



Component and System level tools for modeling modeling of NOx Storage and Reduction

Presented to

CLEERS

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As part of our efforts to simulate and calibrate emission control components we are constructing models for NOx storage and reduction.

- We are developing software and hardware to support each of three phases of modeling in emissions control: development, design and use.
 - Using Bistro™, we construct microkinetics models catalyst components to capture and extrapolate catalyst performance, including degradation.
 - Using Runway™, we simulate exhaust systems to probe sensitivities to operating conditions, cost and control.
- We have commenced construction of models of NOx storage and reduction catalysts that incorporate sulfate poisoning.
 - The models can faithfully represent literature data across a broad range of conditions
 - The models are sensitive to hydrocarbon speciation, making comparisons with tailpipe data difficult

Introduction to TIAX

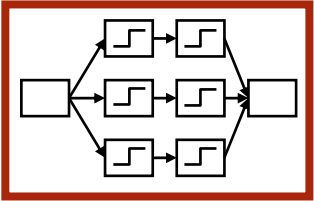
TIAX is a technology and innovation business that works collaboratively with clients and partners to address forefront technical issues.

- **TIAX emerged last year from Arthur D. Little, advancing its 116-year heritage of helping clients realize the exponential power of technology & innovation.**



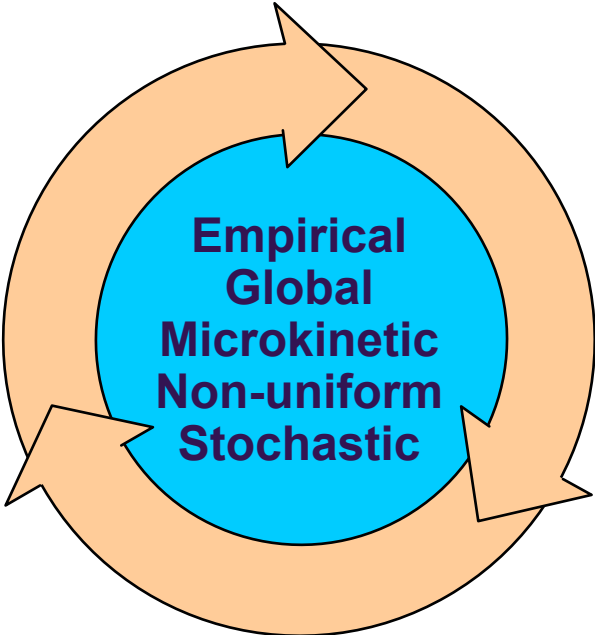
- **TIAX emerged last year from Arthur D. Little, advancing its 116-year heritage of helping clients realize the exponential power of technology & innovation.**
 - Independent company formed in May of 2002
 - >200 scientists, engineers, and industry experts
 - Headquartered in Cambridge, MA, West Coast presence in Cupertino, CA
 - 50 laboratories; ISO 9001 Registered

We are developing software and hardware to support each of these phases of modeling in emissions control.



Hydra™: model reduction

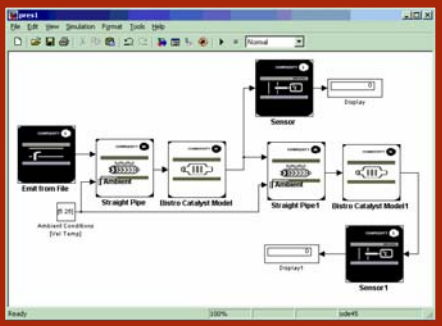
Use



Discovery

Reaction/number	A ₁	E ₁	A ₂	E ₂	A ₃	E ₃	A ₄	E ₄
C ₂ H ₆ → C ₂ H ₅	1.00e+10	0.0	0.0e+00	-45.0	0.0			
C ₂ H ₅ → C ₂ H ₄ + H ₂	6.00e+10	45.0	0.0e+00	-45.0	0.0			
H ₂ + C ₂ H ₅ → C ₂ H ₆ + H ₂	3.00e+10	50.0	1.00e+10	-50.0	0.0			
C ₂ H ₅ → C ₂ H ₄ + H	1.00e+13	50.0	0.0e+00	-50.0	0.0			
C ₂ H ₅ + H → C ₂ H ₆	1.00e+13	45.0	1.00e+10	-50.0	0.0			
C ₂ H ₅ + H → C ₂ H ₄ + H ₂	6.00e+10	45.0	4.00e+10	-50.0	0.0			
C ₂ H ₅ + H → C ₂ H ₃	4.00e+10	55.0	1.00e+10	-55.0	0.0			
C ₂ H ₅ + H → C ₂ H ₂	4.00e+10	100.0	0.0e+00	-47.5	0.0			
C ₂ H ₄ → C ₂ H ₂ + H ₂	4.00e+10	100.0	1.00e+10	-100.0	0.0			
C ₂ H ₄ + H → C ₂ H ₅	6.00e+10	41.0	0.0e+00	-47.5	0.0			
H ₂ → H + H	1.00e+13	0.0	0.0e+00	-45.0	0.0			
C ₂ H ₄ + H → C ₂ H ₃	1.00e+13	25.0	0.0e+00	-45.0	0.0			
H ₂ + H → H ₂	1.00e+13	30.0	0.0e+00	-45.0	0.0			
H ₂ + H → H ₂	1.00e+13	0.0	0.0e+00	-45.0	0.0			
H ₂ + H → H ₂	1.00e+13	30.0	0.0e+00	-45.0	0.0			
H ₂ + H → H ₂	1.00e+13	30.0	0.0e+00	-45.0	0.0			
H ₂ + H → H ₂	1.00e+13	0.0	0.0e+00	-45.0	0.0			
H ₂ + H → H ₂	1.00e+13	0.0	0.0e+00	-45.0	0.0			

