catalysts

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Supplementary Material

Analysis and Model-Based Description of the Total Process of Periodic Deactivation and Regeneration of a VO_x Catalyst for Selective Dehydrogenation of Propane

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A) Kinetic Investigation of the Reaction Network

Table S1. Optimized kinetic parameters for the reaction network of the dehydrogenation of propane.

Parameter	Opt. Value	95% Confidence Intervals	Unit
A_1	−11.002	±2.9%	-
A_2	−12.551	±1.2%	-
A_3	−10.390	±2.7%	-
A_4	−9.012	±2.7%	-
B_1	15.976	±19.5%	-
B_2	13.456	±2.0%	-
B_3	11.667	±6.6%	-
B_4	11.777	±4.4%	-
a_1	0.500	±14.4%	-
a_2	1.130	±1.7%	-
a_3	0.814	±10.8%	-
a_4	0.725	±8.9%	-
b_2	1.051×10^{-4}	±6954%	-
b_3	0.212	±11.7%	-
b_4	0.170	±10.6%	-

Table S2. Preexponential factors and activation energies for the reaction network of the dehydrogenation of propane derived from the optimized parameters (Table S1).

Parameter	Opt. Value	Unit
$k_{0,1}$	2.151	$mol\ kg^{-1}\ s^{-1}\ Pa^{-a_5}$
$k_{0,2}$	0.044	$mol\ kg^{-1} s^{-1}\ Pa^{-(a_1+b_1)}$
$k_{0,3}$	0.064	$mol\ kg^{-1} s^{-1}\ Pa^{-(a_2+b_2)}$
$k_{0,4}$	0.283	$mol\ kg^{-1} s^{-1}\ Pa^{-(a_3+b_3)}$
$E_{A,1}$	94976	$J\ mol^{-1}$
$E_{A,2}$	80908	$J\ mol^{-1}$
$E_{A,3}$	70147	$J\ mol^{-1}$
$E_{A,4}$	70813	$J\ mol^{-1}$

B) – C) Catalyst Deactivation/ Regeneration

Akaike Information Criterion

Since models can only try to approximate the effects measured in experimental data, a reliable methodology for model selection is desirable [1]. A well-known tool for model selection and statistical inference is the coefficient of determination R^2, which is known to be inadequate for nonlinear problems but still widely used in scientific literature [2]. An alternative way for model discrimination introduced by Akaike is the Akaike Information Criterion (AIC), that is based on information theory [3]:

$$AIC = 2p - 2ln\,(L) \tag{S1}$$

This criterion includes the number of parameters of the tested model p and the numerical value of the log-likelihood at its maximum point $ln\,(L)$. This value can be calculated in the case of a nonlinear fit with normally distributed errors with the help of the residuals from the nonlinear least-squares fit RSS_{opt} and their number n [1].

$$ln(L) = 0.5\left(-n\left(\ln(2\pi) + 1 - \ln(n) + \ln\sum_{i=1}^{n} RSS_{opt}\right)\right) \tag{S2}$$

In application the AIC is computed for every candidate model and the one with the smallest value is chosen. This model is supposed to be closest to the unknown reality that generated the measured data. Since the number of parameters is included, this criterion does not favor models with numerous parameters that offer only a slight increase in precision. It has to be noted, that not the absolute value but rather the differences in AIC values among the candidate models is important. If the candidate set does not include a sufficient model also a low AIC value does not guarantee a good fit of the measured data [1].

For an easier comparison, a so called Akaike weight of model i can be calculated [1,2](equation S3)

$$w_i(AIC) = \frac{e^{-0.5\cdot\Delta_i(AIC)}}{\sum_k^K e^{-0.5\cdot\Delta_k(AIC)}} \tag{S3}$$

$\Delta_i(AIC)$ describes the difference between model i and the model with the lowest AIC value, while K represents the overall number of the models compared. These values can be interpreted as the weight of evidence for the respective model. This procedure normalizes the values in a way that the sum of w_i gives 1, and thus makes the results easier to interpret.

The model discrimination in this contribution is based on the Akaike weights w_i of the respective model i.

