Design of Better Performed Diesel Oxidation Catalysts at Reduced Temperature

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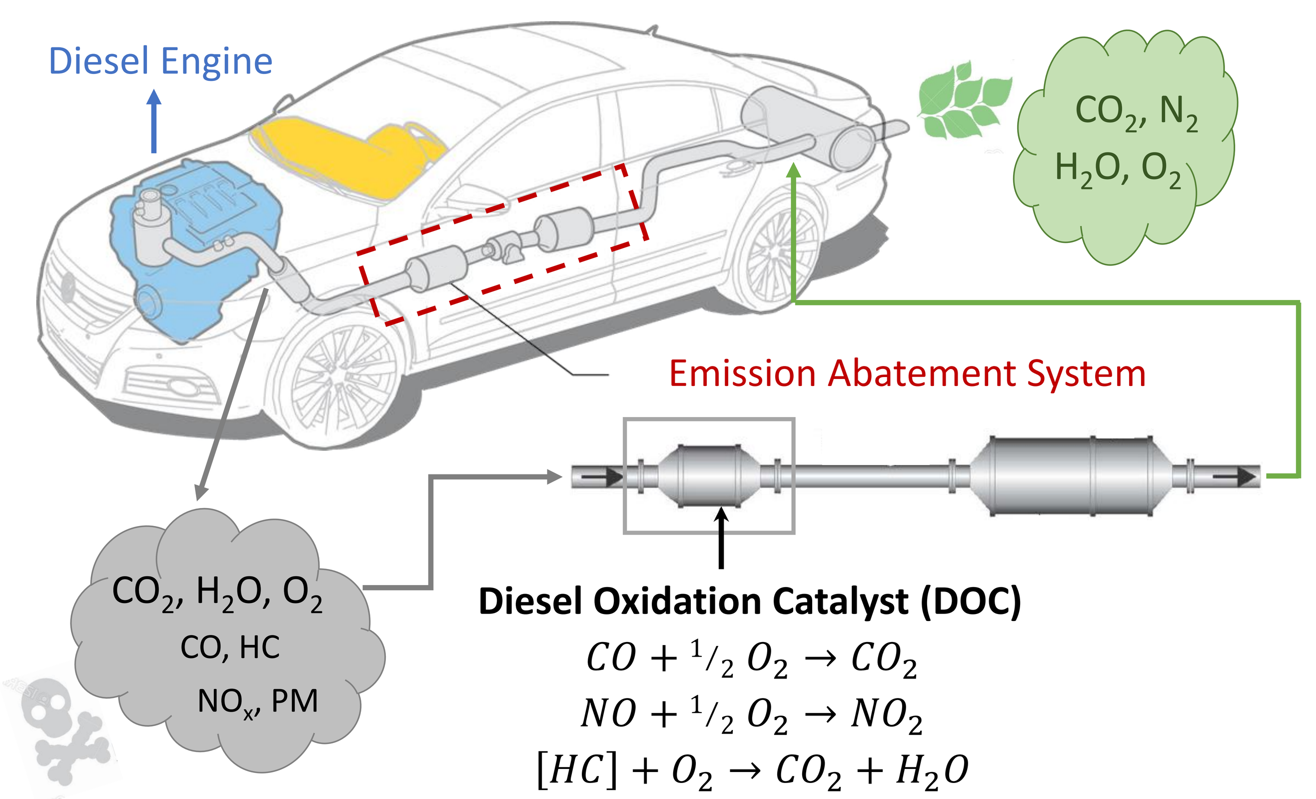
Background and Motivation



$CO + {}^{1}/_{2}\,O_2 \rightarrow CO_2$

$NO + {}^{1}/_{2}\,O_2 \rightarrow NO_2$

$[HC] + O_2 \rightarrow CO_2 + H_2O$

Low Temperature Combustion (LTC) Engines

- Higher fuel efficiency ($\eta_{max} = 1 - T_L/T_H$)
- Lower NOx and particulate matters (PM) emissions

