On parameter fitting of Microkinetic mean-field models for catalytic systems.

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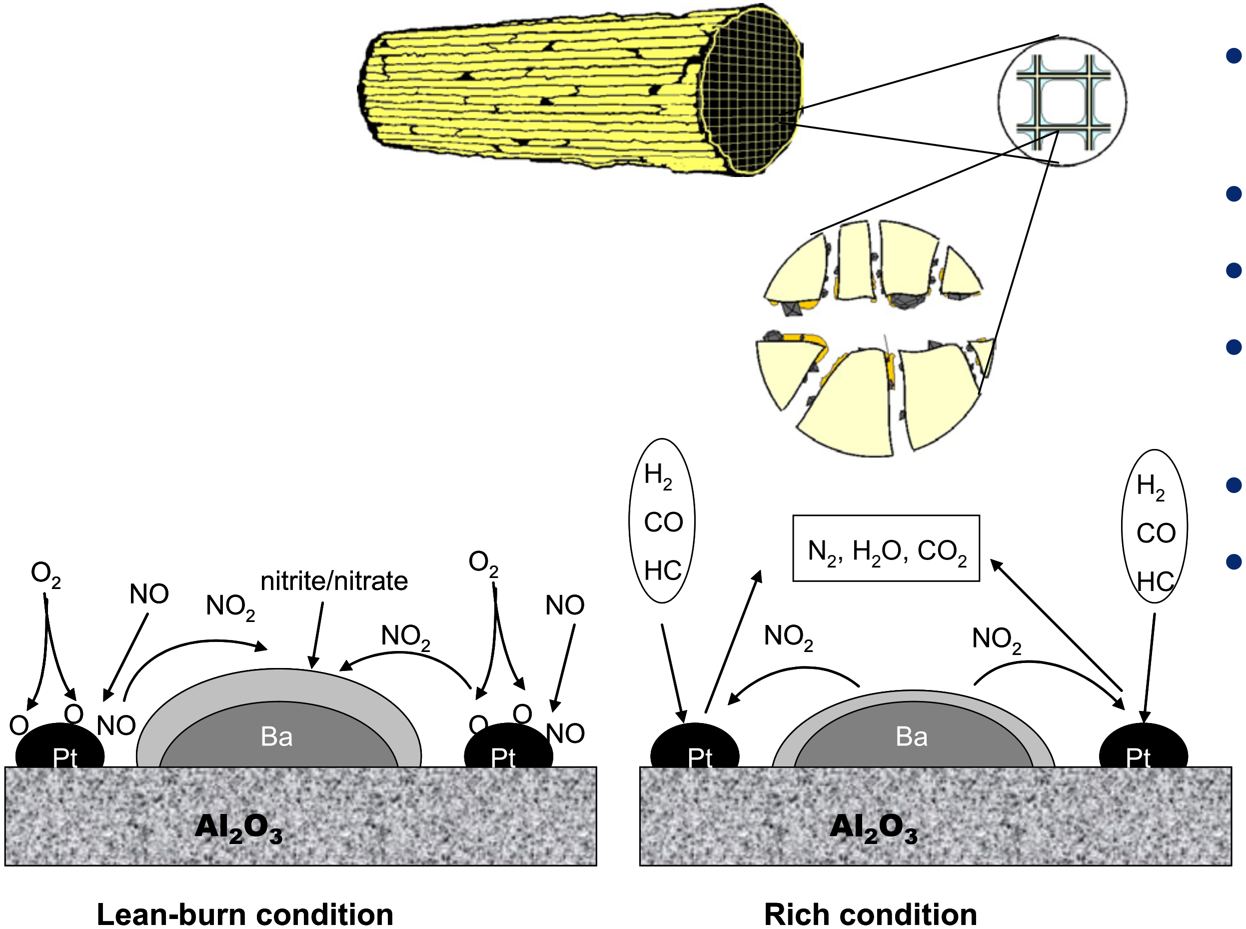
Outline

- System overview
  - NO_X Storage and Reduction (NSR) system
  - Microkinetic model
- Parameter fitting
  - New(?) approach in Microkinetic modeling
  - Fitting results
- Conclusions
- Discussion