Bootstrapping

For estimating the confidence intervals of the estimated parameters of the deactivation and the regeneration kinetics, a bootstrapping algorithm has been used. Bootstrap methods describe resampling algorithms [4,5]. The fundamental idea is, that all information about an underlying population is contained in an observed sample. Statistics about the underlying population can hence be simulated by using random samples from the original sample. Different methods of resampling are possible. The resampling method used in this contribution is semi-parametric resampling [6]. It involves random resampling of the residuals r of a parametric model with the responses $y = (y_1, \dots, y_n)$. A general representation of the model is given in equation S4:

$$y = g(\theta) + r \tag{S4}$$

Fitting of the model gives the estimate $\hat{\theta}$ of the parameters θ and a set of residuals $r_i, i \in \{1, \dots, n\}$. The resampling algorithm is as follows.

1. Sample with replacement from the residuals r. The new set of residuals is called bootstrap errors $r^* = (r_1^*, \dots, r_n^*)$.
2. Generate a bootstrap data set y^* by adding the bootstrap errors to the model values (equation S5):

$$y^* = g(\hat{\theta}) + r^* \tag{S5}$$

3. Fit the model using the estimated optimal parameters $\hat{\theta}$ and the bootstrap data set y^* (equation S6) to obtain a bootstrap estimate $\hat{\theta}^*$:

$$y^* = g(\theta) \tag{S6}$$

4. Repeat Steps 1 – 3 for $B = 1500$ times to obtain the bootstrap distribution of the estimated parameter.

Based on this parameter distribution the confidence intervals of the estimated parameters can be calculated [7]. A non-studentized pivotal method is used [6,8]. This method argues that the behavior of the distribution $W = \hat{\theta} - \theta$ is mirrored by the behavior of $W^* = \hat{\theta}^* - \hat{\theta}$. For a known distribution W it would be possible to find a quantile $w_{\frac{\alpha}{2}}$ such that $P\left(W \leq w_{\frac{\alpha}{2}}\right) = \frac{\alpha}{2}$. A two sided $1 - \alpha$ confidence interval would be

$$\left(\hat{\theta} - w_{\frac{\alpha}{2}}, \hat{\theta} + w_{1-\frac{\alpha}{2}}\right) \tag{S7}$$

Since the "true distribution" W is not known the quantiles $w_{\frac{\alpha}{2}}$ and $w_{1-\frac{\alpha}{2}}$ are replaced by the approximate quantiles $w_{\frac{\alpha}{2}}^*$ and $w_{1-\frac{\alpha}{2}}^*$ from the bootstrap distribution W^*:

$$\left(\hat{\theta}^* - w_{\frac{\alpha}{2}}, \hat{\theta}^* + w_{1-\frac{\alpha}{2}}\right) \tag{S8}$$

In this contribution the 95% confidence intervals have been calculated ($\alpha = 0.05$). An advantage of bootstrapping methods is their simplicity, which allow to adapt them for a wide range of applications. The major disadvantage is that the methods are generally computationally costly. Alternative methods to calculate confidence intervals analytically may be more efficient, such as the nlparci[1] function implemented in MATLAB®. This function deploys the Jacobian, given by the lsqnonlin[2] function that has been used for fitting the models in this contribution (Levenberg-Marquardt algorithm). Problems arise, when the Jacobian is not invertible[3].

Since bootstrapping algorithms are more robust they have been chosen in this study. Nevertheless, the results of the nlparci function can be used for verification of confidence intervals estimated by bootstrapping. Table S3 summarizes the confidence intervals estimated by both methods for the kinetic parameter of the deactivation of the VO_x catalyst with propene. The confidence intervals estimated with the different methods are in good agreement, which proofs the applicability and validity of the applied methodology for this problem.

[1] See https://de.mathworks.com/help/stats/nlparci.html for further information

[2] See https://de.mathworks.com/help/optim/ug/lsqnonlin.html for further information

[3] A non-invertible Jacobian might be singular or singular to working precision. nlparci deploys QR decomposition to the Jacobian. For a non-invertible Jacobian this results in R being not a full upper triangle matrix which can therefore not be inverted.