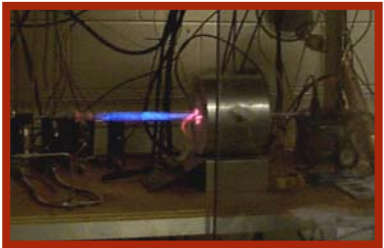
Bistro™: microkinetics modeling



Runway™: system simulation

Design & Manufacture

- Technology Assessments
- Market Assessments
- IP Monetization



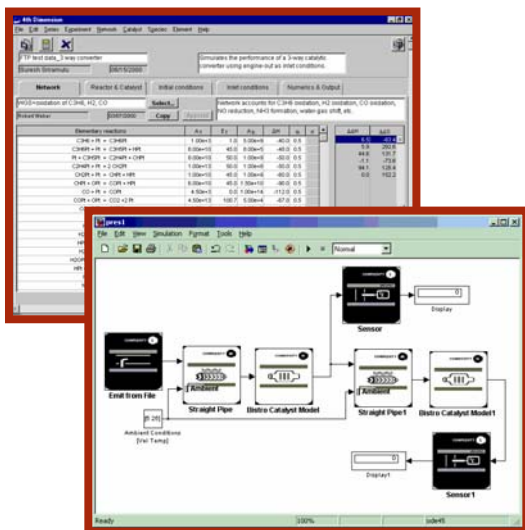
Genex™: rapid calibration



To Bistro™, our component-level modeling tool, we have added Runway™, a tool for simulating emission control systems.

What they are

- Database for managing complex reaction networks
- Matlab-based Numerical simulations of chemical reactors
- Simulink-based System simulations



What they do

- Accurately describe both steady state and transient performance of reacting systems
- Facilitate communication among catalyst chemists chemical engineers and powertrain designers
- Permit extension of reaction networks to account for aging and degradation phenomena

How we use them

- Analysis of literature data on emission control catalysis
- Sensitivity analysis of operating conditions
- Costing studies of both fixed and operating expenses
- Calibration of emission control catalysts
- Simulation of hypothesized systems

Conventional, global catalyst models represent the data over limited ranges and afford no cross-system learning.

- In conventional models the parameters in the empirical rate expressions are just fitting coefficients and have no physical meaning.
- Moreover, the form of conventional models is not well adapted to describe transient performance—neither startup nor acceleration.
- Therefore conventional models cannot be tied to the properties or formulation of the catalysts and must be retuned from scratch for each new system.

Example of a conventional expression used to describe the rate of a reaction catalyzed by a catalytic converter

Functional form forces numerical correlation between parameters, making it difficult to determine accurate values

Based only on observable species, ignores available information about surface species

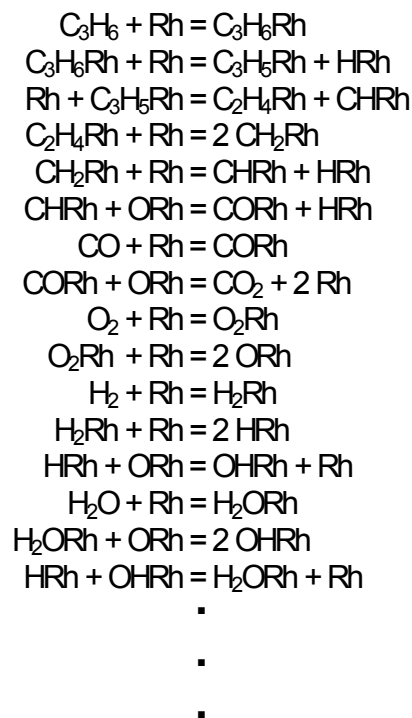
$$r = \frac{k \cdot K \cdot P_{CO} P_{O_2}}{1 + K \cdot P_{CO}}$$

Assumes that adsorption is equilibrated and that surface species are in steady state, precluding accurate description of fast transients

Advanced microkinetics models provide insight into catalyst performance, including degradation, that bears directly on cost, reliability and control.

- Microkinetics models are sets of coupled differential equations built from a fundamental understanding of the chemical steps that occur on the surface of the catalyst.
- The models can be accurate over a wide range of conditions and are intrinsically capable of representing transients.
- The generality and extensibility of microkinetics models allow simulations that can lead to new catalysts which are cheaper and more robust (different metals, lower loading, use protocols).
- Extending a microkinetics model to include other sorts of reactions, notably catalyst degradation, is straightforward.
- Since the models represent many levels of performance, they can be interrogated to devise model-based control.

Microkinetics network for oxidation of propene



Reactions are not assumed to be equilibrated or irreversible

Reaction rates are expressed in Arrhenius form, $r = A \exp(-E_a/RT)$, with parameters derived from transition state theory or fundamental measurements

We have developed Bistro, a platform for creating microkinetics-based models that incorporate much of the credo of catalysis.

Calculate transient performance of chemical reactor using MATLAB.

Export models to Runway™

Specify time dependent or constant inlet conditions

Control solution of the stiff differential equations.

- Thermo-physical properties
- Adiabatic
 - CSTR, PFR, Film PFR
- TPD and TPR
 - CSTR, PFR
 - Sensitivity analysis

- Easy entry of reactions and parameters
- Re-use of previously validated parameters

The screenshot shows the 'Network' tab of the Bistro software. It displays a table of elementary reactions with columns for the reaction equation, forward and reverse pre-exponential factors (A_f , A_b), activation energies (E_f , E_b), enthalpy change (ΔH), and entropy change (ΔS). The interface also includes a menu bar, a toolbar, and various control buttons like 'Select...', 'Copy', and 'Append'.

