Numerical tools and methodologies for generating and refining kinetic models of lean NO_x traps

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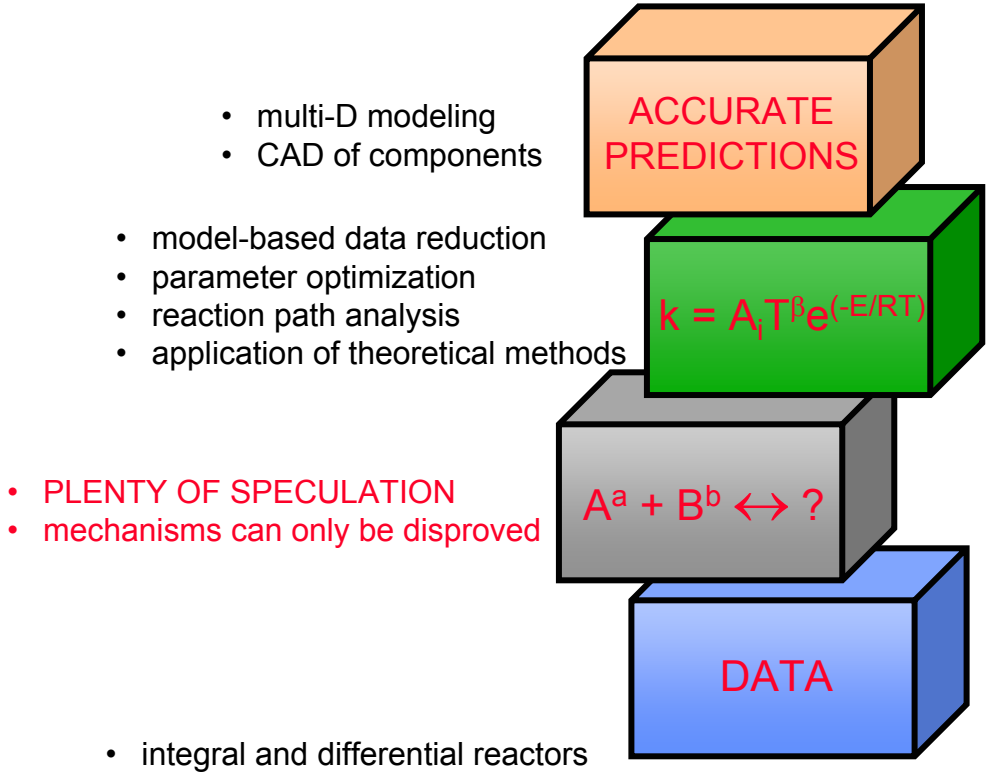
Topics for discussion

- General framework for building and testing kinetic models
  - Data sets, theory, and numerical tools
- Application of transient perfectly stirred reactor code (PSR)
  - Chemkin tool
  - Published mechanisms
  - Pt/Al_2O_3, BaO/Al_2O_3, $Pt/BaO/Al_2O_3$ literature results
  - CLEERS $SCONO_x$ material
- DAKOTA
  - Design optimization, parameter estimation, uncertainty quantification, and sensitivity analysis
- Commercial versus open source (GNU)
  - Chemkin
  - Cantera
- Path forward

Building kinetic models

- **Validate, refine and apply kinetic model**
- **Resolve model parameters**
  - **Theory**
  - **Numerical tools**
- **Formulate mechanistic detail**
  - **Rate laws**
- **Experiments**
  - **Identify major players**
    product species
    adsorbates
  - **Capture critical P, T, C dependencies**



