Exploiting the Underlying Relationships Between Apparent Kinetic Parameters and Surface Coverages

Fernando Vega-Ramon[1], Christopher Hardacre[1], Dongda Zhang[1]*

1 Department of Chemical Engineering, the University of Manchester, Engineering Building, Manchester M13 9PL, United Kingdom
Corresponding author: dongda.zhang@manchester.ac.uk
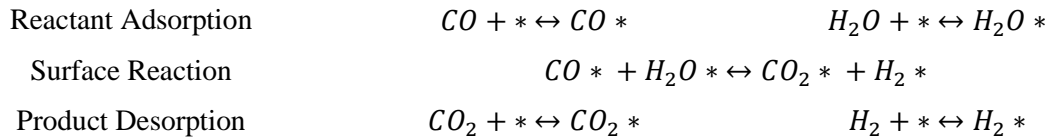
Highlights
- Analytical relationships between power law parameters and surface coverages are demonstrated.
- Parameter estimation framework was developed to infer microkinetic insight from gas-phase data.
- Model fitting, interpretability and thermodynamic consistency suggest validity of methodology.

1. Introduction

Microkinetic modelling techniques have been extensively proposed in literature to aid in the analysis of complex heterogeneous reactions. By considering all possible elementary steps and species, these can aid in the identification of kinetically significant pathways and intermediates. In sharp contrast, generalised power law models neglect the existence of surface intermediates, approximating the rate of reaction in terms of observable states (gas-phase concentrations) and some apparent kinetic parameters (reaction orders and activation energies) which are empirically fit from data. The question on whether it is plausible to mathematically "bridge" these two model structures has been previously examined in literature [1],[2]. In this work, this concept was further explored through the design of in-silico case studies, whereby a mechanism was adopted to construct a microkinetic model and to illustrate the derivation of analytical expressions linking surface coverages to apparent reaction parameters. A parameter estimation framework was then developed to test the validity of these relationships and the microkinetic insight that can be gained from their consideration.

2. Methodology

A simplified, 5-step WGSR reaction mechanism was adopted as the basis of the in-silico case studies. The Arrhenius parameters of the elementary steps were taken from previous work in literature [3], where UBI-QEP and transition state theory methods were used to determine activation energies and pre-exponential factors.

Reactant Adsorption	$CO + * \leftrightarrow CO*$	$H_2O + * \leftrightarrow H_2O*$
Surface Reaction	$CO* + H_2O* \leftrightarrow CO_2* + H_2*$	
Product Desorption	$CO_2 + * \leftrightarrow CO_2*$	$H_2 + * \leftrightarrow H_2*$

Upon parametrising the rate equations of the elementary steps (e.g. via mass-action law), three in-silico datasets were generated by simulating an ideal packed bed reactor under different temperatures (430 K, 440 K and 450 K). It must be highlighted that the generated data includes both gas-phase as well as surface composition profiles. Analytical expressions for the apparent reaction parameters were then developed by considering a rate-limiting step assumption (e.g. Langmuir-Hinshelwood kinetics) and the following logarithmic derivatives

$$r = \vec{r} - \overleftarrow{r} = \frac{k_3 K_1 K_2 P_{CO} P_{H_2O} - \frac{k_3^-}{K_4 K_5} P_{CO_2} P_{H_2}}{\left(1 + K_1 P_{CO} + K_2 P_{H_2O} + \frac{1}{K_4} P_{H_2} + \frac{1}{K_5} P_{CO_2}\right)^2}$$

$$\alpha_i = \left(\frac{\partial \ln \vec{r}}{\partial \ln P_i}\right)_T \qquad \beta_i = \left(\frac{\partial \ln \overleftarrow{r}}{\partial \ln P_i}\right)_T \qquad \overrightarrow{E_{A,app}} = -R \frac{\partial \ln \vec{r}}{\partial (1/T)} \qquad \overleftarrow{E_{A,app}} = -R \frac{\partial \ln \overleftarrow{r}}{\partial (1/T)}$$

Application of the above expressions leads to the result that apparent reaction orders and activation energies are linear combinations of the intermediate surface coverages. Thus, a parameter estimation methodology was designed to directly infer these coverages from the gas- phase in-silico trajectories. Both in-silico data generation and parameter estimation tasks were computationally implemented in *Python* programming language.