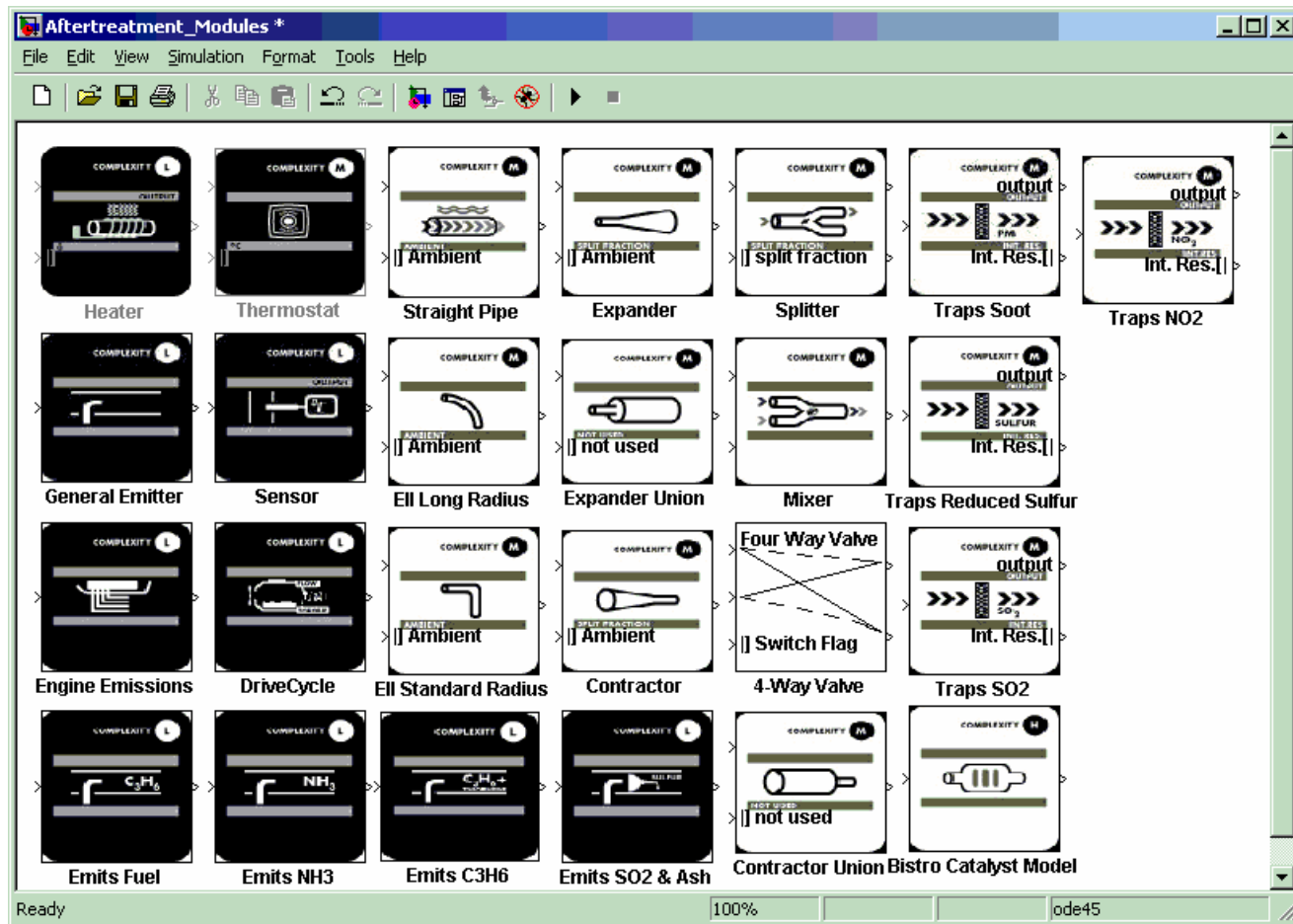
Elementary reactions	A_f	E_f	A_b	ΔH	α	σ	$\Delta\Delta H$	$\Delta\Delta S$
Pt + N2 = N2Pt	1.00e+3	0.0	1.00e+11	-60.0	0.5	-1	-19.9	-80.3
NO + Pt = NOPt	1.00e+3	0.0	1.00e+9	-90.0	0.5		53.9	19.9
NOPt + Pt = NPt + OPt	5.00e+13	70.0	3.00e+15	-146.5	0.5		-72.3	-260.8
N2Pt + Pt = 2 NPt	3.40e+10	130.0	1.00e+12	-25.0	0.5	1	-20.4	-41.8
NOPt + NPt = N2Pt + OPt	1.00e+13	100.0	2.00e+11	-122.0	0.5	2	210.0	-55.4
O2 + 2 Pt = O2Pt2	4.00e+3	0.0	1.00e+9	-37.6	0.5	-2		
O2Pt2 = 2 OPt	5.42e+12	4.1	8.00e+15	-170.0	0.5	-2		
NOPt + OPt = NO2Pt2	1.00e+9	120.0	2.00e+11	-120.0	0.5			
NO2 + 2 Pt = NO2Pt2	1.00e+3	0.0	1.00e+9	-70.0	0.5	2		
2 NO + O2 + BaO2 = BaN2O6	1.00e+0	60.0	1.00e+17	-140.0	0.5			
BaN2O6 + 4 Pt = BaO2 + 2 NOPt + 2 OPt	1.00e+10	120.0	1.00e+17	-210.0	0.5	1		
NO + OPt = BaO2 + Pt	1.00e+10	60.0	1.00e+8	-37.6	0.5			
NO2 + 4 Pt = BaO2 + 2 NO2Pt2	1.00e+7	100.0	1.00e+15	-100.0	0.5	-1		

At the bottom of the interface, summary values are shown: $\Delta H = -63.7$ kJ/mol, $\Delta S = 227.1$ J/mol K, and $T = 700.0$ K.