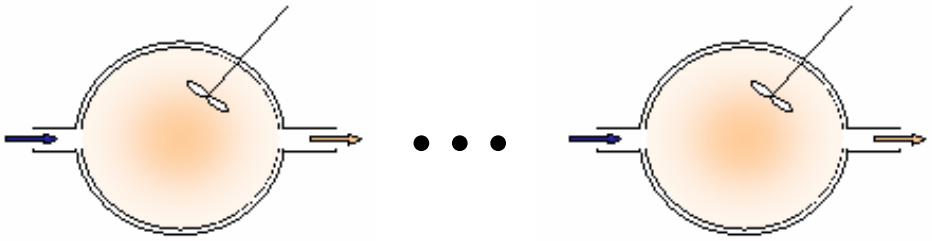
- multi-D modeling
- CAD of components

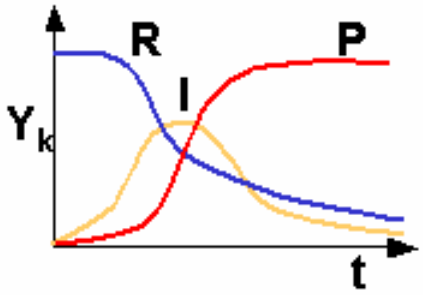
- model-based data reduction
- parameter optimization
- reaction path analysis
- application of theoretical methods

- PLENTY OF SPECULATION
- mechanisms can only be disproved

- integral and differential reactors
- thin films, packed beds, wash-coated
- steady state, transient, isothermal, TPR, TPD
- gas analysis, electron and photon spectroscopies

Lean NOx traps as perfectly stirred reactors





- **Chemkin**
  - **Collection of problem-independent algorithms to manage computation and provide information**

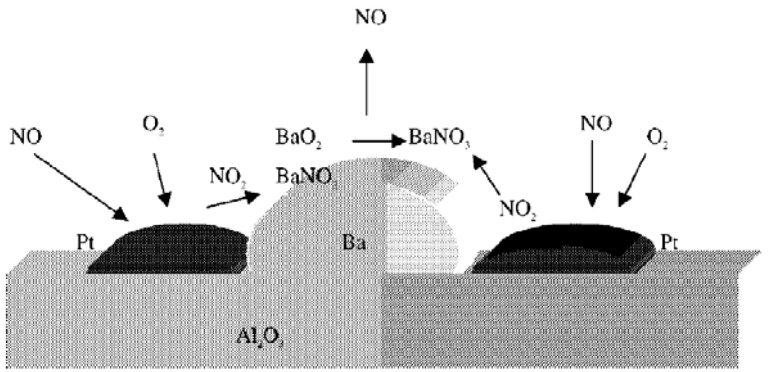
    species, reactions, thermodynamic and transport properties
  - **Suite of 0-, 1-, and 2-D reacting flow simulators**

- **Have a transient PSR model**
  - **Linked in series**
  - **User defined**

    T, [C] profiles, active area fraction
  - **Equations integrated over V_R as opposed to M_{cat}**
- **Need a transient plug flow model**
  - **Pore diffusion, surface transport**

Evaluation of published mechanisms

- **Mechanisms are scarce and often not transferable**
  - **Tuned to a particular data set**
  - **Pt/Al_2O_3 most abundant**
    TWC, catalytic combustion, POX
    NO reduction still debatable
  - **BaO/Al_2O_3 + $Pt/BaO/Al_2O_3$**
    high degree of speculation
    only 1 published as of 2003
- **Conversion to Chemkin formulation not trivial**
  - **Pseudo-first order TOF space to mass action kinetics**
  - **Transport of NO_2(s) between Pt(s) and $BaONO_3$(s) not available in PSR model**



