Microkinetics modeling of NOx SCR

Presented to
Diesel Cross Cut

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Arthur D. Little, Inc.
Acorn Park
Cambridge, Massachusetts
02140-2390

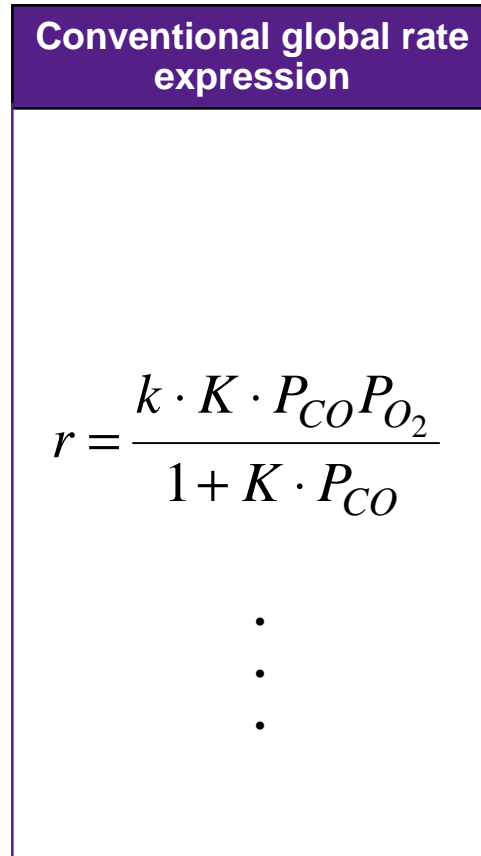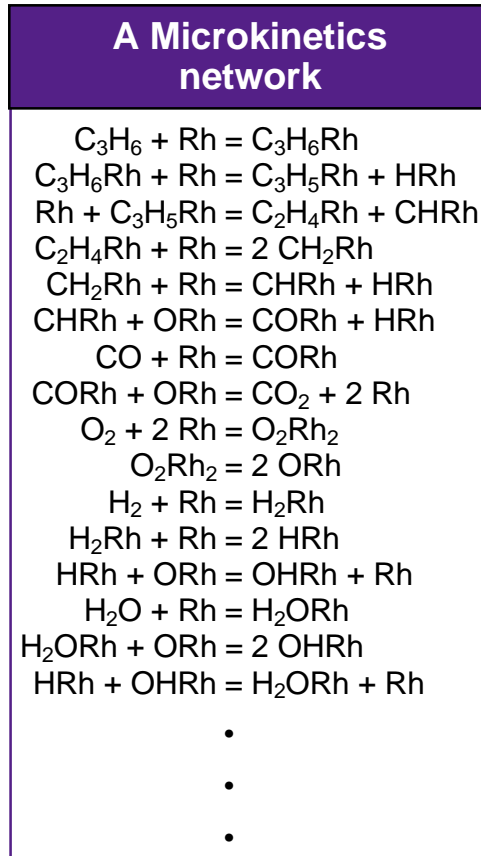**Microkinetics models can suggest ways to improve the formulation and operation of NOx SCR catalysts.**

- In microkinetics models the hypothesized reaction network is represented by many elementary steps and solved numerically.

- A NOx SCR network needs to accommodate NOx reduction, reductant oxidation and the formation of spectator species

- We are in the process of refining our network for SCR, including ammonia storage.

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In microkinetics models the hypothesized reaction network is represented by many elementary steps and solved numerically.

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

A Microkinetics network
$C_3H_6 + Rh = C_3H_6Rh$
$C_3H_6Rh + Rh = C_3H_5Rh + HRh$
$Rh + C_3H_5Rh = C_2H_4Rh + CHRh$
$C_2H_4Rh + Rh = 2\ CH_2Rh$
$CH_2Rh + Rh = CHRh + HRh$
$CHRh + ORh = CORh + HRh$
$CO + Rh = CORh$
$CORh + ORh = CO_2 + 2\ Rh$
$O_2 + 2\ Rh = O_2Rh_2$
$O_2Rh_2 = 2\ ORh$
$H_2 + Rh = H_2Rh$
$H_2Rh + Rh = 2\ HRh$
$HRh + ORh = OHRh + Rh$
$H_2O + Rh = H_2ORh$
$H_2ORh + ORh = 2\ OHRh$
$HRh + OHRh = H_2ORh + Rh$
$\bullet$
$\bullet$
$\bullet$

Conventional global rate expression
$$r = \frac{k \cdot K \cdot P_{CO}P_{O_2}}{1 + K \cdot P_{CO}}$$
$\bullet$
$\bullet$
$\bullet$

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

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

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

Microkinetics

We construct microkinetics networks by building up the chemistry under the constraints of absolute rate theory and thermodynamics.