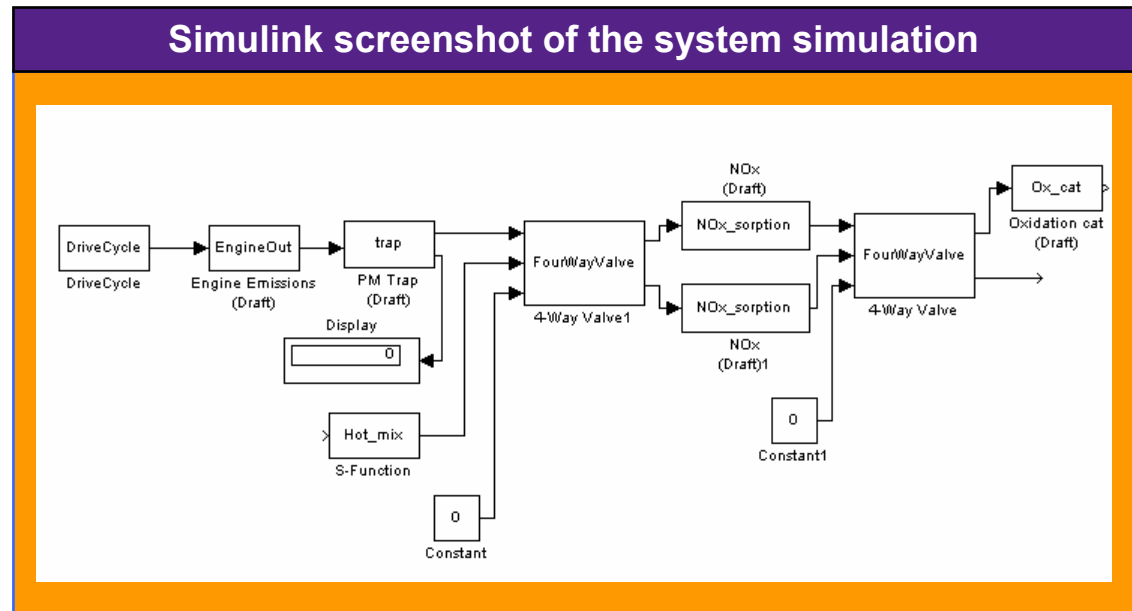
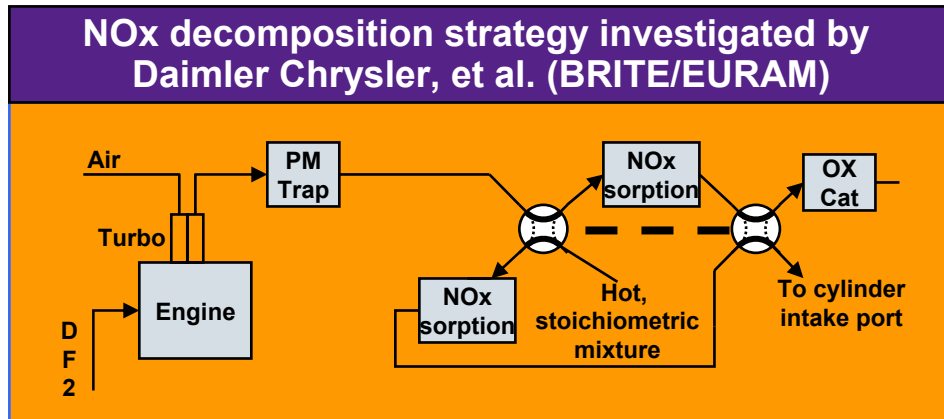


Runway™ Overview

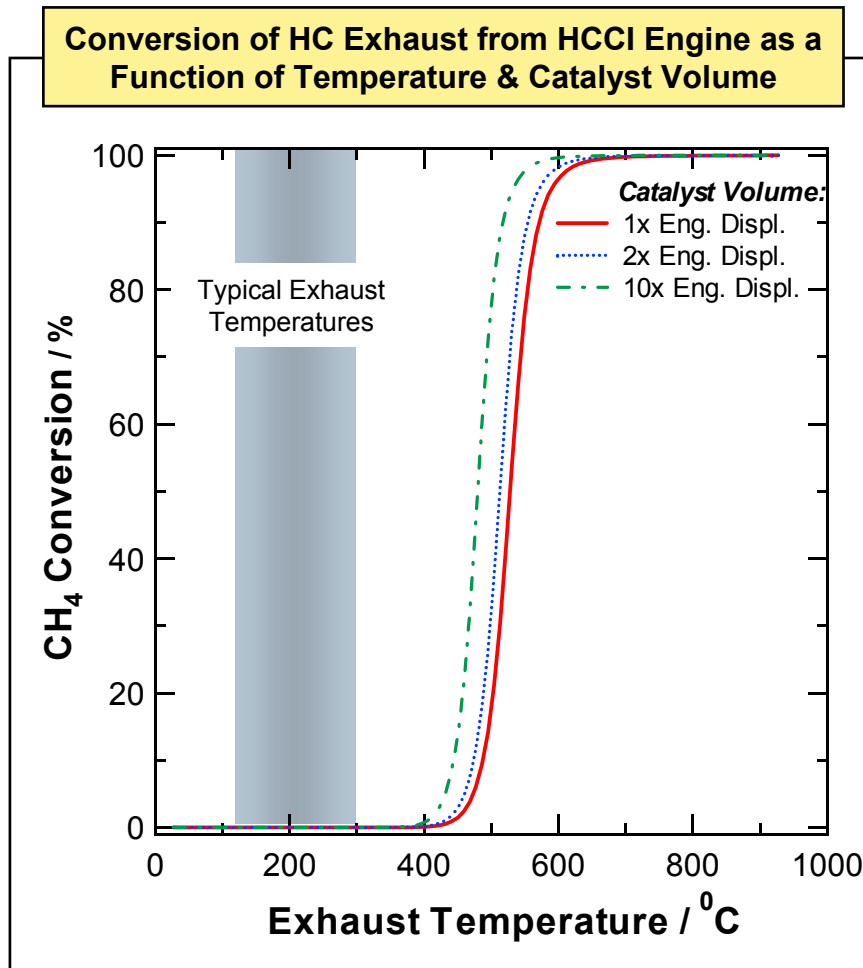
To facilitate the simulation of complete emission control systems, we created Runway, a set of modules that run in Simulink®.



