A model-based experimental design study for the development of kinetic models of methanol oxidation on silver catalyst

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Abstract

Partial oxidation of methanol to formaldehyde on silver catalyst represents an important industrial process due to the versatility of formaldehyde as an intermediate in chemical synthesis. The development of kinetic models is essential for a quantitative description of the concentration of the chemical species involved in the process as well as for process design and optimisation purposes. However, the development and identification of reliable kinetic models is strictly related to the execution of informative experiments, allowing for the elucidation of the complex reaction pathways involved in the oxidation process and providing a precise estimation of the kinetic parameters for each model proposed in the study. In this paper a model-based design of experiments (MBDoE) approach is used for planning optimally informative experiments for the development of kinetic models of methanol oxidation on silver catalyst. Experiments are carried out in microreactor platforms where better reaction temperature control, accelerated heat and mass transfer and enhanced mixing of reactants can be achieved.

Keywords

Model-based design of experiments, kinetic modeling, microreactor technology.

1. Background

The partial oxidation of methanol to formaldehyde on silver catalyst represents an important industrial reaction due to the versatile role of formaldehyde as an intermediate in chemical synthesis. Throughout the years numerous research efforts have been devoted into this reaction system to understand the catalytic behavior of silver and the possible reaction mechanisms occurring at the surface [1,2]. A microkinetic model of methanol oxidation on silver, based on a Langmuir-Hinshelwood mechanism, has been recently proposed [3]. The model successfully explains both surface science experiments and kinetic experiments at industrial conditions applying physically realistic parameters. However, a simplification of the original model was required in order to be applied for reactor engineering purposes [4], given the high number of kinetic parameters and the complexity of the rate expressions. The accurate quantitative description of the concentration of the chemical species involved in the process is related to the availability of *i*) a reliable kinetic mechanism, defining the mathematical structure of the kinetic model; *ii*) the precise estimation of the set of kinetic parameters for the model. Model-based design of experiments (MBDoE) techniques can be used for discriminating among possible rival kinetic mechanisms [5] and/or for improving parameter estimation precision [6], avoiding non-informative regions of the experimental design space. The model identification problem is treated as an optimal control problem where the best operating conditions in terms of manipulated inputs and sampling scheduling are detected also taking into account limitations (constraints) on the experimental facilities.
In this study, MBDoE techniques are used for the identification of kinetic models of methanol oxidation on silver providing: *i*) a discrimination of candidate kinetic models from experimental data; *ii*) a quantitative approach for ranking of the experiments based on the evaluation of Fisher information matrix (FIM), underlining the most informative experimental conditions to be used in the experimentation. The methanol oxidation reaction is carried out in a microstructured reactor fabricated in silicon by etching and where Ag catalyst was deposited by sputtering [7]. Microfluidic devices represent the ideal platforms for the identification of kinetic models [8], allowing for a better temperature control, accelerating heat and

mass transfer and ensuring an excellent mixing of the reactants. Furthermore, they enable online measurement acquisition and easy control of the process for a quick and stable generation of process data to be used for model development.

2. Methods

2.1 Reaction mechanisms

In the identification study the simplified model proposed by Andreasen [4] was used as a reference model (Model 1) and two additional simplified kinetic models of increasing level of complexity (Model 2, Model 3) were considered. The set of reactions involved in the proposed models are shown in Table 1. According to Model 1, reactions (1) and (2) constitute the base (global) mechanism. Model 2 includes (1,2) and the combustion reactions for both CH_3OH and CH_2O as given by reactions (3) and (4) respectively. Model 3 includes the combustion reactions (3,4) for CH_3OH and CH_2O (like Model 2) but the global methanol oxidation reaction (1) used in Model 1 and 2 was split into a dehydrogenation step (5) and a selective oxidation step (6) assuming a power-law model for the kinetic expressions.

Table 1 Set of reactions involved in the proposed kinetic models.