NO_X Storage and Reduction (NSR)



- Used for automotive emission control
- Monolith reactor
- Alumina washcoat
- Different active sites (Pt, BaO)
- Complex system
- Transient conditions
  - Switching between storage (lean) and reduction (rich) conditions

Objectives

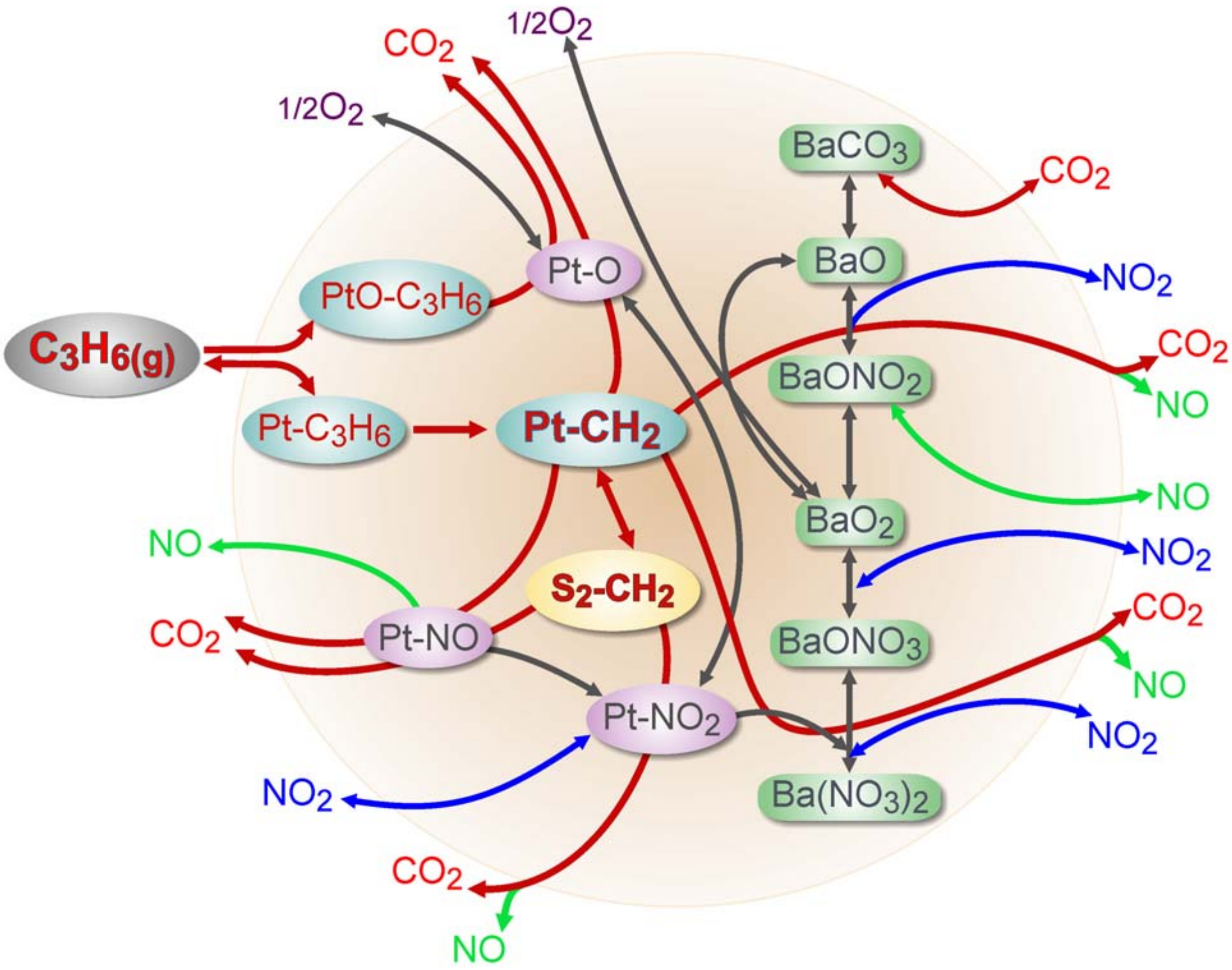
- Modelling objective
  - Increased understanding of NSR systems
    - By using detailed kinetic models:
      - Study unobservable phenomena and set up hypothesis about the NSR system
      - Suggest new experiments to verify hypothesis
- Objective of this study
  - Increase effectiveness during fitting
  - Improve model assessment