Runway affords a flexible architecture that can be “wired” rapidly into a wide range of aftertreatment concepts.

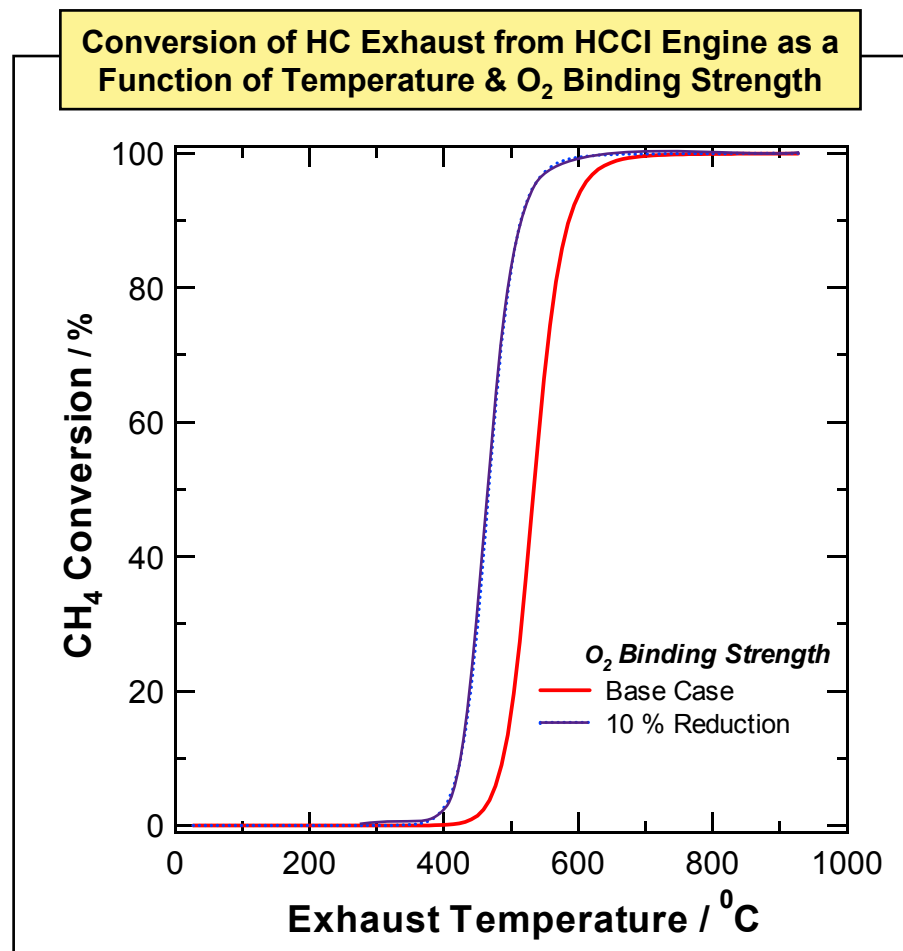


Our modeling suggests that HC emissions control for HCCI engines will prove challenging owing to the low exhaust temperatures.



- Kinetics model based on NREL work
- Assumed a Pt-based catalyst with loading of 60g/ft³ Pt with 1.5 nm dia. Pt particles
- Exhaust conditions: 0.5 % CH₄, 7 % O₂, 0.5 % CO
- Assumed fast heat transfer between catalyst and gas
- Simulation corresponds to an experiment with a temperature programmed reactor.

Modeling suggests that catalysts which weaken oxygen adsorption (such as some lean-NOx catalysts) might enhance low-temperature HC oxidation.



- At low temperature, oxygen fragments poison the catalyst surface.
- Reducing the binding strength of oxygen will reduce the poisoning effect thereby allowing oxidation of CH₄.
- Assumed a Pt-based catalyst with loading of 60g/ft³ Pt with 1.5 nm dia. Pt particles
- Exhaust conditions: 0.5 % CH₄, 7 % O₂, 0.5 % CO
- Catalyst volume: 1x engine displacement

A network for NO_x storage was constructed from information available in the literature¹ concerning NO_x - BaO interaction.