Table S3. Optimized parameters of model C5 to describe the coking behavior of the VO_x catalyst using propene.

Parameter	Opt. Value	Confidence Intervals			Unit
		nlparci	bootstrapping		
c_{max}	17.695	$\pm 1.61\%$	-1.54%	$+1.35\%$	$\% \left(\frac{\mathrm{kg_{coke}}}{\mathrm{kg_{cat}}} \times 100\right)$
α	0.275	$\pm 1.94\%$	-2.05%	$+1.55\%$	-
k_0	9.59×10^5	$\pm 34.44\%$	-29.71%	$+33.72\%$	$(\mathrm{kg_{coke}kg_{cat}^{-1}min^{-1}})^{1-h}$
E_A	139022	$\pm 1.78\%$	-1.92%	$+1.35\%$	$\mathrm{J\ mol^{-1}}$
h	1.106	$\pm 2.32\%$	-2.79%	$+1.47\%$	-
k_{des}	3.22×10^{-3}	$\pm 3.24\%$	-2.24%	$+4.09\%$	$\mathrm{min^{-1}}$
c_0	5.994	$\pm 5.21\%$	-4.47%	$+5.17\%$	$\% \left(\frac{\mathrm{kg_{coke}}}{\mathrm{kg_{cat}}} \times 100\right)$

It has to be noted, that there are other methods for estimating confidence intervals via bootstrapping which are described in literature [9].

As an example, the distribution of the bootstrap parameters $\hat{\theta}^*$ together with the optimal parameter $\hat{\theta}$ and the estimated confidence intervals are illustrated in Figure S1. The numbers in the bins of the histograms in Figure S1 have been normalized by dividing them by $B = 1500$ to get the frequencies, that are easier to interpret. The optimal parameters are also listed in Table 8.

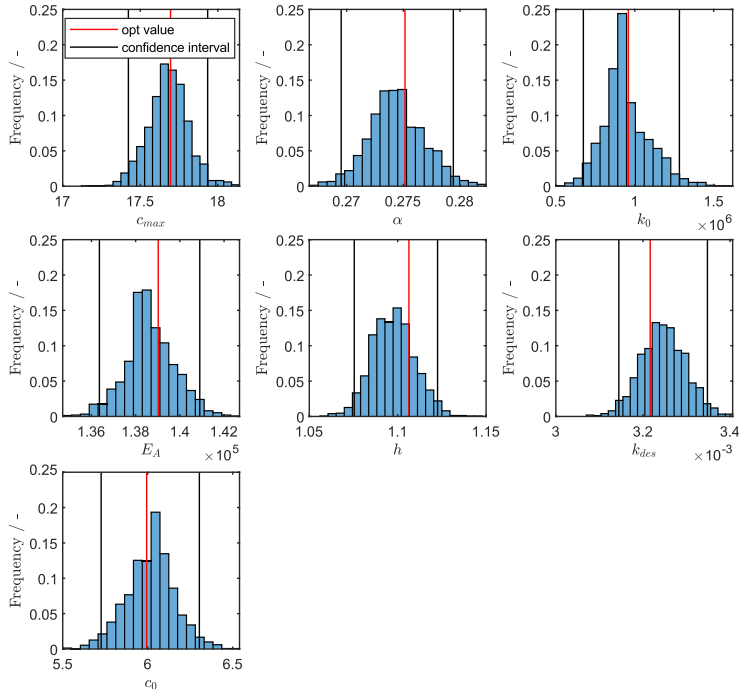

Figure S1. Histograms of the distribution of the parameters of the bootstrapping process of model (C5) of the deactivation of the VO_x catalyst with propene.

D) Periodic Experiments and Validation

The diagrams in Figure S2 and Figure S3 illustrate the results of the periodic experiments 2) and 3) described in section "Results and Discussion - Periodic Experiments and Validation". The experimental conditions are summarized in Table 15. Periodic experiment 1) is illustrated in Figure 15.