Microkinetic model

- Adapted from previous work [1-3]
  - Tanks in series
  - Mass transport by film model
  - Detailed kinetics
- Applied to new experiments [4]
  - C_3H_6 as reducing agent

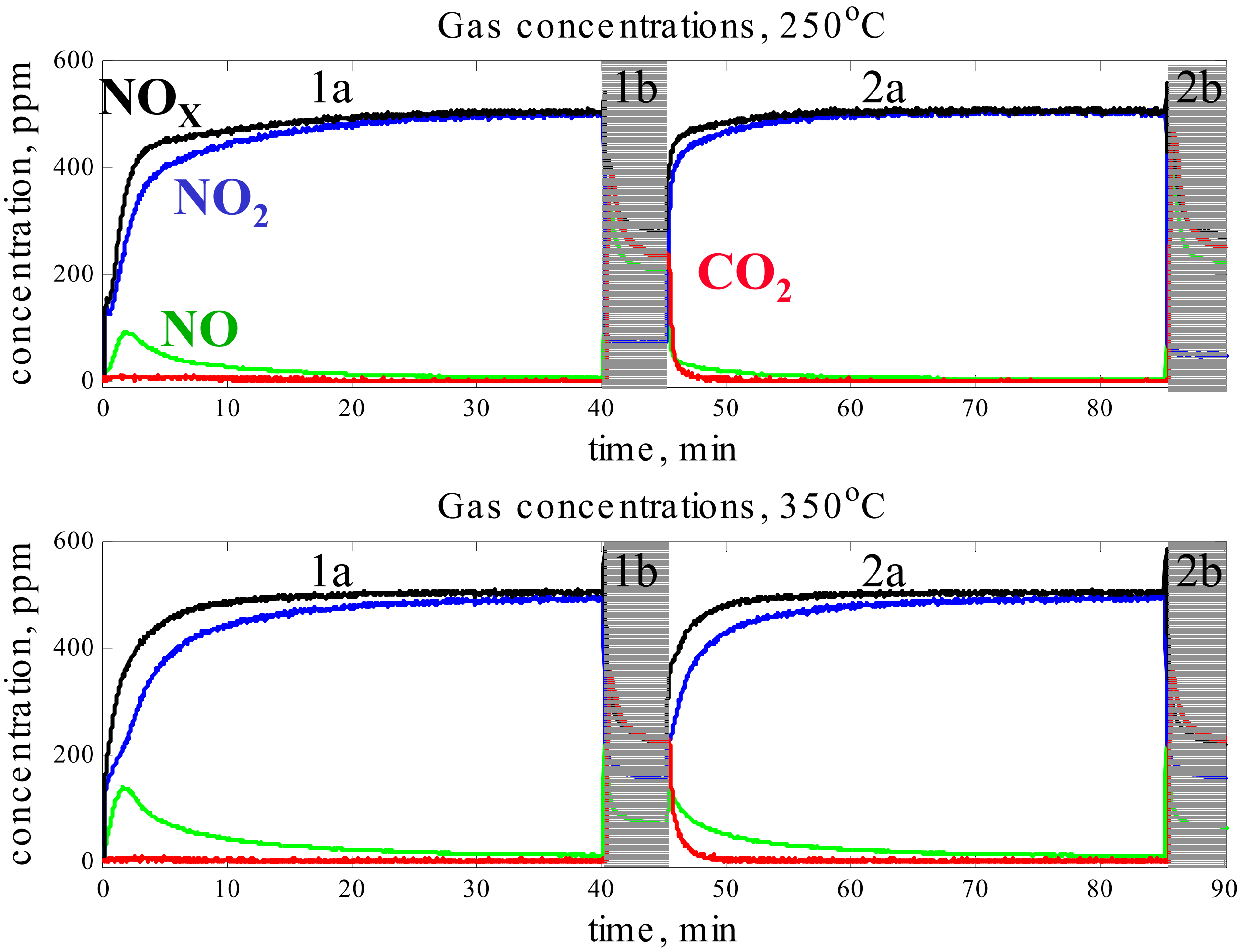
1. Westerberg, B. et al., Chem. Eng. J., 2003. **92**(1-3)
2. Olsson, L. et al., J. Phys. Chem. B, 2001. **105**(29)
3. Olsson, L. et al., Catal. Today, 2002. **73**(3-4)
4. Abdulhamid, H. et al., Top. Catal. 2004. 30-31(1)

