

# EXTENT-BASED MODEL IDENTIFICATION OF SURFACE CATALYTIC REACTION SYSTEMS

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## INTRODUCTION

### CONTEXT

Kinetic model identification and estimation of reaction and mass-transfer parameters are important tasks for monitoring, control and optimization of industrial processes. The Extent-based Model Identification has been developed to separate effects of reaction, mass transfer and flows for homogeneous and gas-liquid reaction systems [1]. Measurements are transformed into extents, which are modeled individually, decomposing the identification task into sub-problems of lower complexity [2].

## THEORY

### MASS BALANCE EQUATIONS

$$\begin{cases} \dot{\mathbf{n}}_g(t) = \mathbf{W}_{m,g} \boldsymbol{\zeta}_m(t) + \mathbf{W}_{in,g} \mathbf{u}_{in,g}(t) - \omega_g(t) \mathbf{n}_g(t), & \mathbf{n}_g(0) = \mathbf{n}_{g0} \\ \dot{\mathbf{n}}_s(t) = \mathbf{N}_r^T \mathbf{r}(t) + \mathbf{N}_a^T \boldsymbol{\xi}_a(t) + \mathbf{W}_{m,s} \boldsymbol{\zeta}_m(t), & \mathbf{n}_s(0) = \mathbf{n}_{s0} \end{cases}, \quad \omega_g(t) = \frac{u_{out,g}(t)}{m_g(t)},$$

where  $\mathbf{n}_g$  and  $\mathbf{n}_s$  are numbers of moles in gas and solid phases,  $\boldsymbol{\zeta}_m$  are mass-transfer rates,  $\mathbf{u}_{in,g}$  and  $u_{out,g}$  are inlet and outlet flow rates of gas,  $m_g$  is the mass of gas,  $\boldsymbol{\xi}_a$  are adsorption/desorption flows and  $\mathbf{r}$  are rates of surface reaction.

### LINEAR TRANSFORMATION TO EXTENTS

Extents of mass transfer  $\mathbf{x}_{m,g}$ , inlet  $\mathbf{x}_{in,g}$  and initial conditions  $x_{ic,g}$  in phase G and extents of reaction  $\mathbf{x}_r$ , adsorption  $\mathbf{x}_a$  and mass transfer  $\mathbf{x}_{m,s}$  in phase S are given by

$$\begin{bmatrix} \mathbf{x}_{m,g}(t) \\ \mathbf{x}_{in,g}(t) \\ x_{ic,g}(t) \end{bmatrix} = \begin{bmatrix} \mathbf{M}_g \\ \mathbf{F}_g \\ \mathbf{i}_g^T \end{bmatrix} \mathbf{n}_g(t) = \begin{bmatrix} \mathbf{W}_{m,g} & \mathbf{W}_{in,g} & \mathbf{n}_{g0} \end{bmatrix}^+ \mathbf{n}_g(t),$$

$$\begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_a(t) \\ \mathbf{x}_{m,s}(t) \end{bmatrix} = \begin{bmatrix} \mathbf{R} \\ \mathbf{A} \\ \mathbf{M}_s \end{bmatrix} (\mathbf{n}_s(t) - \mathbf{n}_{s0}) = \begin{bmatrix} \mathbf{N}_r^T & \mathbf{N}_a^T & \mathbf{W}_{m,s} \end{bmatrix}^+ (\mathbf{n}_s(t) - \mathbf{n}_{s0}),$$

which results in

$$\begin{cases} \dot{\mathbf{n}}_g(t) = \mathbf{W}_{m,g} \mathbf{x}_{m,g}(t) + \mathbf{W}_{in,g} \mathbf{x}_{in,g}(t) + \mathbf{n}_{g0} x_{ic,g}(t) \\ \dot{\mathbf{n}}_s(t) = \mathbf{N}_r^T \mathbf{x}_r(t) + \mathbf{N}_a^T \mathbf{x}_a(t) + \mathbf{W}_{m,s} \mathbf{x}_{m,s}(t) + \mathbf{n}_{s0} \end{cases}.$$

### PRESENT WORK

For the analysis of surface catalytic reaction systems, it is important to separate the effects of transport phenomena, chemisorption and reactions. The Extent-based Model Identification has been extended to gas-solid (G-S) systems involving catalytic processes at the surface of solid catalysts. This procedure allows separating model identification and parameter estimation for the adsorption/desorption of each substrate/product and for each solid-phase reaction.