Build reaction networks from simpler subnetworks	Estimate parameters from absolute rate theory	Ensure thermodynamic consistency

Build reaction networks from simpler subnetworks

1) NO adsorption/desorption
2) O_2 adsorption/desorption
3) N_2 adsorption/desorption
4) H_2 adsorption/desorption
5) NH_3 adsorption/desorption
6) NO surface reactions
7) Hydrogen oxidation
8) Ammonia decomposition

Estimate parameters from absolute rate theory

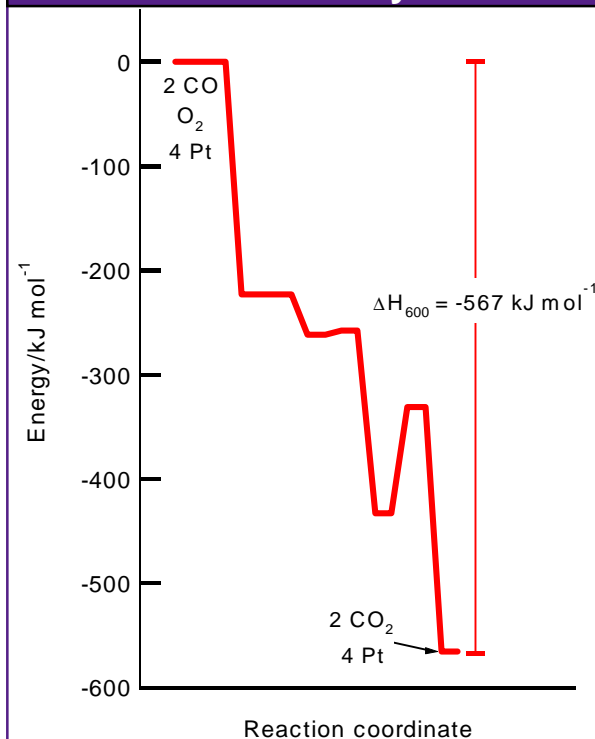$$AM \rightleftharpoons AM^{\ddagger} \rightleftharpoons A + M$$

$$r_d = \frac{k_B T}{h} \frac{Q''_{AM^{\ddagger}}}{Q'_{AM}} \exp\left(-\frac{\Delta E^{0\ddagger}}{k_B T}\right)\theta_{AM}$$

$$\frac{Q''_{AM^{\ddagger}}}{Q''_{AM}} \approx 1$$

$$r_d = \frac{k_B T}{h} \exp\left(-\frac{\Delta E^{0\ddagger}}{k_B T}\right)\theta_{AM}$$

$$A \approx 10^{-13} s^{-1}$$

Ensure thermodynamic consistency

Energy/kJ mol^{-1} vs Reaction coordinate. 2 CO, O_2, 4 Pt → 2 CO_2, 4 Pt. $\Delta H_{600} = -567$ kJ mol^{-1}

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Transition state theory provides excellent first guesses for the values of pre-exponential factors for elementary steps.

Molecular Adsorption	
$A + * \rightarrow A*$	$r = A\left[\exp{-\left(E_a / k_B T\right)}\right]P_A \theta*$
Mobile transition state	$A = 10^3 / Pa$ s
Immobile transition state	$A = 10^1 / Pa$ s

Molecular Desorption	
$A* \rightarrow A + *$	$r = A\left[\exp{-\left(E_a / k_B T\right)}\right]\theta_{A*}$
Similar freedom for adsorbed & transition states	$A = 10^{13} / $ s
More rotational & translational freedom for transition state	$A = 10^{16} / $ s

Dissociative Adsorption	
$A_2 + 2* \rightarrow 2A*$	$r = A\left[\exp{-\left(E_a / k_B T\right)}\right]P_{A2}(\theta*)^2$
Mobile transition state	$A = 10^3 / Pa$ s
Immobile transition state	$A = 10^1 / Pa$ s

Associative Desorption	
$2A* \rightarrow A_2 + 2*$	$r = A\left[\exp{-\left(E_a / k_B T\right)}\right]\theta_{A*})^2$
Mobile adsorbed & transition states w/full rotational freedom	$A = 10^8 / $ s
Mobile adsorbed & transition states w/o rotation	$A = 10^{11} / $ s
Immobile adsorbed & transition states	$A = 10^{13} / $ s
Immobile species with more rotational & translational freedom for transition state	$A = 10^{16} / $ s

To assist in the construction of microkinetics networks, we have created ADL Bistro.