Reactions	Model 1	Model 2	Model 3
$CH_3OH + 1/4O_2 = CH_2O + 1/2H_2 + 1/2H_2O$ (1)	√	√	-
$CH_2O + 1/2O_2 = H_2 + CO_2$ (2)	√	√	√
$CH_3OH + 3/2O_2 = 2H_2O + CO_2$ (3)	-	√	√
$CH_2O + O_2 = H_2O + CO_2$ (4)	-	√	√
$CH_3OH = CH_2O + H_2$ (5)	-	-	√
$CH_3OH + 1/2O_2 = CH_2O + H_2O$ (6)	-	-	√
$H_2 + 1/2O_2 = H_2O$ (7)	√	√	√
Number of kinetic parameters (N_θ)	6	10	12

Hydrogen oxidation reaction (7) has also been included in each reaction mechanism. Although this reaction is known to occur only at higher temperatures [8], it has been primarily considered to represent the low hydrogen concentrations observed in the experiments. The reaction rate expressions for reactions (1,2) are the one proposed in [4], while power law kinetic expressions have been used for the other reactions involved in the proposed mechanisms.

2.2 Optimal design of experiments: mathematical formulation

The microstructured reactor was modelled in the gPROMS environment [9] as a plug flow reactor (PFR):

$$\frac{1}{\tau}\frac{\partial c_i}{dz} = -\sum_{j=1}^{N^{reaz}} \nu_{ij} r_j \qquad (8)$$

where c_i is the species concentration, r_j and v_{ij} are the reaction rate and the stoichiometric coefficient of the *i*-th species in the *j*-th reaction respectively, while τ is the residence time. Equations (8), together with the reaction rate expressions, represent a system of partial differential equations (PDEs) which can be written in the general form as:

$$\mathbf{f}\left(\dot{\mathbf{x}}(z), \mathbf{x}(z), \mathbf{u}, \boldsymbol{\theta}, z\right) = 0 \qquad \hat{\mathbf{y}}(z) = \mathbf{g}\left(\mathbf{x}(z)\right) \qquad (9,10)$$

with the set of boundary (initial) conditions $\mathbf{x}(0) = \mathbf{x}_0$, where $\mathbf{x}(z)$ and $\dot{\mathbf{x}}(z)$ are the N_x-dimensional vectors of space-dependant state variables (here the concentrations c_i) and spatial derivatives respectively, $\mathbf{u}$ are the manipulated (input) variables (of dimensions N_u), $\boldsymbol{\theta}$ is the N_θ-dimensional set of unknown model parameters to be estimated, and z is the axial coordinate. The symbol ^ is used to indicate the estimate of a variable (or of a set of variables): thus, $\mathbf{y}(z)$ is the vector of measured values of the outputs, while $\hat{\mathbf{y}}$ is

the vector of the corresponding values estimated by the model. MBDoE techniques aim at decreasing the model parameter uncertainty region predicted by model as the solution of the optimisation problem:

$$\boldsymbol{\varphi}^{\text{opt}} = \arg\min_{\boldsymbol{\varphi}\in D}\left\{\psi\left[\mathbf{V}_\theta(\boldsymbol{\theta},\boldsymbol{\varphi})\right]\right\} = \arg\min_{\boldsymbol{\varphi}\in D}\left\{\psi\left[\mathbf{H}_\theta^{-1}(\boldsymbol{\theta},\boldsymbol{\varphi})\right]\right\} \tag{11}$$

subject to (9,10) and to a n_φ-dimensional set of constraints on design variables, usually expressed as:

$$\varphi_i^l \le \varphi_i \le \varphi_i^u \qquad i = 1 \ldots n_\varphi \tag{12}$$

with lower (superscript *l*) and upper (superscript *u*) bounds on the elements of $\boldsymbol{\varphi}$, defining the design space *D* (i.e. the operating range of experimental decision variables). The design optimisation (11) is carried out by acting on the n_φ-dimensional experiment design vector $\boldsymbol{\varphi}$:

$$\boldsymbol{\varphi} = \left[\mathbf{y}_0, \mathbf{u}(t)\right]^{\mathrm{T}} \tag{13}$$