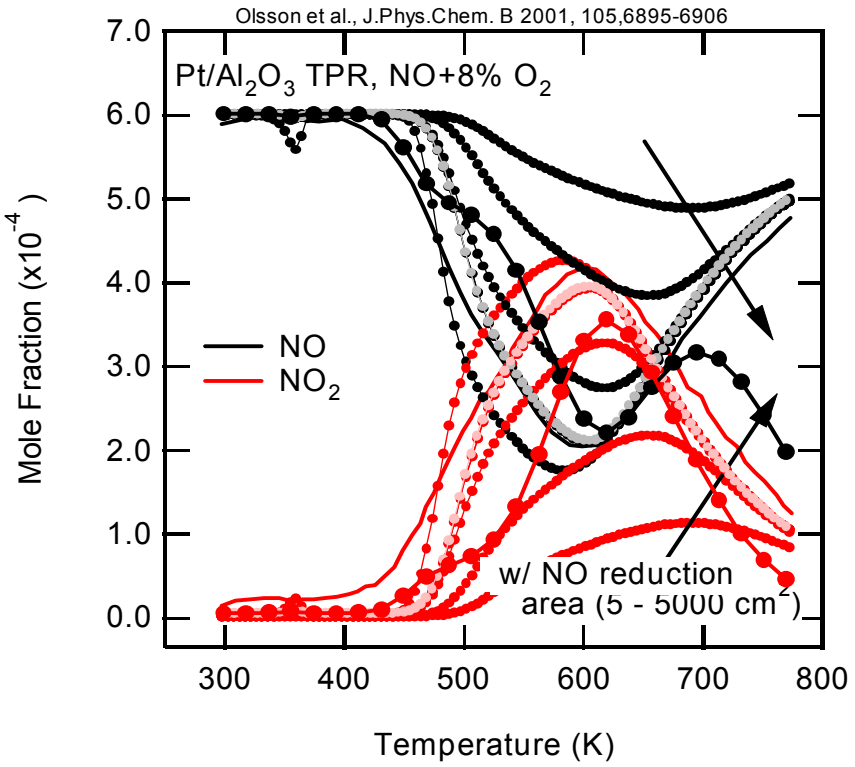
Olsson et al. (storage)
- adsorption/desorption of O_2, NO, NO_2
- surface reactions O(s), NO(s), NO_2(s)
- transport of NO_2(s) from Pt(s) to $BaONO_3$(s)

Deutschmann et al. (reduction)
- adsorption/desorption of H_2, CO, H_2O, CO_2
- surface reactions
  H(s), OH(s), O(s), C(s), CO(s), CO_2(s)

Hoebink et al. (NO reduction)
- desorption of N_2
- surface reactions NO(s), N(s), O(s)