Disadvantages:

- Higher CO and hydrocarbon (HC) emissions
- Low exhaust temperature (~150˚C) decreases diesel oxidation catalyst (DOC) activity

Improved catalyst needed:

- To increase DOC activity at low temperature
- To decrease emissions without sacrificing fuel efficiency

Methods

Microkinetic Model

$$R_i = \left(k_{f,i}\prod_{j\in P_{IS}} P_j \prod_{j\in\theta_{IS}} \theta_j\right) - \left(k_{r,i}\prod_{j\in P_{FS}} P_j \prod_{j\in\theta_{FS}} \theta_j\right)$$

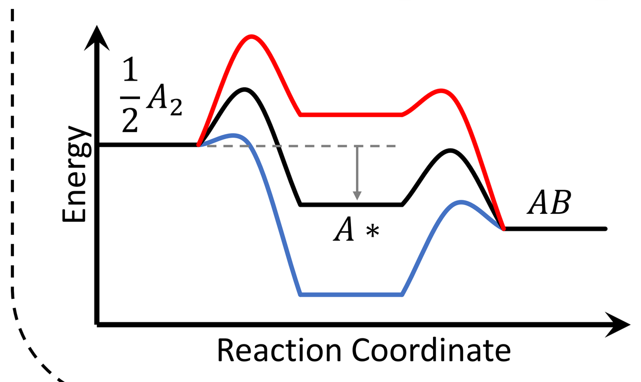
$$\frac{d\theta_j}{dt} = \sum_{n\in R_{FS}} s_n r_n - \sum_{n\in R_{IS}} s_n r_n = 0$$

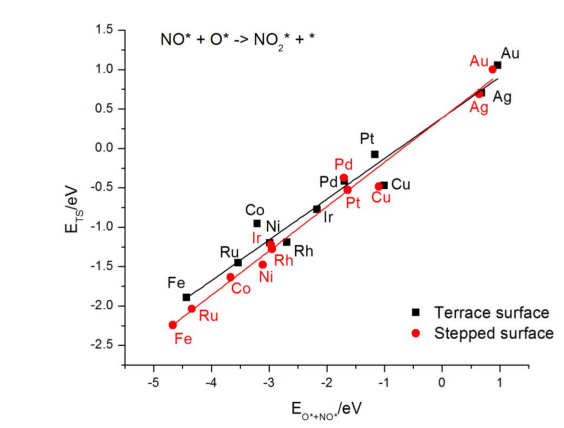
$$k = \frac{k_B T}{h} exp\left(-\frac{E_a - T\Delta S}{k_B T}\right)$$

Scaling Relations

- Between adsorption energies of different intermediates
- Between activation barriers and reaction energies (BEP relation)

descriptors: E_1 and/or E_2





Production Rate = function(*1 or 2 Energetic Descriptor*), show catalytic activity trend

Computational Screening

Catalysts Activity Trend from Microkinetic Models

Reaction Condition: P = 1 atm, 90 ppm NO, 4500 ppm CO, 10 ppm NO_2, 500 ppm CO_2, 10% O_2, balance N_2