which includes the N_y-dimensional set of initial conditions $\mathbf{y}_0$ on the measured variables and the manipulated inputs $\mathbf{u}$ (which may be also approximated by discrete piecewise constant or piecewise linear functions in the spatial domain). In (11) $\mathbf{V}_\theta$ and $\mathbf{H}_\theta$ are the variance-covariance matrix of model parameters and the Fisher information matrix (FIM), respectively, where $\mathbf{H}_\theta$ is defined by

$$\mathbf{H}_\theta(\boldsymbol{\theta},\boldsymbol{\varphi}) = \mathbf{H}_\theta^0 + \sum_{k=1}^{N_{\text{exp}}}\sum_{i=1}^{N_y}\sum_{j=1}^{N_y} s_{ij}\left[\frac{\partial\hat{y}_i(z_k)}{\partial\theta_l}\frac{\partial\hat{y}_j(z_k)^T}{\partial\theta_m}\right]_{l,m=1\ldots N_\theta} \tag{14}$$

In (14) s_{ij} is the *ij*-th element of the $N_y \times N_y$ inverse matrix of measurements error and $\mathbf{H}_\theta^0$ is the prior information matrix, taking into account the preliminary statistical information about the parametric system before the N_{exp} trials are carried out. According to (11), the experiment is designed so as to minimise a measurement function ψ of $\mathbf{V}_\theta$. The particular form of the measurement function represents the design criterion selected in order to maximise the expected information content of the experiment as predicted by the model. The most common design criteria are the so-called alphabetical ones, i.e. A-, D-, E-optimal criteria (minimising the trace, the determinant and the maximum eigenvalue of $\mathbf{V}_\theta$ respectively [10]), or they are based on singular values decomposition [11].

2.3 Ranking of experiments based on information evaluation

In order to evaluate the relative amount of information which can be obtained for the estimation of the *M*-th model parameters from the *i*-th experiment the following RFI (Relative Fisher Information) index can be computed:

$$RFI_{ij} = \frac{\left\|\mathbf{H}_{ij}\right\|}{\sum_{i=1}^{N_{\text{exp}}}\left\|\mathbf{H}_{ij}\right\|} = \frac{\left\|\mathbf{H}_{ij}\right\|}{\mathbf{H}_j} \tag{15}$$

where $\mathbf{H}_i^M$ is the FIM related to the *i*-th experiment for the *M*-th competitive model evaluated from (14) and $\mathbf{H}^M$ is the global information obtained from the N_{exp} experiments for the identification of the *M*-th model according to a norm $\|\ .\ \|$. In this study, the Frobenius norm has been used as a suitable matrix norm. The utility of (15) is that it allows for a ranking of the available (already executed) experiments, underlining the most informative regions of the design space *D* to be exploited for model identification. A generalised A-optimal design can be defined as

$$\boldsymbol{\varphi}^{\text{opt}} = \arg\max_{\boldsymbol{\varphi}\in D}\left\{tr\left(\sum_{i=1}^{N_{\text{exp}}}\sum_{j=1}^{N_M}\mathbf{H}_{ij}\right)\right\}. \tag{16}$$

The interesting feature of (16) is that it allows for the simultaneous maximisation of the information content of a number of experiments for a set of N_M candidate models.

2.4 Available experimental data set and model discrimination

In this case study the elements of the design vector $\boldsymbol{\varphi}$ (13) which can be optimised by MBDoE are:

1. Composition of reactants in terms of molar fractions: methanol (0.07-0.16), oxygen (0.03-0.10) and water (0.02-0.22) modelled as initial conditions $\mathbf{y}_0$;
2. Temperature T (725 K < T < 825 K) modelled as manipulated input **u**;
3. Pressure P (159000-165000 Pa) modelled as manipulated input **u**;
4. Flowrate F (25-27 mL/min) modelled as manipulated input **u**.