Reactions	A _f	E ₀	A _r
H ₂ + Pt = H ₂ Pt	1.00 × 10 ³	0.0	5.00 × 10 ⁹
H ₂ Pt + Pt = 2 HPt	5.00 × 10 ¹²	2.0	1.00 × 10 ¹²
H ₂ O + Pt = H ₂ OPt	1.00 × 10 ³	0.0	1.00 × 10 ⁹
H ₂ OPt + OPt = 2 OHPt	1.00 × 10 ¹²	30.0	9.00 × 10 ¹³
HPt + OPt = OHPt + Pt	5.00 × 10 ¹³	30.0	2.00 × 10 ¹³
HPt + OHPt = H ₂ OPt + Pt	5.00 × 10 ¹³	56.0	5.00 × 10 ¹¹
O ₂ + 2 Pt = O ₂ Pt ₂	4.00 × 10 ³	0.0	1.00 × 10 ⁹
O ₂ Pt ₂ = 2 OPt	5.42 × 10 ¹²	4.1	8.00 × 10 ¹⁵
NO + Pt = NOPt	1.00 × 10 ³	0.0	1.00 × 10 ¹²
Pt + N ₂ = N ₂ Pt	1.00 × 10 ³	0.0	5.00 × 10 ⁸
NOPt + Pt = NPt + OPt	5.00 × 10 ¹⁰	70.0	3.00 × 10 ¹⁵
N ₂ Pt + Pt = 2 NPt	3.40 × 10 ⁵	121.0	1.00 × 10 ¹²
NOPt + NPt = N ₂ + OPt + Pt	1.00 × 10 ¹²	87.7	3.00 × 10 ¹
NOPt + HPt = NHPt + OPt	1.00 × 10 ¹⁰	83.6	1.00 × 10 ¹²
CO + Pt = COPt	4.50 × 10 ³	0.0	1.00 × 10 ¹⁵
COPt + OPt = CO ₂ + 2 Pt	4.50 × 10 ¹³	100.7	5.00 × 10 ⁴
COPt + NOPt = CO ₂ + NPt + Pt	1.00 × 10 ⁹	0.0	1.00 × 10 ⁹
BaN ₂ O ₆ + 4 Pt = BaO ₂ + 2 NOPt + 2 OPt	1.00 × 10 ¹²	60.0	1.00 × 10 ¹⁸
BaO + OPt = BaO ₂ + Pt	1.00 × 10 ¹³	0.0	1.00 × 10 ¹⁰
NOPt + OPt = NO ₂ Pt ₂	1.00 × 10 ¹¹	70.0	2.00 × 10 ¹¹
BaN ₂ O ₆ + 4 Pt = BaO ₂ + 2 NO ₂ Pt ₂	1.00 × 10 ¹²	60.0	1.00 × 10 ¹⁸
NO ₂ + 2 Pt = NO ₂ Pt ₂	1.00 × 10 ³	0.0	1.00 × 10 ¹⁰
2 NO + O ₂ + BaO ₂ = BaN ₂ O ₆	1.00 × 10 ⁶	100.0	1.00 × 10 ¹³
2 NO ₂ + BaO ₂ = BaN ₂ O ₆	1.00 × 10 ⁶	100.0	1.00 × 10 ¹³
NOPt + COPt = CO ₂ + NPt + Pt	1.00 × 10 ¹⁰	10.0	1.00 × 10 ⁴
COPt + NO ₂ Pt ₂ = NOPt + CO ₂ + 2 Pt	1.00 × 10 ¹¹	30.0	1.00 × 10 ⁴

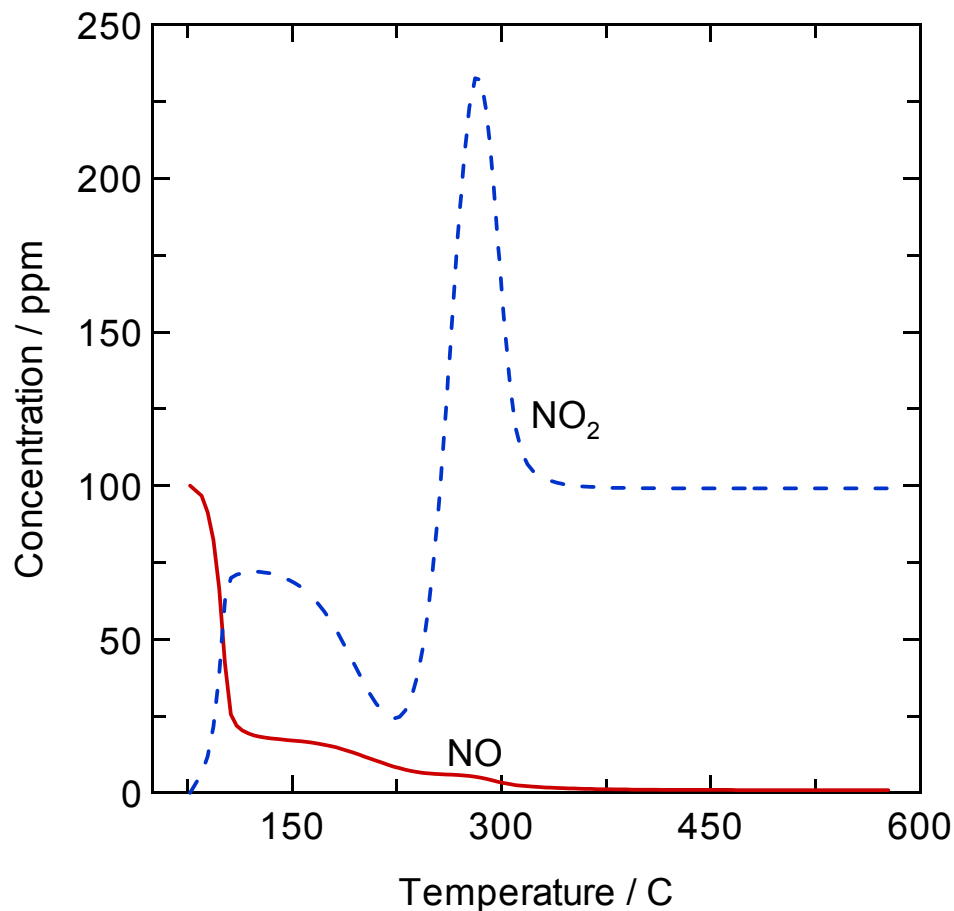
1. H. Mahzoul, J.F. Brilhac, P.Gilot, (1999)

In agreement with experimental observations, our model generates a large desorption of NO₂ around 300°C.