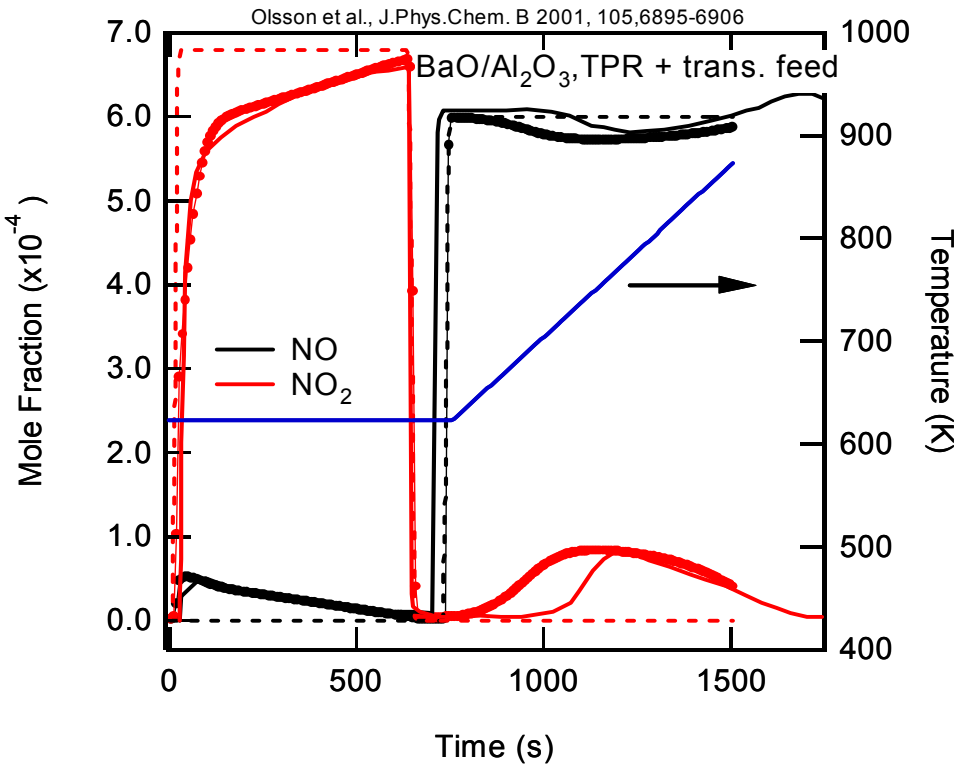
TPR of NO + O_2 over Pt/Al_2O_3

- **Chemkin prediction**
  - **Good agreement obtained by**
    adjusting active area
    number of PSRs in series
- **Investigate the importance of NO reduction**
  - **Poor agreement**
    creates shoulder region at low T
    NO conversion too extreme at high T
- **WHY?**
  - **NO submodel not transferable?**
  - **Better agreement by retuning the modified mechanism?**
  - **NO reduction not important?**



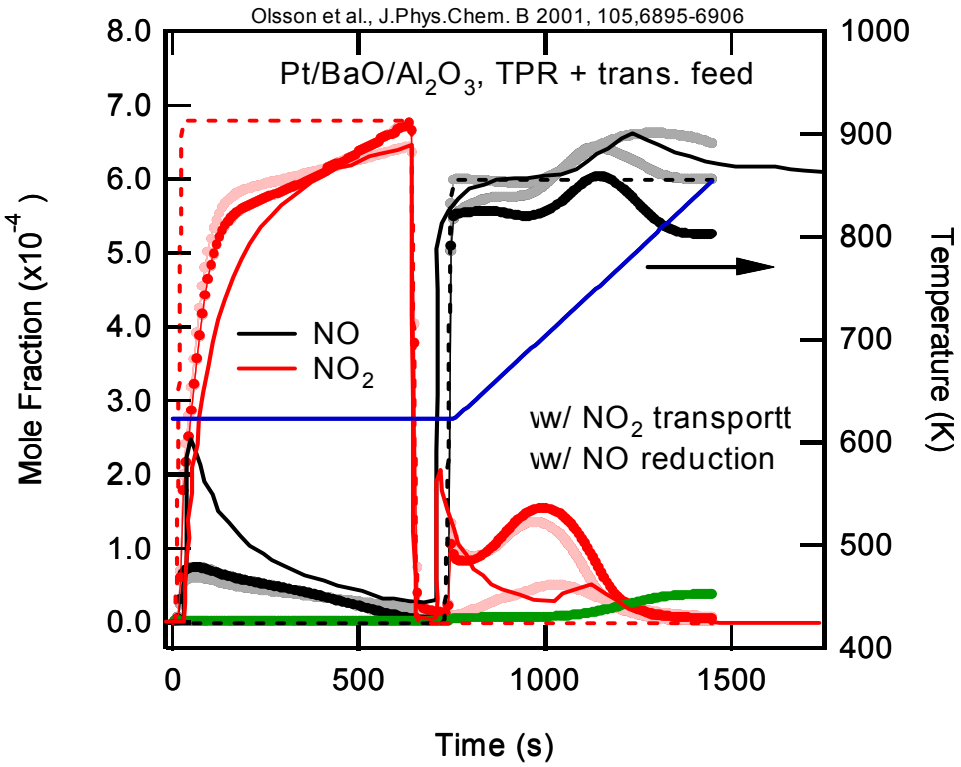
TPR (+ transient feed) of NO and NO_2 over BaO/Al_2O_3

- **Experimental condition**
  - **NO_2 exposure followed by NO**
  - **Linear temperature ramp**
- **Observation**
  - **NO formed during initial storage period**
    postulate surface oxidation
  - **Broad NO_2 desorption peak**
    postulate coverage dependence
- **Chemkin prediction**
  - **Good agreement with trends**
  - **Marginal agreement with peak shapes and positions**