The ranges of operability shown in parenthesis in the above represent the currently investigated design space D, where P and F have been basically kept constant during the trials. Concentration measurements are available as molar fractions of CH_3OH, O_2, CH_2O, H_2, H_2O and CO_2 at the inlet and outlet of the reactor and they are assumed to be corrupted by Gaussian noise with zero mean and a standard deviation of 1% on the reading. Preliminary data from N_{exp}= 21 experiments from the microreactor system were available in order to discriminate among the rival models (Model 1, Model 2 and Model 3) where the effect of temperature (T) and feed composition (CH_3OH, O_2 and H_2O molar fraction $\mathbf{y}^0$) on final products (CH_3OH, O_2, H_2O, CH_2O, H_2, CO_2) was investigated:

1. Experiments E1-5: T varied from 725 to 826 K (y^{CH3OH}=0.10, y^{O2}=0.04, y^{H2O}=0.07);
2. Experiments E6-9: T varied from 725 to 826 K (y^{CH3OH}=0.15, y^{O2}=0.06, y^{H2O}=0.11);
3. Experiments E10-21: T kept at 733 K, variable y^{CH3OH} (range 0.07-0.14, E10 to E14), y^{O2} (range 0.03-0.10, E15 to E17) and y^{H2O} (range 0.02-0.21, E18 to E21).

In all these performed experiments He was used as an inert, the volumetric flow rate was kept at F = 26.5 mL/min and the pressure at P = 1.6 atm. The reaction channel length containing the catalyst was 12.5 mm long and 0.12 mm high.

Model discrimination was carried out from experimental data by assessing the lack-of-fit for each proposed model in terms of χ^2 obtained after parameter estimation is carried out. The Akaike information criterion (AIC) in the form

$$\mathrm{AIC} = 2N_\theta - 2\ln\chi^2 \tag{17}$$

was also used to investigate the trade-off between fitting capability (χ^2) and model complexity in terms of number of model parameters (N_θ).

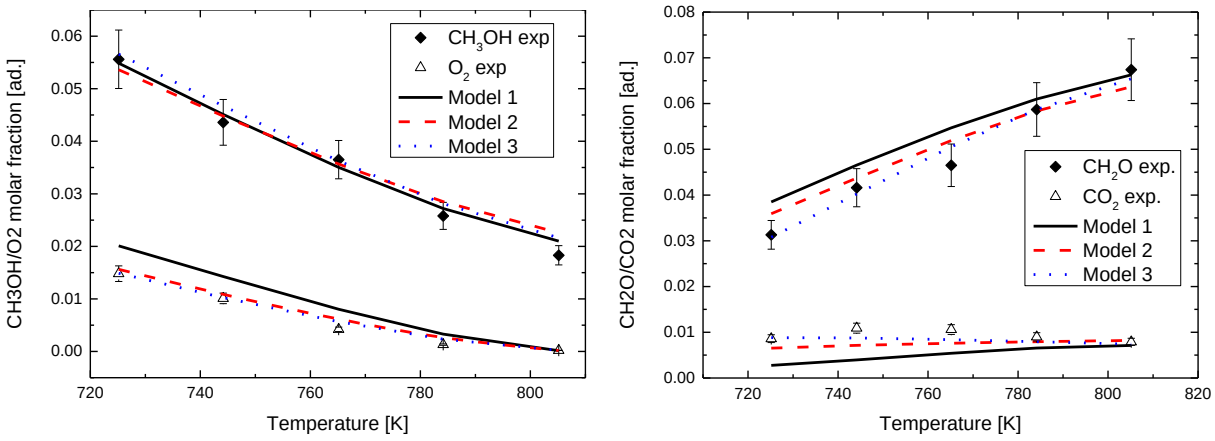
Results and discussion

Results after model discrimination are shown in Table 2. Model 3 is the one providing the most satisfactory results when using the lack-of-fit criteria, underlined by the lower χ^2. However, it also represents the most complex model in terms of number of model parameters, as clearly indicated by the relatively high *AIC* value, which tends to promote the use of Model 1 (the simplest model).