What it is	What it does	How we are using it
• A database for creating reaction networks connected to • MatLab code for simulating chemical reactors 	• Accurately describes both steady state and transient performance of chemical reactors • Facilitates communication among Chemists and Chemical Engineers • Permits easy extension of reaction networks to account for aging and degradation phenomena	• Development of novel aftertreatment systems for Diesel engines • Sizing of a vent catalyst for a fast cooking oven • Debottlenecking of a process for making an agrochemical • Estimating heat release rates for exothermic reactions

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A NOx SCR network needs to accommodate NOx decomposition, reductant oxidation and the formation of spectator species.

The literature provides spectroscopic and kinetic evidence for:

- Surface mono- and dinitrosyl species

- Site blockage by adsorbed oxygen

- Formation of site-blocking nitrites or nitrates

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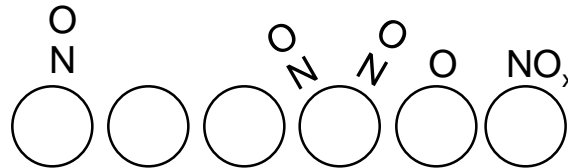
We have constructed a NOx decomposition network that is broadly consistent with the literature.

	A_f	E_0	A_r	ΔH
$NO + Cu = NOCu$	6.00×10^2	35.0	1.00×10^{13}	-69.0
$NO + NOCu = NOCuON$	6.00×10^2	35.0	1.00×10^{13}	-39.0
$NOCuON + Cu = N_2OCu + OCu$	1.00×10^{12}	0.0	1.00×10^{13}	-97.0
$N_2O + Cu = N_2OCu$	6.00×10^2	0.0	1.00×10^{13}	-29.0
$O_2Cu + Cu = 2\ OCu$	1.00×10^{11}	2.5	1.00×10^{13}	-74.0
$O_2 + Cu = O_2Cu$	1.00×10^3	42.0	1.00×10^{13}	-80.0
$N_2OCu + Cu = N_2Cu + OCu$	2.00×10^9	10.0	2.00×10^9	-150.0
$N_2 + Cu = N_2Cu$	1.00×10^3	20.0	1.00×10^{13}	-20.0
$NOCu + OCu = NO_2Cu + Cu$	1.00×10^{13}	10.0	1.00×10^{13}	-10.0