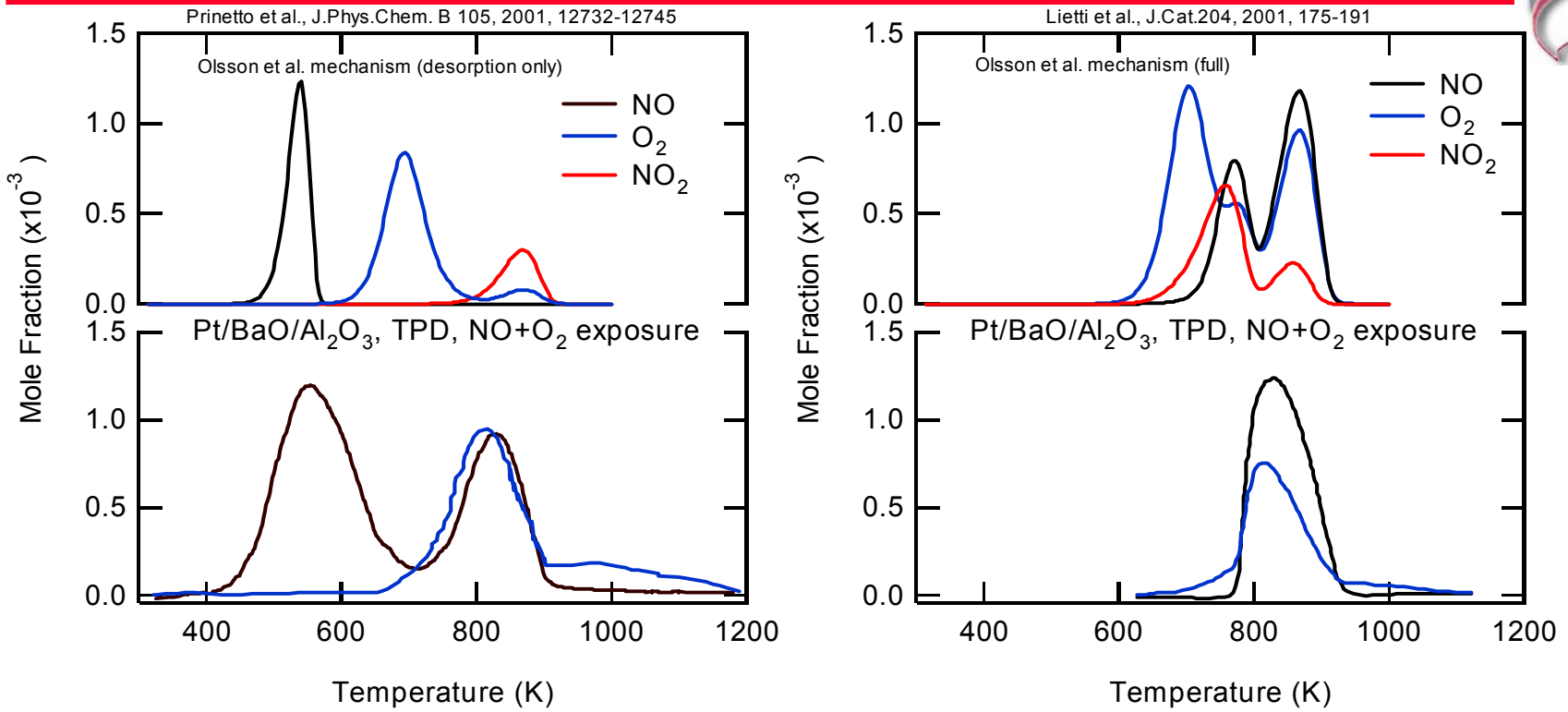


TPR (+ transient feed) of NO and NO_2 over $Pt/BaO/Al_2O_3$

- **Experimental condition**
  - **NO_2 exposure followed by NO**
  - **Linear temperature ramp**
- **Observation**
  - **NO_2 desorption at low T**
    postulate spill over effect
- **Chemkin prediction**
  - **Behaves like BaO material without spillover**
  - **Predict low T NO_2 desorption with spillover**
  - **NO reduction does not enhance prediction**
  - **Marginal agreement with peak shapes and positions**