Table 2 Results from model discrimination for Model 1, 2 and 3.

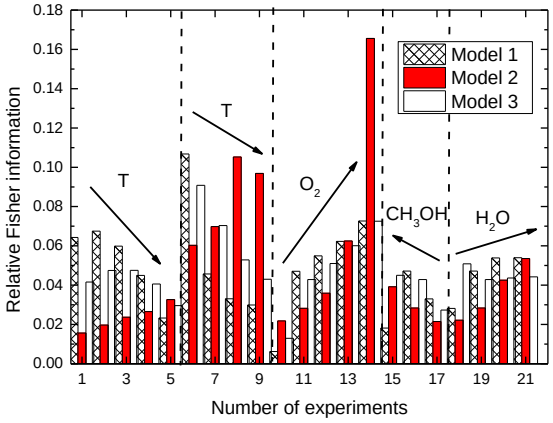
Model	χ^2	N_θ	***AIC***
Model 1	9762	6	-6.4
Model 2	7721	10	2.1
Model 3	6874	12	6.3

However, the superiority of Model 3 becomes apparent from the results shown in Figure 1, where molar fraction profiles predicted by the models are shown as a function of temperature. Model 1 (solid line) is ineffective on representing oxygen (Figure 1a) but also formaldehyde and CO_2 concentrations (Figure 1b) in a reliable way, while methanol profiles are always represented in a satisfactory way by all the proposed models. Interestingly, the representation of both oxygen and methanol concentration as a function of the investigated temperature was significantly improved by including the combustion reactions in the model formulation (Model 2 and 3) as compared to the original model formulation (Model 1). Furthermore, it is clear that a better representation of both CO_2 and CH_2O can be realised if competitive dehydrogenation and selective oxidation steps are included (Model 3). The possible explanation is that Model 3 in this case provides a better approximation of the complex kinetic mechanism occurring at the catalyst surface, where methoxide is formed as an intermediate [1].

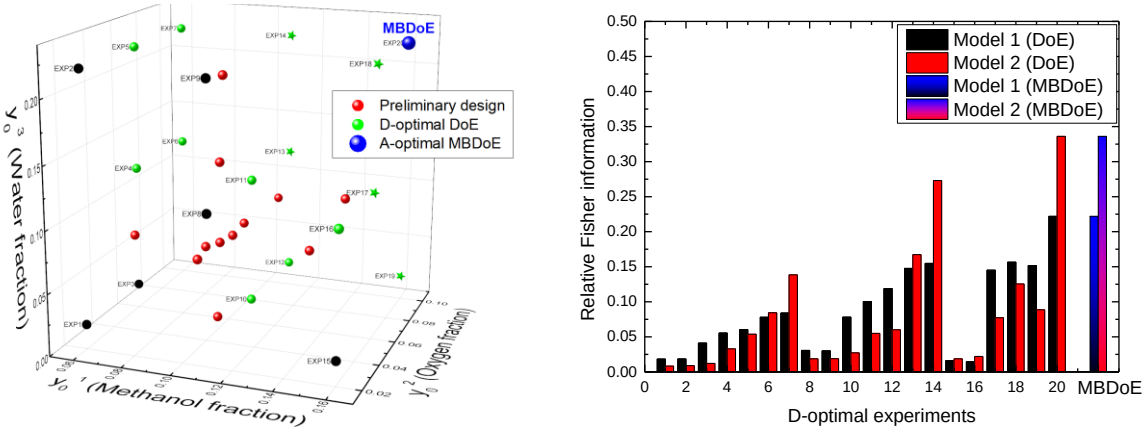


(a) (b)

Figure 1. Relative performance of candidate kinetic models after model identification in terms of molar fractions. (a) CH_3OH, O_2 molar fractions; (b) CH2O, CO2 molar fractions. The experimental points are indicated by symbols including error bars.