If  $\mathbf{u}_{in,g}(t)$  and  $\omega_g(t)$  are known,  $\mathbf{x}_r(t)$  and  $\mathbf{x}_a(t)$  can be computed as follows:

$$\begin{cases} \dot{\mathbf{x}}_{m,g}(t) = \mathbf{u}_{in,g}(t) - \omega_g(t) \mathbf{x}_{m,g}(t), & \mathbf{x}_{m,g}(0) = \mathbf{0}, & \dot{x}_{ic,g}(t) = -\omega_g(t) x_{ic,g}(t), & x_{ic,g}(0) = 1, \\ \mathbf{x}_{m,g}(t) = \mathbf{W}_{m,g}^+ (\mathbf{n}_g(t) - \mathbf{W}_{in,g} \mathbf{x}_{m,g}(t) - \mathbf{n}_{g0} x_{ic,g}(t)), & & \mathbf{x}_{m,s}(t) = \mathbf{x}_{m,g}(t) + \int_0^t \omega_g(\tau) \mathbf{x}_{m,g}(\tau) d\tau, \end{cases}$$

$$\begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_a(t) \end{bmatrix} = \begin{bmatrix} \mathbf{N}_r^T & \mathbf{N}_a^T \end{bmatrix}^+ (\mathbf{n}_s(t) - \mathbf{n}_{s0} - \mathbf{W}_{m,s} \mathbf{x}_{m,s}(t)).$$

### INCREMENTAL MODEL IDENTIFICATION

For the  $i$ th reaction, the following minimization problem is solved:

$$\begin{cases} \min_{\mathbf{k}_{r,i}} J_{r,i} = (\hat{\mathbf{x}}_{r,i} - \mathbf{x}_{r,i}(\mathbf{k}_{r,i}))^T \mathcal{W}_{r,i} (\hat{\mathbf{x}}_{r,i} - \mathbf{x}_{r,i}(\mathbf{k}_{r,i})), \\ \text{s.t. } \dot{\mathbf{x}}_{r,i}(t, \mathbf{k}_{r,i}) = r_i(\mathbf{n}_s(t), \mathbf{k}_{r,i}), & \mathbf{x}_{r,i}(0, \mathbf{k}_{r,i}) = \mathbf{0}, \end{cases}$$

where  $\hat{\mathbf{x}}_{r,i}$  and  $\mathbf{x}_{r,i}$  are computed and simulated extents of reaction at  $H$  time instants and  $\mathbf{k}_{r,i}$  are rate parameters.

For the  $j$ th adsorption/desorption process, the following problem is solved:

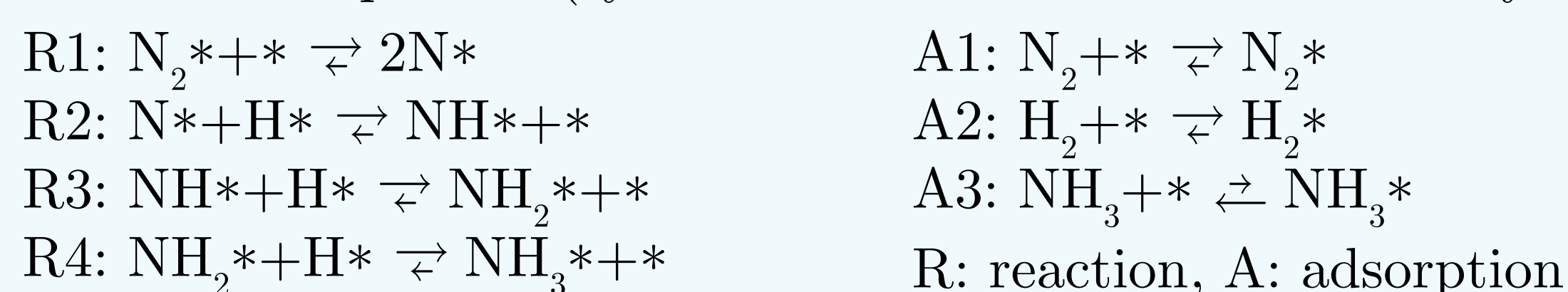
$$\begin{cases} \min_{\mathbf{k}_{a,j}} J_{a,j} = (\hat{\mathbf{x}}_{a,j} - \mathbf{x}_{a,j}(\mathbf{k}_{a,j}))^T \mathcal{W}_{a,j} (\hat{\mathbf{x}}_{a,j} - \mathbf{x}_{a,j}(\mathbf{k}_{a,j})), \\ \text{s.t. } \dot{\mathbf{x}}_{a,j}(t, \mathbf{k}_{a,j}) = \boldsymbol{\xi}_{a,j}(\mathbf{n}_s(t), \mathbf{k}_{a,j}), & \mathbf{x}_{a,j}(0, \mathbf{k}_{a,j}) = \mathbf{0}, \end{cases}$$

where  $\hat{\mathbf{x}}_{a,j}$  and  $\mathbf{x}_{a,j}$  are computed and simulated extents of adsorption at  $H$  time instants and  $\mathbf{k}_{a,j}$  are rate parameters.

## CASE STUDY

### SIMULATED SYSTEM

Haber-Bosch process (synthesis of ammonia with iron catalyst) in a CSTR:



Let  $\Omega = \{\text{N}_2^*, \text{H}_2^*, \text{NH}_3^*, \text{N}^*, \text{NH}^*, \text{NH}_2^*, *\}$  be the set of species at the catalyst surface and  $\Phi = \{\text{N}_2, \text{H}_2, \text{NH}_3\}$  the set of gas species just above the catalyst surface. Then,

$$\mathbf{c}_s(t) = \frac{\mathbf{n}_s(t)}{A}, \quad c_{tot} = \sum_{i \in \Omega} c_{s,i}(t), \quad \theta_{s,i}(t) = \frac{c_{s,i}(t)}{c_{tot}}, \quad i \in \Omega,$$

where the catalyst area  $A = 216 \text{ m}^2$  and  $c_{tot} = 5.1 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2}$  for this simulation [3].