Reaction Mechanism

$CO(g) + * \leftrightarrow CO*$

$NO(g) + * \leftrightarrow NO*$

$O_2(g) + * \leftrightarrow O_2*$

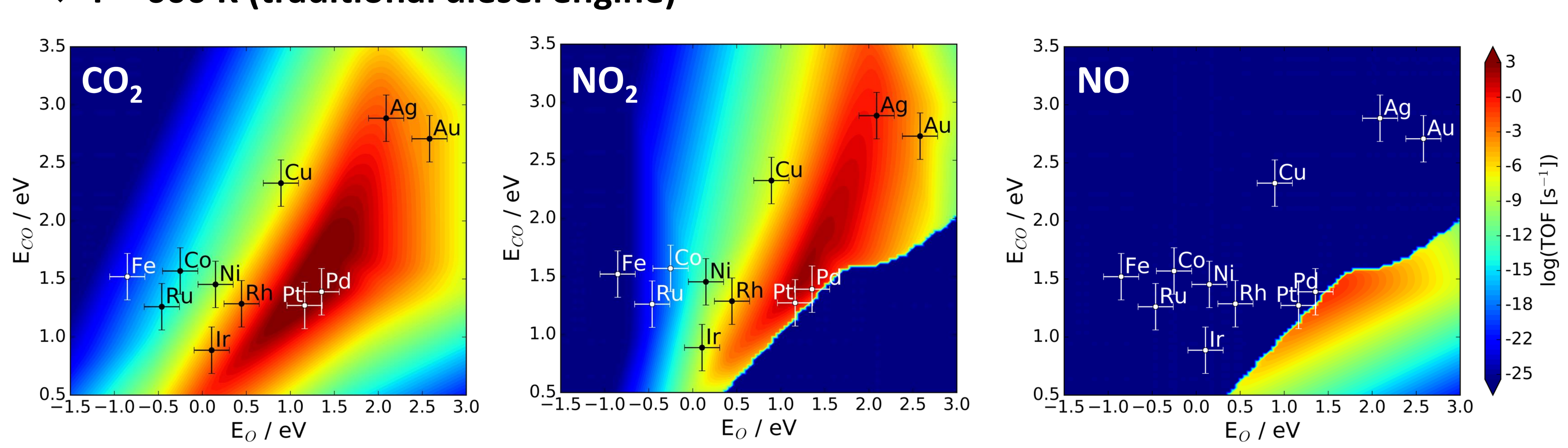
$O_2* + * \leftrightarrow 2O*$

$CO* + O* \leftrightarrow CO_2(g) + 2*$

$NO* + O* \leftrightarrow NO_2(g) + 2*$

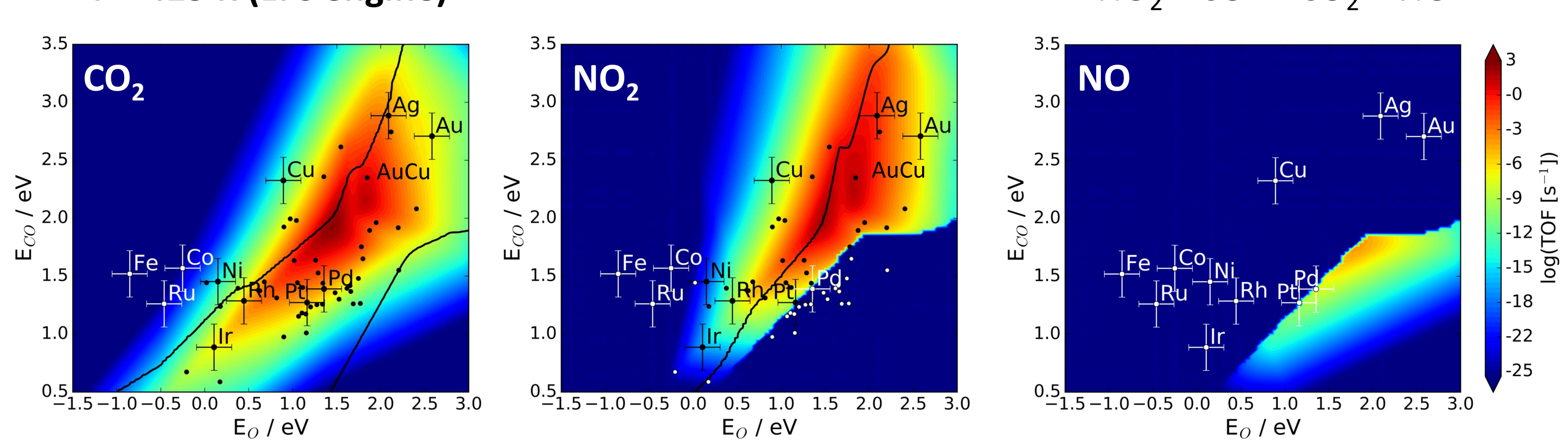
Descriptors: E_O and E_{CO}

❖ **T = 600 K (traditional diesel engine)**