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In particular, the simulation supports the hypothesis that the oxygen left by decomposed NO participates in the formation of surface NOx.
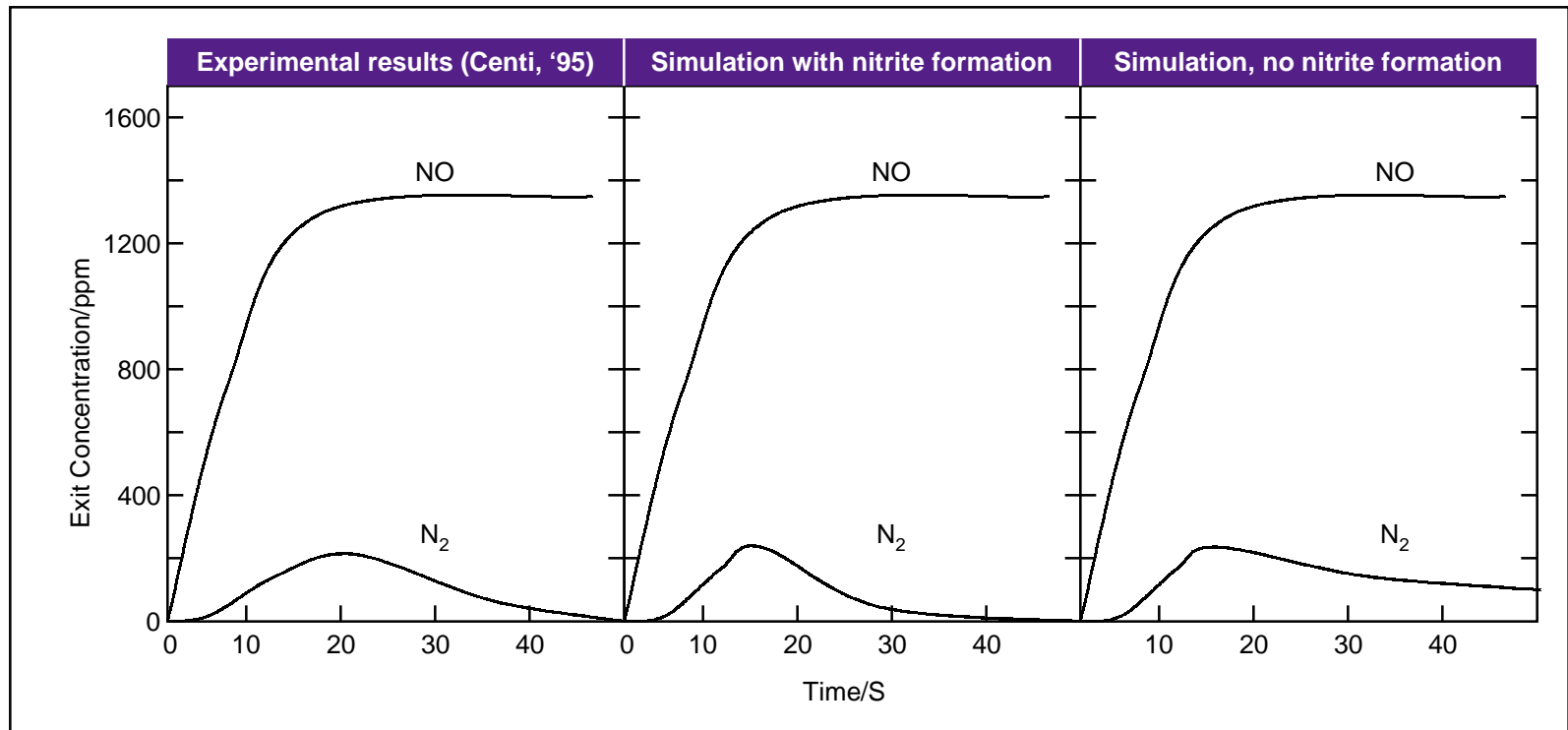
We are in the process of refining our network for SCR, including ammonia storage.

- Without a direct interaction between M-NO and M-NHx the model shows only ammonia decomposition.

- We are implementing ammonia storage by invoking acid sites in the oxide-supported catalyst.

	A_f	E_0	A_r	ΔH
NO + Cu = NOCu	6.00×10^2	35.0	1.00×10^{13}	-69.0
NO + NOCu = NOCuON	6.00×10^2	35.0	1.00×10^{13}	-39.0
NOCuON + Cu = N_2OCu + OCu	1.00×10^{12}	0.0	1.00×10^{13}	-97.0
N_2O + Cu = N_2OCu	6.00×10^2	0.0	1.00×10^{13}	-29.0
O_2Cu + Cu = 2 OCu	1.00×10^{11}	2.5	1.00×10^{13}	-74.0
O_2 + Cu = O_2Cu	1.00×10^3	42.0	1.00×10^{13}	-80.0
N_2OCu + Cu = N_2Cu + OCu	2.00×10^9	10.0	2.00×10^9	-150.0
N_2 + Cu = N_2Cu	1.00×10^3	20.0	1.00×10^{13}	-20.0
NOCu + OCu = NO_2Cu + Cu	1.00×10^{13}	10.0	1.00×10^{13}	-10.0
H_2 + Cu = H_2Cu	1.00×10^4	0.0	1.00×10^9	-43.0
H_2Cu + Cu = 2 HCu	4.00×10^{12}	2.0	1.00×10^{12}	-43.0
HCu + OCu = HOCu + Cu	5.00×10^{13}	30.0	1.00×10^{13}	-62.0
HCu + HOCu = H_2OCu + Cu	5.00×10^{13}	56.0	5.00×10^{11}	-43.0
H_2O + Cu = H_2OCu	1.00×10^4	0.0	1.00×10^{10}	-24.0
NH_3 + Cu = NH_3Cu	1.00×10^3	30.0	1.00×10^9	-20.0
NH_3Cu + Cu = NH_2Cu + HCu	1.00×10^{11}	50.0	2.00×10^{10}	-45.0
NH_2Cu + Cu = NHCu + HCu	1.00×10^{11}	70.0	2.00×10^{10}	-15.0
NHCu + Cu = NCu + HCu	4.00×10^9	70.0	8.00×10^8	-15.0
N_2Cu + Cu = 2 NCu	1.00×10^{13}	0.0	1.00×10^{13}	-15.0

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