### MEASUREMENTS

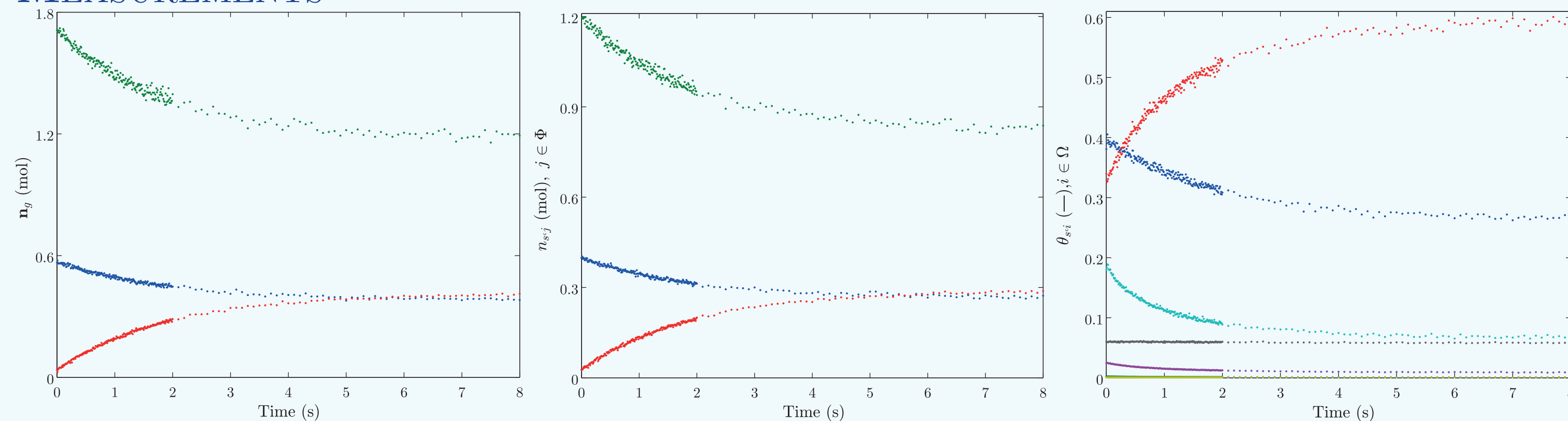


Figure 1 - Left: numbers of moles in the gas phase ( $\text{N}_2$ : blue;  $\text{H}_2$ : green;  $\text{NH}_3$ : red); Middle: numbers of moles of gas species just above the catalyst surface ( $\text{N}_2^*$ : blue;  $\text{H}_2^*$ : green;  $\text{NH}_3^*$ : red); Right: coverage of species at the catalyst surface ( $\text{N}_2^*$ : blue;  $\text{N}^*$ : green;  $\text{H}^*$ : red;  $\text{NH}^*$ : cyan;  $\text{NH}_2^*$ : violet;  $\text{NH}_3^*$ : yellow;  $*$ : black). Measurements with zero-mean Gaussian noise of standard deviation of 1% with respect to the maximum concentration of each species.

## REFERENCES

- [1] Bhatt et al., Ind. Eng. Chem. Res. 49 (2010), 7704.
- [2] Srinivasan et al., 1st IFAC Workshop on Thermodynamic Foundations of Mathematical Systems Theory, Lyon (2013).
- [3] Dumesic and Trevino, J. Catal. 116 (1989), 119.