Operating Conditions

[NO] = 1000 ppm
[H₂O] = 10 %
[CO₂] = 10 %
[O₂] = 12 %
Balance N₂

SV = 30,000 h⁻¹
4 C min⁻¹
Noble metal area = 300 cm²/cm³
BaO area = 15000 cm²/cm³
CSTR Reactor



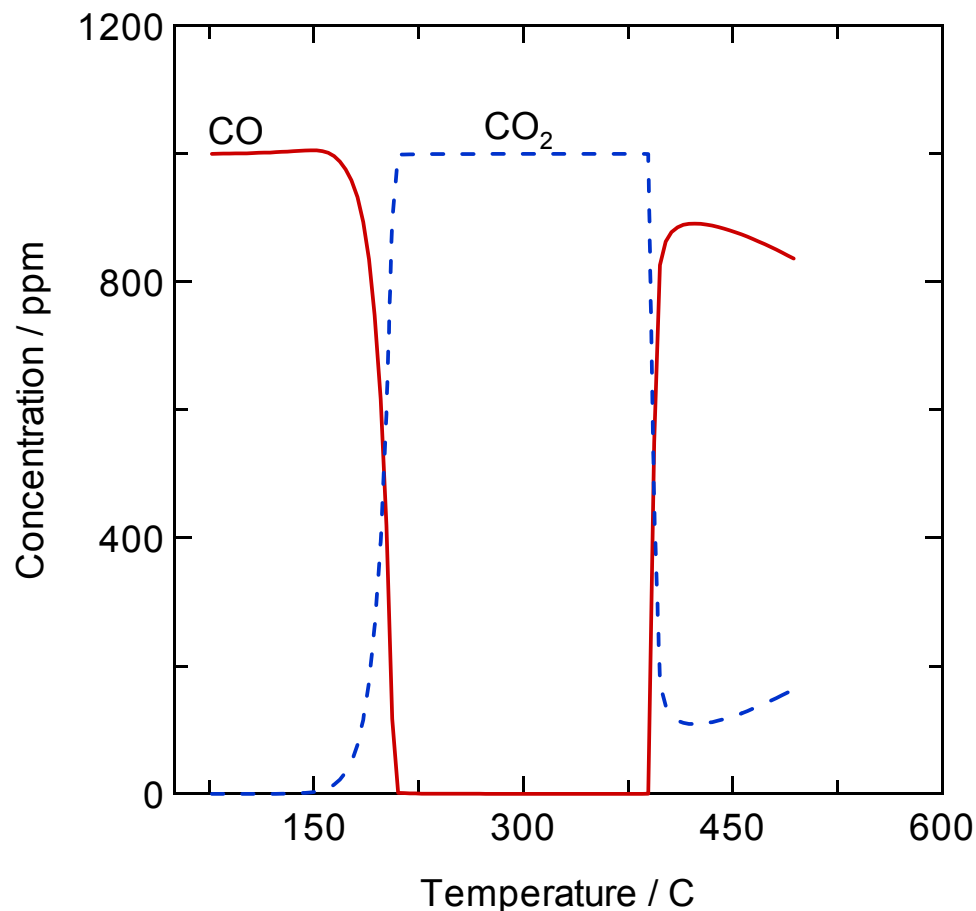
The model also captures well the reducibility of the NO_x storage component.

Operating Conditions

[NO] = 1000 ppm
[H₂O] = 10 %
[CO₂] = 10 %
[O₂] = 12 %
Balance N₂

SV = 30,000 h⁻¹
4 C min⁻¹
Noble metal area = 300 cm²/cm³
Ba(NO₃)₂ area = 1000 cm²/cm³
CSTR Reactor