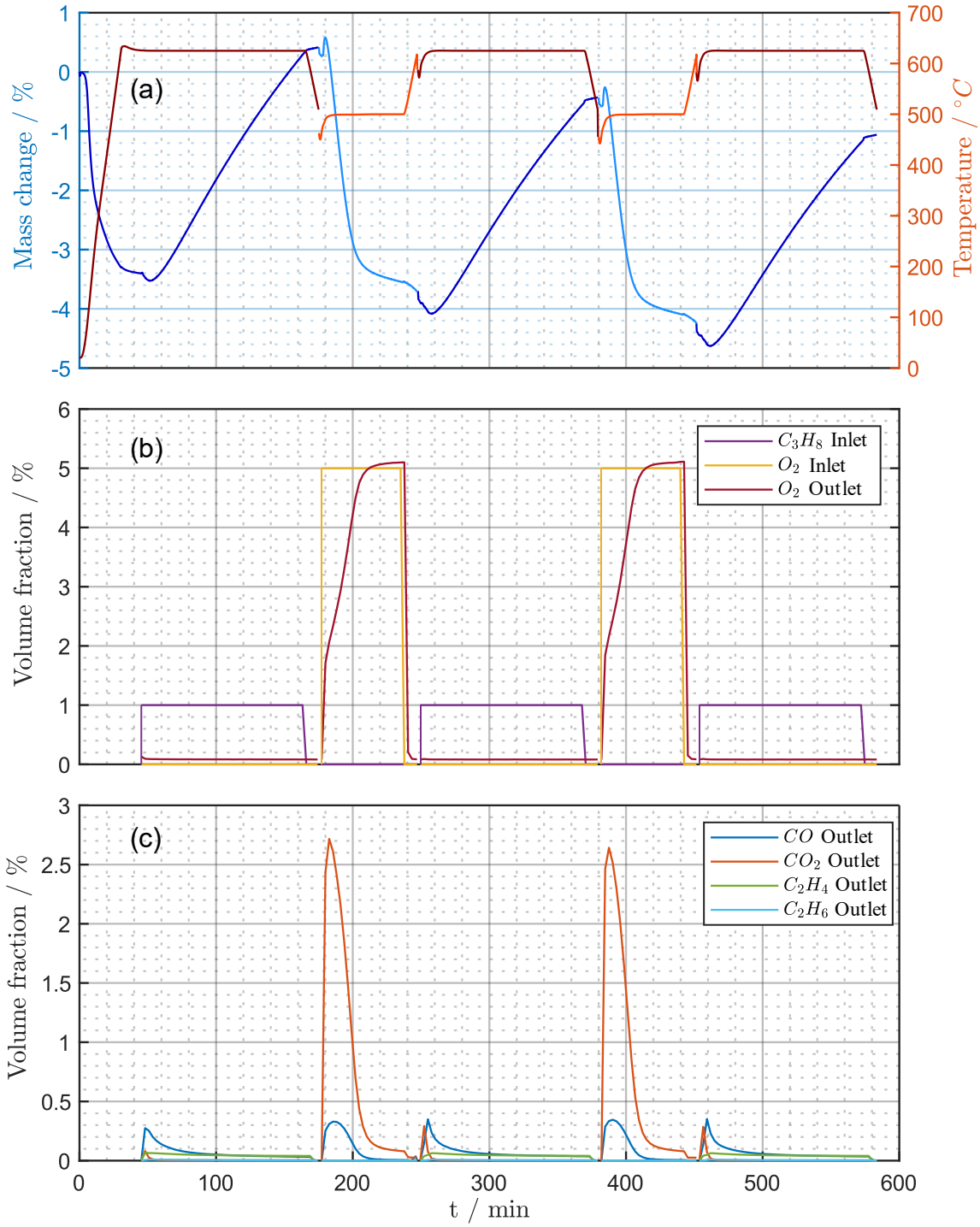

Figure S2. Measurements during periodic experiments: (a) mass changes (TGA) and temperature, (b) oxygen and propane concentrations, (c) CO, CO_2, ethene and ethane concentrations for periodic experiment (2).