### LINEAR TRANSFORMATION TO EXTENTS

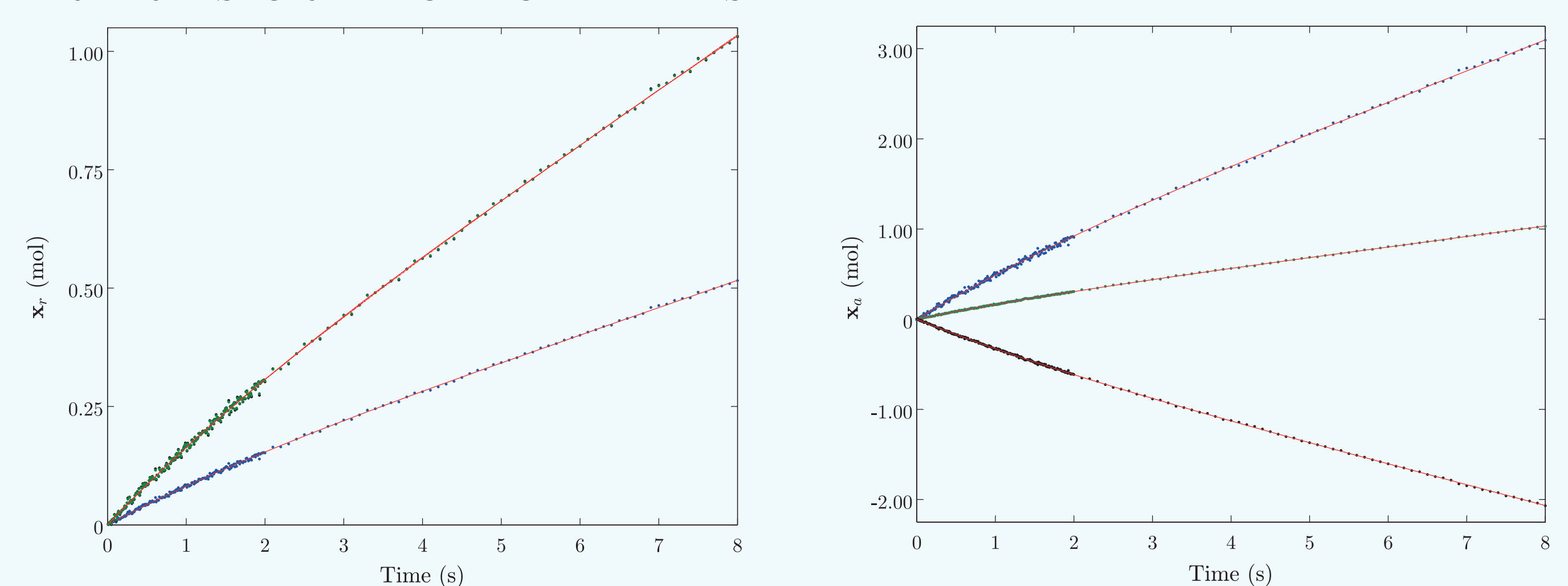


Figure 2 - Left: extents of reaction on the solid surface (R1: blue; R2-4: green); Right: extents of adsorption (A1: green; A2: blue; A3: black). Red lines represent extents simulated with estimated rate parameters.

### INCREMENTAL MODEL IDENTIFICATION

Table 1: Summary of the results of Incremental Model Identification (<sup>a</sup>:  $\text{mol}^{-1} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ; <sup>b</sup>:  $\text{mol}^{-2} \cdot \text{m}^{-4} \cdot \text{s}^{-1}$ ; <sup>c</sup>:  $\text{s}^{-1}$ ).

Step	Identified model	Parameter	True	Estimation CI (99%)
R1	$r_1 = A k_1 c_{s,\text{N}_2^*} c_{s,*}$	$k_1^{\text{a}}$	$1.380 \cdot 10^9$	$[1.376, 1.382] \cdot 10^9$
R2	$r_2 = A k_2 c_{s,\text{N}^*} c_{s,\text{H}^*}$	$k_2^{\text{a}}$	$9.900 \cdot 10^{10}$	$[9.864, 9.922] \cdot 10^{10}$
R3	$r_3 = A k_3 c_{s,\text{NH}^*} c_{s,\text{H}^*}$	$k_3^{\text{a}}$	$1.072 \cdot 10^9$	$[1.069, 1.074] \cdot 10^9$
R4	$r_4 = A k_4 c_{s,\text{NH}_2^*} c_{s,\text{H}^*}$	$k_4^{\text{a}}$	$8.000 \cdot 10^9$	$[7.991, 8.031] \cdot 10^9$
A1	$\xi_{a,1} = A k_{a,1} c_{s,\text{N}_2} c_{s,*}$	$k_{a,1}^{\text{a}}$	$1.480 \cdot 10^6$	$[1.478, 1.483] \cdot 10^6$
A2	$\xi_{a,2} = A k_{a,2} c_{s,\text{H}_2} (c_{s,*})^2$	$k_{a,2}^{\text{b}}$	$4.922 \cdot 10^{12}$	$[4.908, 4.936] \cdot 10^{12}$
A3	$\xi_{a,3} = -A k_{a,3} c_{s,\text{NH}_3^*}$	$k_{a,3}^{\text{c}}$	$6.100 \cdot 10^5$	$[6.090, 6.109] \cdot 10^5$

## CONCLUSIONS

- Rate models for reactions and adsorption/desorption processes were correctly identified and rate parameters were estimated within confidence interval.
- Fast catalytic systems require large amount of measurements.
- Perspectives: systems with higher number of intermediate species.