(a)



(b) (c)

Figure 2. Ranking of experiments in terms of RFI. (a) Preliminary experiments: ranking of information for Model 1, 2 and 3. (b) D-optimally designed experiments (green spheres), MBDoE optimally designed experiment (blue sphere) and preliminary experiments (red spheres) in terms of $\mathbf{y}_0$ (T = 800K). Experiments with low information are indicated by black spheres, experiments with high information are indicated by green stars. The optimally designed experiment is indicated by the blue sphere. (c) Ranking of experiments designed by DoE and MBDoE.

The availability of the models thus identified from the experimental data allows the definition of the best experimental conditions to be used in order to estimate the model parameters with the greatest precision. An example is given in Figure 2a, where relative Fisher Information (RFI) is evaluated for a ranking of the preliminary experiments (E1-E21). Each proposed model shows a different response in terms of RFI to a change in experimental conditions. In particular:

1. an increment in temperature would be beneficial for Model 2, but would be unhelpful for the estimation of Model 1 and Model 3 kinetic parameters;
2. an increment on oxygen concentration is beneficial for the identification of all the proposed models;
3. an increase in methanol concentration is beneficial for the identification of Model 2 and 3, while a maximum in the information level is realised for Model 1;
4. an increment in water concentration increase the information for Model 1 and 2, while does not really affect Model 3 information.

A screening of the design space *D* allows to identify the most significant experimental regions to be investigated for the identification of a given model. In Figure 2b the preliminary design (E1-E21) points are indicated by red spheres and compared to points generated by a D-optimal design (DoE, green/black spheres and green stars) and by a model-based design of experiments (MBDoE, blue sphere). DoE is based on a quadratic regression model, while MBDoE is based on the proposed detailed kinetic models as a result of the optimisation (16). Figure 2c shows the most informative experimental regions, identified by the highest values of RFI. The optimal experimental settings dictated by MBDoE are:

- T = 800 K, P = 165000 Pa, F = 26 mL/min;
- methanol, oxygen and water initial molar fractions: $\mathbf{y}^0 = [0.16 \quad 0.10 \quad 0.22]^T$.

Highly informative experiments are always characterised by high CH_3OH, O_2 and H_2O concentrations (blue sphere and green stars in Figure 2b), while experiments at low methanol concentration in the feed should always be avoided (black spheres), as they would provide a very limited amount of information.

Conclusions

A discrimination of simplified kinetic models of methanol oxidation on silver has been carried out, underlining a better representation of experimental results when dehydrogenation and a selective oxidation step are included in the model formulation, paving the way to new (possible) model formulations. Furthermore, a new model-based design of experiments (MBDoE) methodology has been proposed and applied for a ranking of the available experiments showing the best experimental conditions to be used for a precise estimation of the set of kinetic parameters of the proposed candidate models.

List of abbreviations used

AIC = Akaike Information Criterion
FIM = Fisher Information Matrix
MBDoE = Model-based Design of Experiments
PFR = Plug Flow Reactor
RFI = Relative Fisher Information

Acknowledgements

Funding from EPSRC grant (EP/J017833/1) is gratefully acknowledged.

References

1. Wachs I E, Madix R J (1978) Surf Sci 76:531
2. Robb D A, Harriott P (1974) J Catal 35:176–183
3. Andreasen A, Lynggaard H, Stagelman C, Stolze P (2003) Surf Sci 544:5
4. Andreasen A, Lynggaard H, Stagelman C et al. (2005) Applied Cat 189:267
5. Schwaab M, Silva F M, Queipo C A et al. (2006) Chem Eng Sci 61:5791
6. Franceschini G, Macchietto S (2008) Chem Eng Sci **63**:4846
7. Cao E, Gavriilidis A (2005) Catal Today 110:154
8. Schubert H, Tegtmeyer U, Schlögl R (1998) Catal Lett 28:383
9. Process Systems Enterprise (2011) London: Process Systems Enterprise 1-72
10. Pukelsheim F (1993) J Wiley & Sons, New York (U.S.A.)
11. Galvanin F, Bezzo F, Macchietto S (2007) Ind Eng Chem Res 46:871