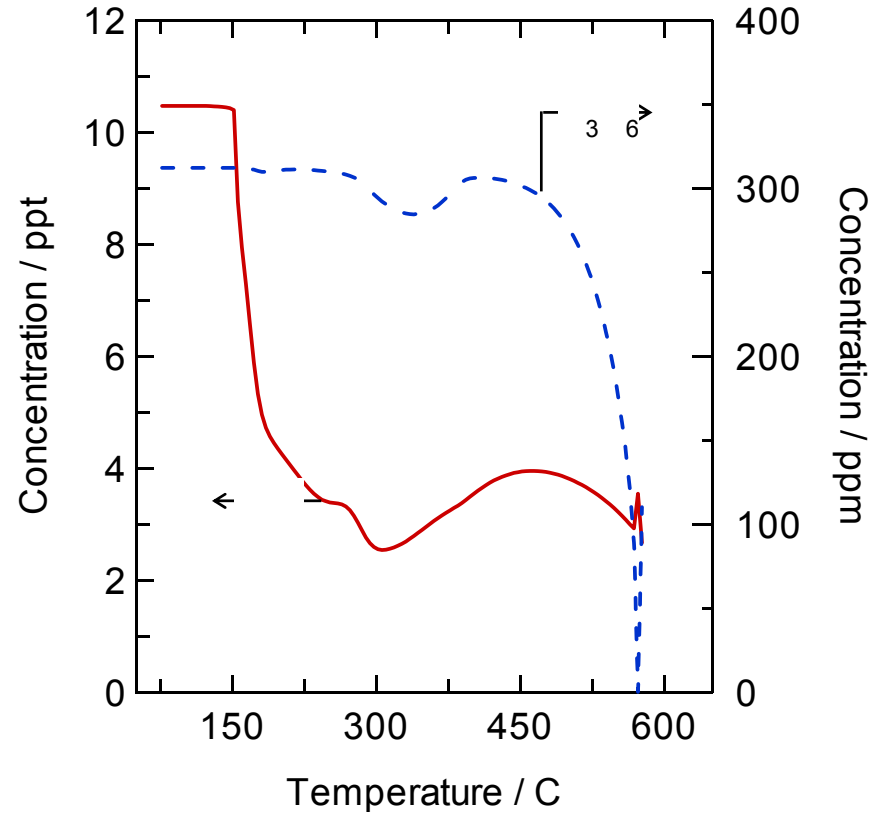
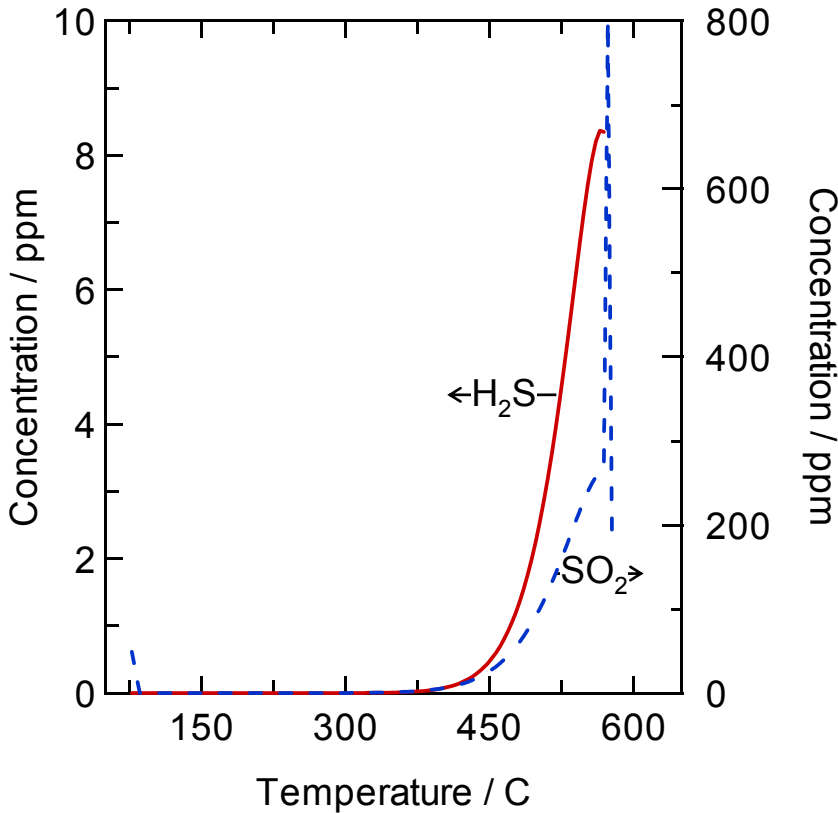
In this simulation, the initial conditions were set such that the initial concentration of Ba(NO₃)₂ was 3 times more than that of the noble metal.



We are just starting to model the interaction of SO₂ and SO₃ with the PGM and NOx storage components.

Reactions	A _f	E ₀	A _r
SO ₂ + 2 Pt = Pt ₂ SO ₂	1.00 × 10 ³	0.0	1.00 × 10 ⁹
Pt ₂ SO ₂ + Pt = PtS + 2 OPt	1.00 × 10 ¹²	158.8	1.00 × 10 ¹⁰
Pt ₂ SO ₃ + Pt = Pt ₂ SO ₂ + OPt	1.00 × 10 ¹¹	33.4	1.00 × 10 ¹⁰
SO ₃ + 2 Pt = Pt ₂ SO ₃	1.00 × 10 ³	0.0	1.00 × 10 ⁹
H ₂ S + 2 Pt = H ₂ SPt ₂	1.00 × 10 ³	0.0	1.00 × 10 ⁹
H ₂ SPt ₂ = HSPt + HPt	1.00 × 10 ¹¹	0.0	1.00 × 10 ¹⁰
HSPt + Pt = HPt + PtS	1.00 × 10 ¹⁰	0.0	1.00 × 10 ¹⁰
BaO ₂ + SO ₂ = BaSO ₄	1.00 × 10 ²	30.0	1.00 × 10 ⁹
BaO ₂ + Pt ₂ SO ₂ = BaSO ₄ + 2 Pt	1.00 × 10 ¹⁰	30.0	1.00 × 10 ⁸
Al ₂ O ₃ + SO ₂ = Al ₂ O ₃ SO ₂	1.00 × 10 ²	20.0	1.00 × 10 ⁹
BaSO ₄ + H ₂ = BaO ₂ + H ₂ S + O ₂	5.00 × 10 ⁻¹	100.0	1.00 × 10 ¹
2 BaO + O ₂ = 2 BaO ₂	1.00 × 10 ²	30.0	1.00 × 10 ¹¹

In agreement with experimental measurements, the model predicts breakthrough (release) of SO₂ and H₂S at high temperatures.



We are learning that:

- Microkinetics can successfully incorporate data from a broad range of sources to create accurate models
- Indeed, the more information the better, particularly if you have a computational grid
- Hydrocarbon speciation is important and we still have a paucity of information, particularly during transients