Reaction mechanism



- 35 reactions
- 12 ads species
- 3 different sites (Pt, BaO, $S2=Al_2O_3$)

Experimental data



- **Inlet concentrations:**
  - 500 ppm NO_2 (constant)
  - 222 ppm C_3H_6 during rich periods (regeneration) marked by grey
- **2 cycles:**
  1a. Storage from "clean" surface
  1b. 1st regeneration
  2a storage from regenerated cat.
  2b 2nd regeneration
- **2 temperatures**
  - 250°C & 350°C

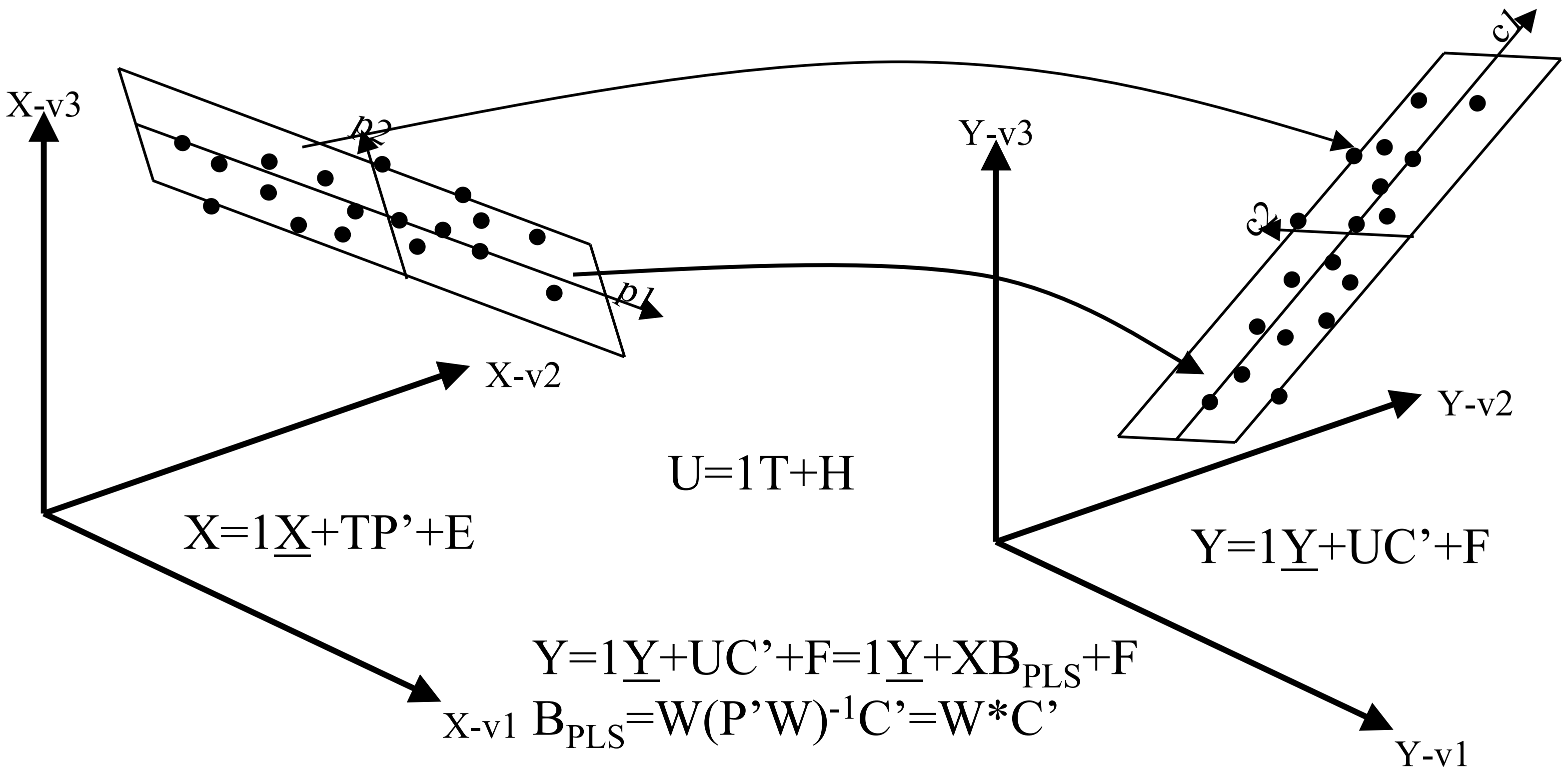
Model implementation

- Matlab 6.5
  - Ode15s: solves only for 12 adsorbed species (in all tanks)
    - Assumes no gas phase accumulation: gas conc. (y, ys) calculated analytically
  - lsqnonlin