❖ **T = 425 K (LTC engine)**

$NO_2 + CO \rightarrow CO_2 + NO$

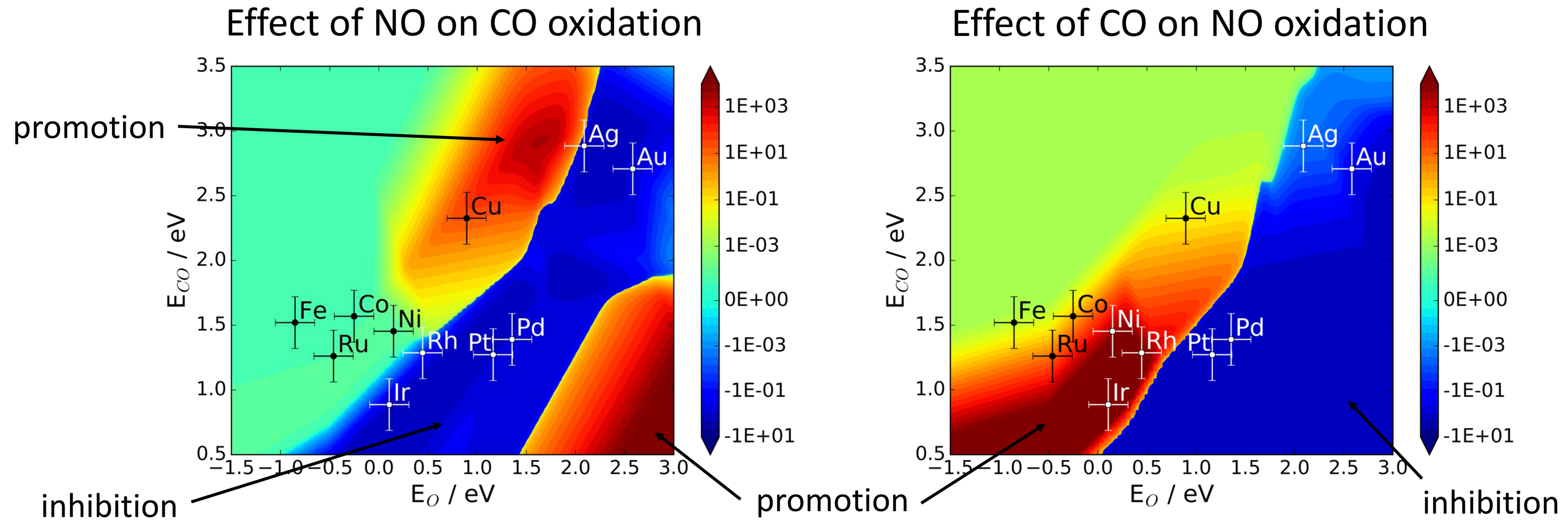


Alloy Screening

- Bulk alloys of noble metals Cu, Ag, Au with more reactive Pd, Pt, Ni metals populate the empty area with high predicted oxidation activity

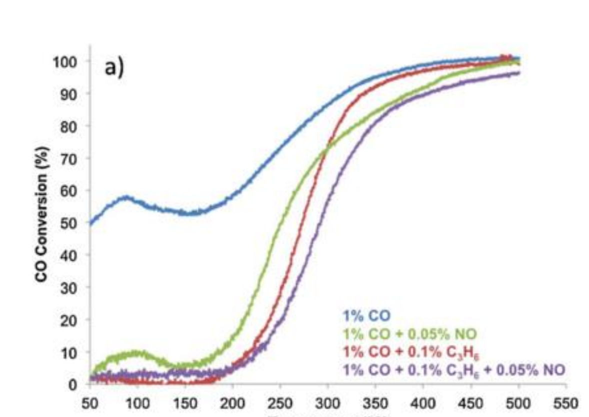
Mutual Inhibition/Promotion Effect between CO & NO