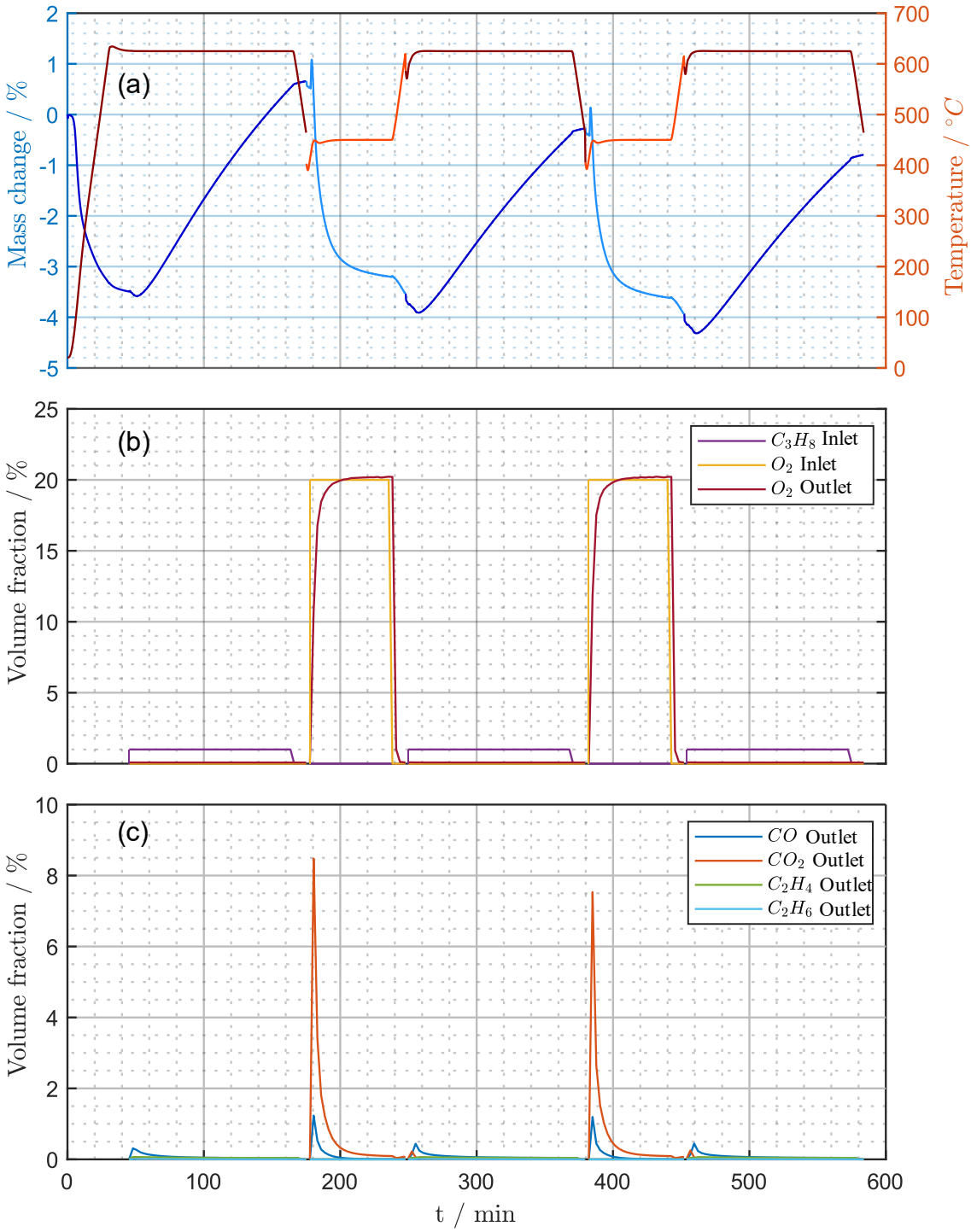

Figure S3 Measurements during periodic experiments: (a) mass changes (TGA) and temperature, (b) oxygen and propane concentrations, (c) CO, CO_2, ethene and ethane concentrations for periodic experiment (3).

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