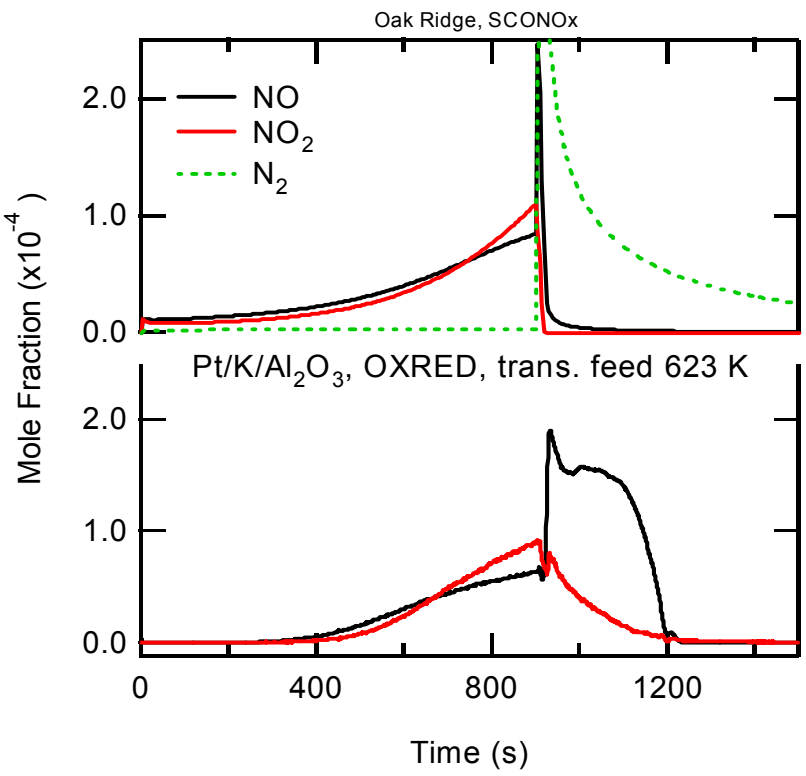


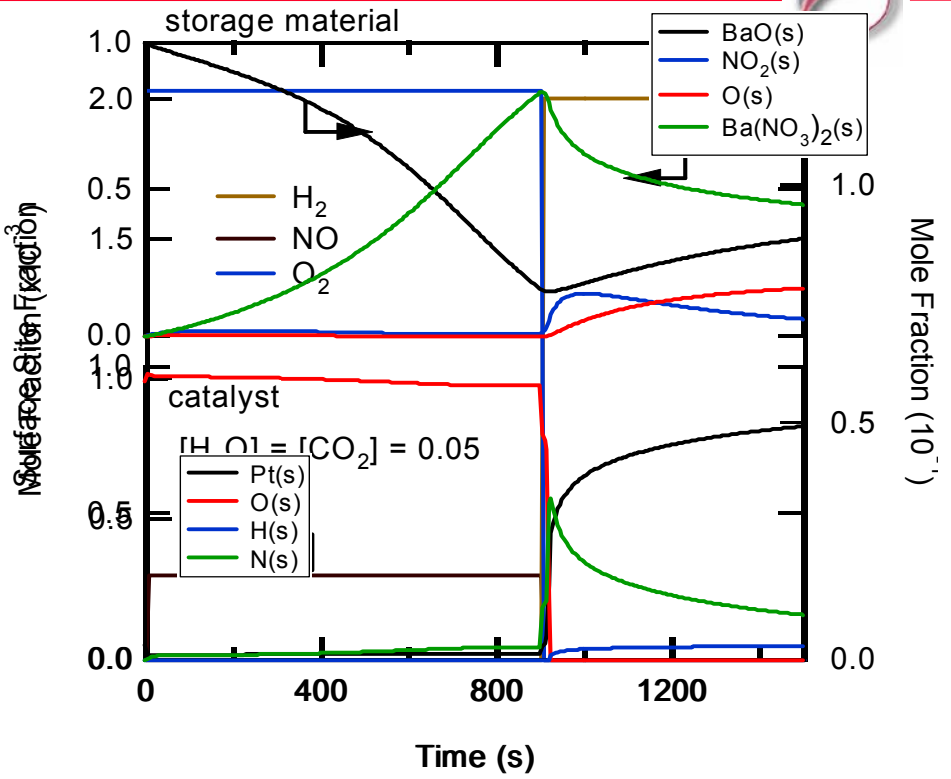
Simulating TPD experiments



- **Key technique for extracting adsorbate energetics from data**
  - **True TDP experiment samples irreversible desorption and surface reaction**
- **Predicted behavior strongly dependent on initial state of surface**
  - **Site fractions of adsorobates must be known or resolved recursively**
- **Cannot reconcile U. di Torino data with Olsson mechanism**

Oxidation-reduction cycle of SCONOx catalyst at 627 K

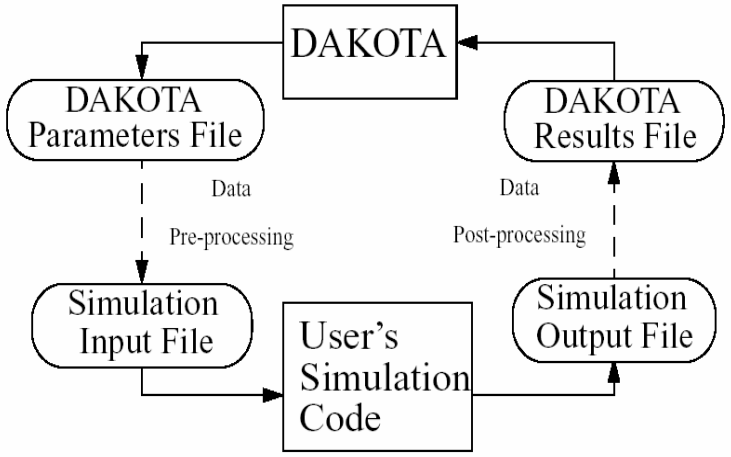




- **Combined Olsson+Deutschmann+Hoebink mechanism**
  - **Missing H_2O and CO_2 reactions with BaO ($BaCO_3$, $Ba(OH)_2$, etc…)**
- **Capture significant trends in data**
  - **NO / NO_2 cross over in oxidation cycle + large reductant-induced NO spike**

Extracting model parameters and more…

- **Model-based data reduction**
  - **Simulation code**
- **DAKOTA**
  - **Numerous methods and strategies**
  - **Parameter study and optimization**
    gradient and non-gradient based
    local and global search routines
    sophisticated bounds control
  - **Uncertainty quantification**
    effects of error propagation
    define regions of validity for model
  - **Sensitivity analysis**
- **Flexible code interface**