Define as: $\eta_i = \frac{\mathrm{TOF}_{CO+NO}}{\mathrm{TOF}_i} - 1, \quad i = \{CO, NO\}$



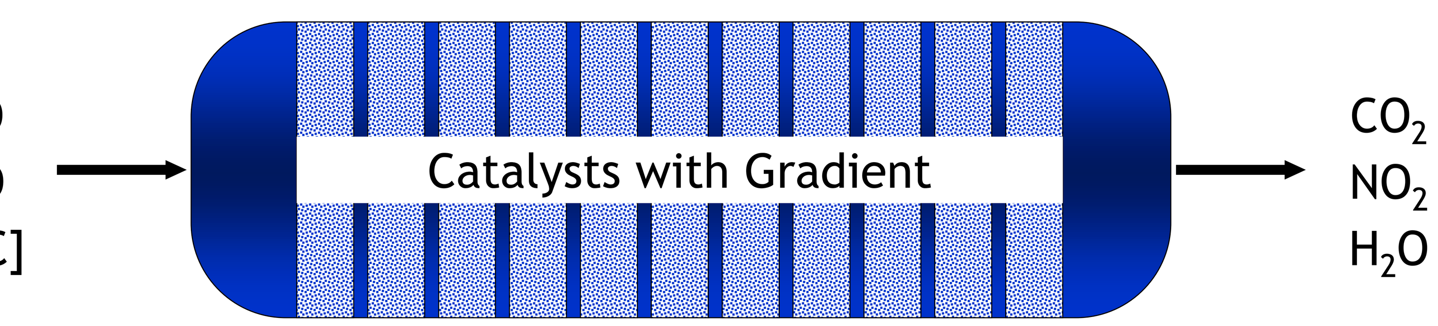
Experimental Validation

- Au-CuO/SiO_2 is an excellent low temperature CO oxidation catalyst, but it suffers from NO and HC inhibition.



Reactor Model with Composition Gradient

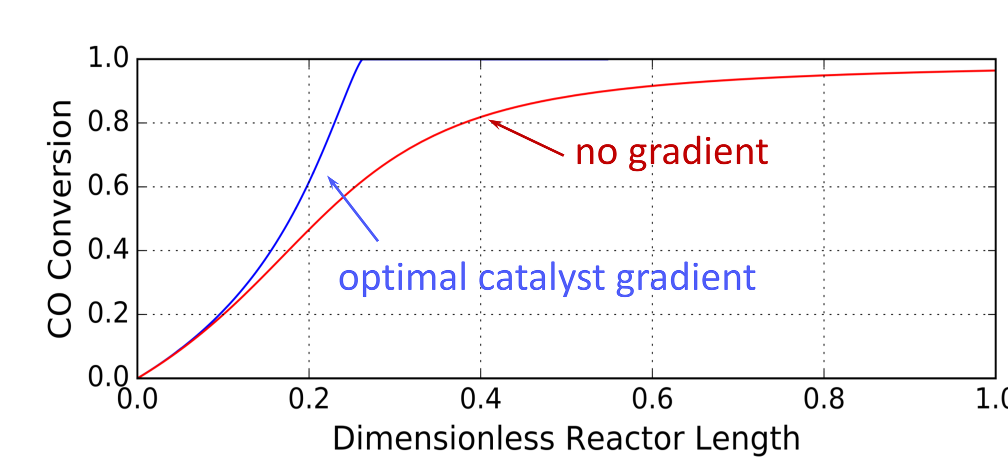
- Reaction conditions influence the position of the top of the volcano.
- Optimal catalyst composition varies with temperature, feed concentration, pressure, etc.



