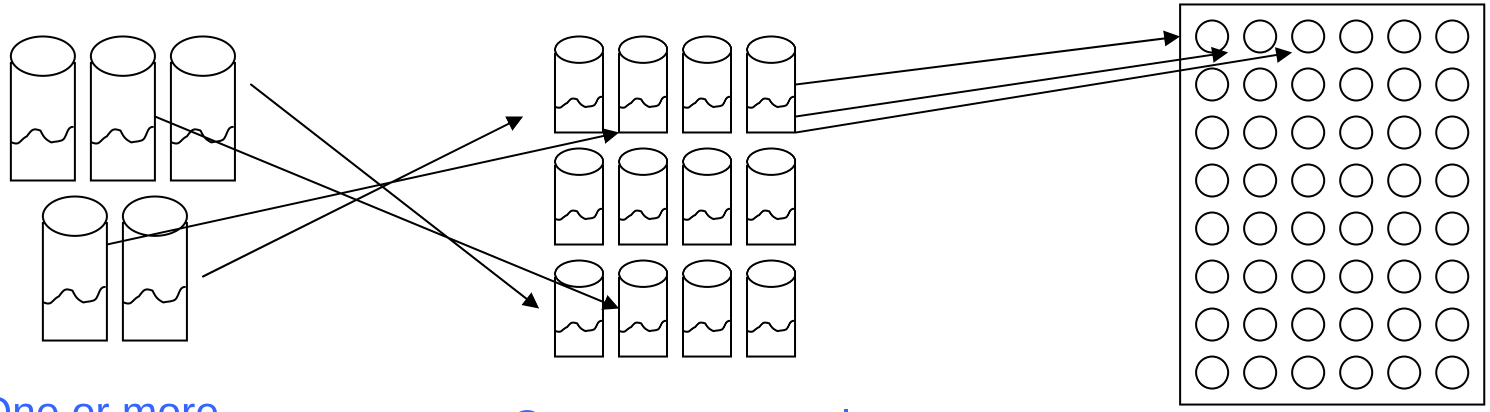
Assuming thorough usage of the HC-SCR technology in the market would yield NO_x emission reductions > 300 000 tons per year.

1 Orehowsky, G., "Emission Standards for Locomotives and Locomotive Engines," Presentation at *Workshop on Locomotive Emissions and System Efficiency*, 2001, Jan. 30–31, Argonne National Lab., Argonne, IL.

Plate Designer

Tool for Helping Chemist Prepare Plates
Output -- XML for eBrowser, Text File for Robots

Stocks -- Mixtures -- Replicates --



One or more chemicals mixed together. Density/Purity tracked. Chemicals must be in reg system

One or more stocks mixed together. Primary component specified by mM, mmoles or wt%

Single Mixture used multiple times in same plate or experiment

imagination at work

Combinatorial Chemistry Lab

eBrowser

- Accepts Plate Designs in XML format
- Accepts Results/Reaction conditions in XML format
- Stores Files
- Associates Chemicals with Results
- Generates Reports
- Outputs data to EXCEL
- Complex searches including by chemical structure/sub-structure