    - Large scale, using PCG, trust region
    - Log of pre-exponentials
    - Centered pre-exponentials
    - Scaled parameters

$$k = Ae^{\frac{-Ea}{RT}} = Ae^{\frac{-Ea}{RT_0}} e^{\frac{-Ea}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)} = k_{ref} e^{\frac{-Ea}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)}$$

$$\theta_{scaled} = \frac{\left(\theta_{un-scaled} - \theta_{mean}\right)}{weight}, \quad \theta = k_{ref}, Ea$$

Latent Variable modelling: Partial Least Squares (PLS)



$U=1T+H$

$X=1\underline{X}+TP'+E$

$Y=1\underline{Y}+UC'+F$

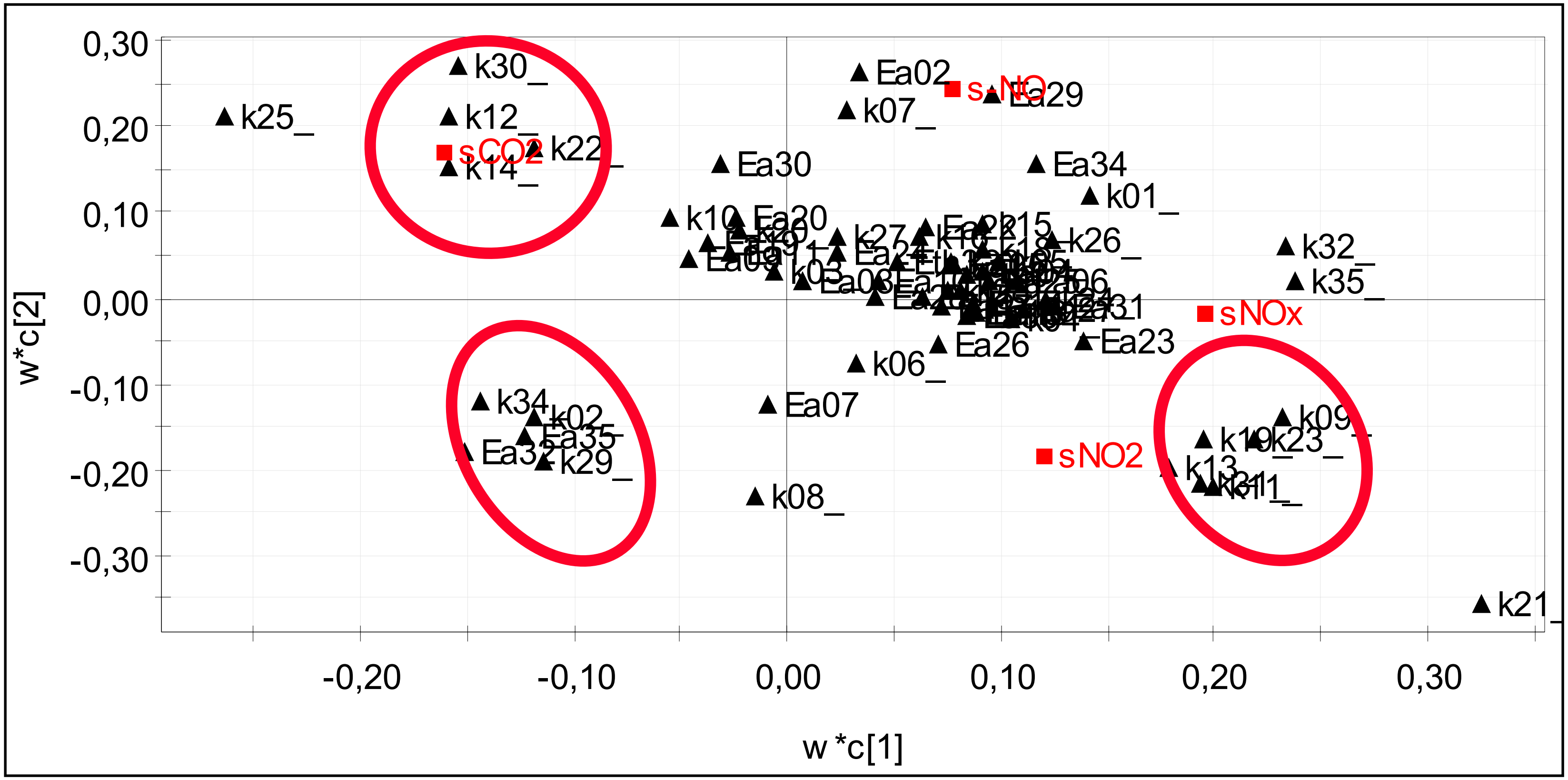
$Y=1\underline{Y}+UC'+F=1\underline{Y}+XB_{PLS}+F$