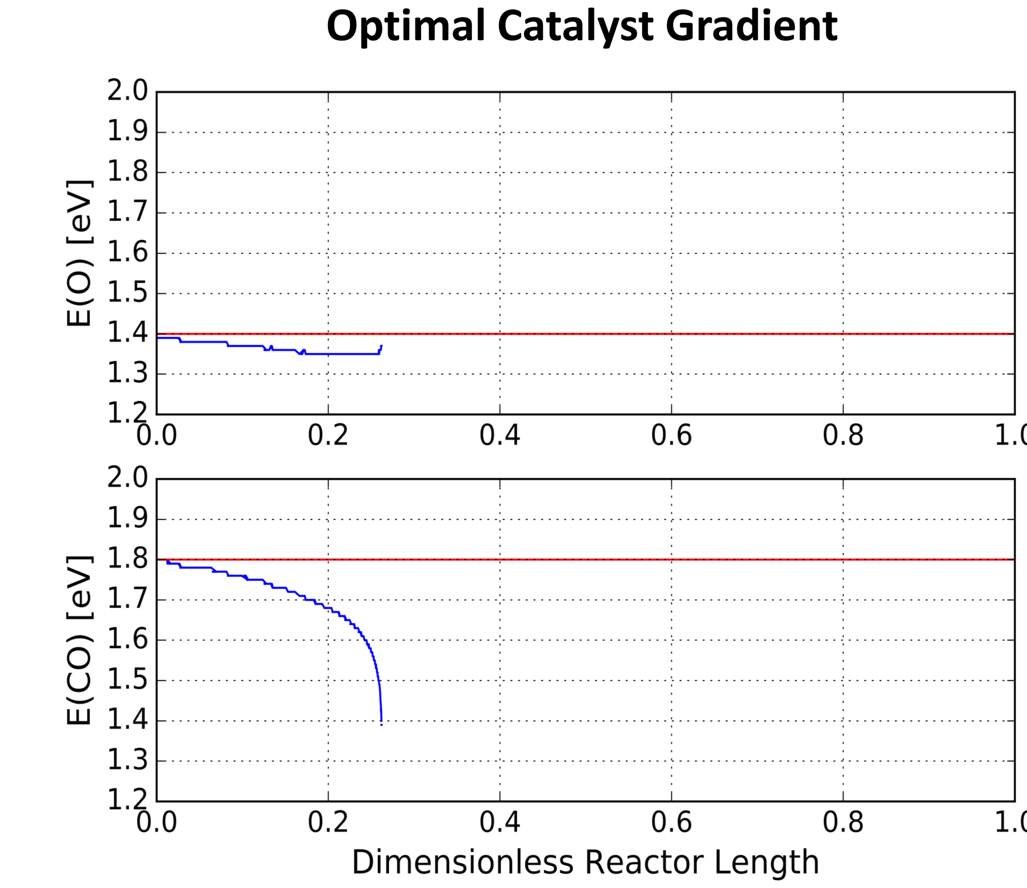
Preliminary Reactor Model

Assume 1-dimensioanl PFR, under steady-state condition:

- Mass balance: $\frac{dX_i}{dz} = \frac{TOF_i \times \rho_{sites}}{F_{i,0}}$
- Heat balance: $\frac{dT}{dz} = \frac{\sum_{j=1}^{q} TOF_{ij} \times \rho_{sites} \times [-\Delta H_{Rxij}(T)]}{\sum_{i=1}^{m} F_i C p_i}$
- Constant density of sites ρ_{sites}



Optimal Catalyst Gradient



- An optimal catalyst gradient design has the potential to reduce the required number of catalytic sites (metal content) by 70%, while still achieving identical CO oxidation performance.

References

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Acknowledgement

Funding: NSF/DOE

Computational Resources: CACDS, XSEDE, NERSC