$$\min_{\theta,A} \sum_{i=1}^{N_p} (P_{i,E} - P_{i,m})^T \Lambda (P_{i,E} - P_{i,m})$$

$$\text{st.} \quad \frac{dP_{CO}}{d\tau} = A \exp\left(\frac{-\overrightarrow{E_{app}}}{RT}\right) \prod P_i^{\alpha_i} - A^- \exp\left(\frac{-(\overrightarrow{E_{A,app}} - \Delta H_{overall})}{RT}\right) \prod P_i^{\beta_i}$$

$$\alpha_{CO} = 1 - 2\theta_{CO} \qquad \alpha_{H_2O} = 1 - 2\theta_{H_2O} \qquad \alpha_{H_2} = -2\theta_{H_2} \qquad \alpha_{CO_2} = -2\theta_{CO_2}$$

$$\beta_{CO} = -2\theta_{CO} \qquad \beta_{H_2O} = -2\theta_{H_2O} \qquad \beta_{H_2} = 1 - 2\theta_{H_2} \qquad \beta_{CO_2} = 1 - 2\theta_{CO_2}$$

$$\overrightarrow{E_{A,app}} = \overrightarrow{E_{A,3}} + \Delta H_{R1} \cdot (1 - \theta_{CO}) + \Delta H_{R2} \cdot (1 - \theta_{H2O}) + \Delta H_{R4} \cdot \theta_{H_2} + \Delta H_{R5} \cdot \theta_{CO2}$$

3. Results and discussion

From the fitting results in Fig. 1, it appears that the lower-complexity power law model can well replicate the microkinetic model simulation, with a mean absolute percentage error below 2% across the three datasets.
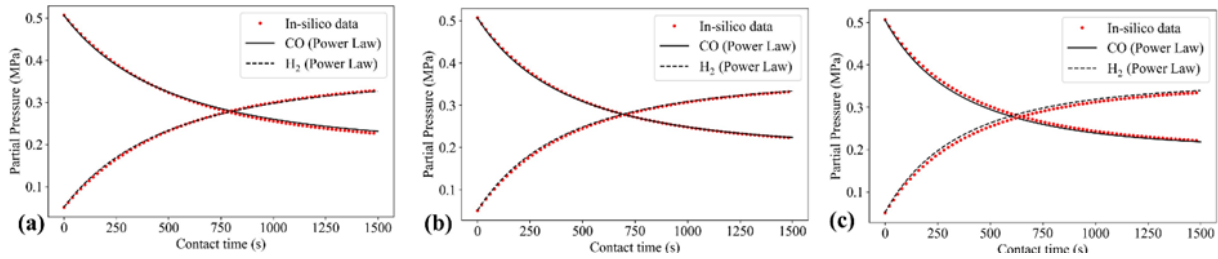

Figure 1. Power law model fitting results for synthetic data at (a) 430 K; (b) 440K; (c) 450K

More importantly, the estimated coverages give quantitative insight on the relative concentrations of surface intermediates. The coverages of molecularly adsorbed products were found to be negligible, whereas adsorbed H_2O is the most abundant species followed by CO. The parameter estimation framework can also provide insight on the effect of temperature on surface composition. In this case, the decreasing occupancy of adsorbed reactants with increasing temperature is well-captured, whereas the coverages of the adsorbed products remain relatively negligible throughout the whole temperature range. Coverages can also be fitted "dynamically", allowing them to change along the process trajectory; the retrieved parameters well-describe the evolution of surface occupancy in the in-silico datasets, with the coverage of H_2O decreasing sharply with conversion while the decrease in CO coverage was comparatively less substantial. These findings are in agreement with the in-silico surface coverage profiles generated by the "ground-truth" microkinetic model.

4. Conclusions

A kinetic modelling methodology incorporating varying degrees of abstraction was successfully applied to develop analytical relationships between surface intermediate concentrations and apparent reaction orders. The validity of these expressions was tested through the design of in-silico parameter estimation case studies. The results indicate that the proposed framework is robust, being able to retrieve microkinetic information under a variety of simulated temperatures and gas-phase compositions.

References

[1] Golodets, G. (1979) *Theor. Exp. Chem.,* 14(4), 367–373
[2] Kagawa, S. (1982) *React. Kinet. Catal. Lett.* 19(3–4), 285–288
[3] Callaghan, C. A. (2006) *PhD Thesis, Worcester Polytechnique Institute*

Keywords

Surface coverage; Reaction order; Parameter estimation; Power law