$B_{PLS}=W(P'W)^{-1}C'=W^{*}C'$

Parameter assessment

- Jacobian $\partial f/\partial \theta$
  - Evaluated for ALL adjustable parameters (not only fitted ones)
- Latent Variable (LV) method:
  - Partial Least Squares (PLS) using J as "X"
    and f (simulated-observed gas phase concentrations) as “Y”
- Outcomes:
  1. Correlation structure !
  2. Number of independent directions (# parameters to fit) !
  3. Which parameters to choose !

LV example: "loading" plot



Fit methodologies using LV

1. Use loading plot (previous slide) to pick parameters that span the experimental space
2. Use LV model loadings and perform fitting in transformed coordinates ("scores")

- Benefits:
  - Practical: less function calls
  - Theoretical: Hessian approximation by J'J is better if parameters are uncorrelated

Alternative approach to microkinetic modelling

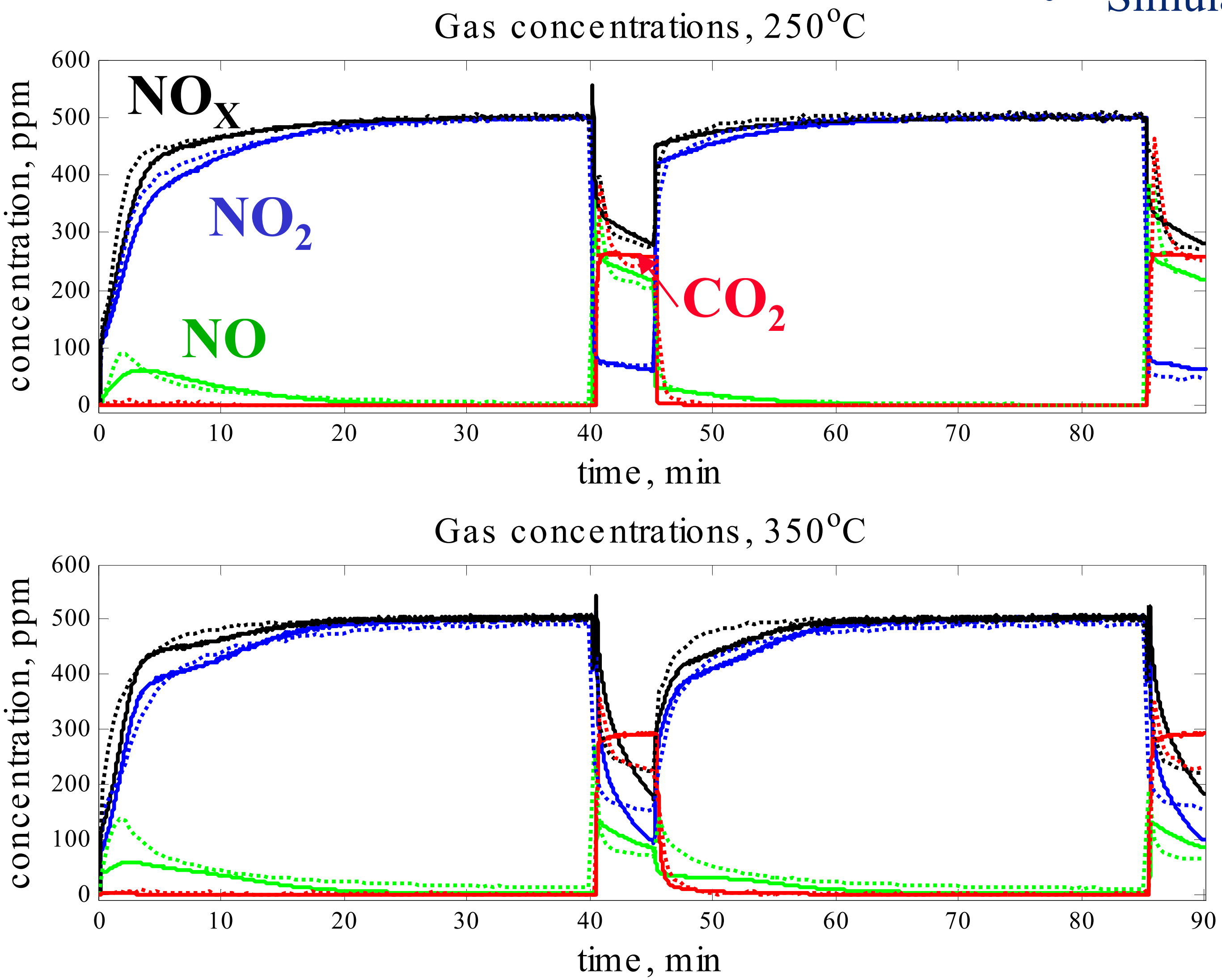
- **Old maxim:**

  "Use the obtainable parameters and fit the rest"
- **Alternative maxim:**

  "Fit only parameters that span the experimental space"

Fit results

- Experimental-dotted
- Simulated-solid lines



Conclusions

- LV Methodology works well
- Parameter values far from optimum puts demand on search algorithm

Discussion
Objective function

- How to implement your intuition?
  - Different weights for different:
    - Experiments
    - Gas phase species
    - Time points
  - Objective function extended beyond residual (exp-sim)
    - How has "a priori" knowledge been incorporated before at EUROKIN?
      - Coverage (unobservable)
      - Reaction rate ratios, assumed rate limiting step, assumed steady state (time dependent!)
      - Signal shape characteristics (e.g. “smooth”, rounded increase in NO_2 during storage)

Discussion
Search algorithm

- lsqnonlin uses gradients
  - Assumes proximity of optimal parameters
  - Finds local optima
- Search algorithms capable of finding global optima!
  - What other methods have been tried at EUROKIN?
    - Simulated Annealing? Simplex methods?
    - Benefits and drawbacks?
      - Convergence, number of function calls, …

Discussion
Experiments

- Better initial parameter estimates
  - "Probe reactions" (TPD, TPR, isotopes, "intelligent" step changes)
    - Using final mechanism
- Spanning the parameter space
  - Simulations using experimental design
  - Pick experiments that exposes the model sensitivity
    - Parameter dependent
    - Catalyst condition dependent ("experimental history")
- Experiences at EUROKIN?

END

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