  - **Script driven or compiled**



- Rely on data, theory, and thermodynamics to provide appropriate constraints for search algorithms
- Non-negative Ea
- Thermodynamically consistent
- Appropriate bounds on A_i

Alternatives to commercial codes

- **DAKOTA**
  - **Available for download from SNL website**
  - **C++ open source (GNU)**
- **Cantera**
  - **Chemkin and Surface Chemkin analog**
  - **Link to download @ Prof. David Goodwin website (Cal. Tech.)**
  - **C++ open source (GNU), also runs under Python engine**
  - **Reaction path analysis tools**
    key to mechanism reduction and generating artificial kinetic maps
  - **Simulation tools beginning to emerge**
- **Others?**
  - **Warnatz group, Germany**

Path forward

- **Continue to search and catalog open literature for relevant information**
  - **Modelable data sets**
  - **Theoretical results (first principles calculations)**
- **Take Chemkin applications coupled to DAKOTA as far as possible**
  - **Transient PSR models**
  - **Equilibrium calculations (phase diagram)**

    $BaCO_3$, $Ba(OH)_x$, etc …
- **Create a transient plug flow model**
  - **Pore diffusion / reaction and surface transport models**

- **Develop and refine detailed kinetic models for lean NO_x traps**
  - **Standardize and benchmark both kinetic mechanisms and models**