

Parameter Estimation of an Empirical Kinetic Model for CO Preferential Oxidation

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Abstract. In this work the application of genetic algorithms (GA) for solving the parameter estimation problem in a nonlinear empirical kinetic model for CO preferential oxidation is reported. Kinetic models with nonlinear rate equations often suffer of considerable parameter uncertainty which can lead to inaccurate predictions. Here, after the parameter vector is obtained, a statistical study is performed in order to show how accurate the parameter estimations are determined. The unknown model parameters are obtained by fitting the model predictions against our laboratory observations measured under a range of experimental conditions using a novel Au/TiO₂ catalyst.

Keywords: CO-PrOx, Parameter estimation, Confidence intervals, Confidence regions

1 Introduction

The growing implementation of fuel cells for new portable electronic devices has moved research into improving reformers for in-situ hydrogen production, separation and purification. It is well-known that Pt-based anodes of PEM fuel cells are easily poisoned by CO. In this context, CO preferential oxidation (CO-PrOx) is the method of choice for the final step of hydrogen purification in small-scale applications due to its fairly simple implementation, lower operation costs and minimal loss of H₂ [1].

Catalysts based on oxide-supported gold nanoparticles have been reported to be highly active for the CO-PrOx reaction with good selectivity levels, operating at temperatures similar to those of the fuel cell (PEM-type, around 80°C) [2]. This fact makes them suitable candidates for this purpose since the integration of the PrOx reactor and the fuel cell into the same cooling circuit becomes straightforward.

An appropriate design of the CO-PrOx reactor for hydrogen purification requires the implementation of a mathematical model of the reactor. To these ends, the rates of the reactions taking place over the catalyst have to be properly quantified. Aiming this modeling task, we report in this work the parameters of simple mass-action kinetics

fitted to adjust our own laboratory measurements under a well-defined range of operating conditions of practical interest.

To estimate the parameters involved, several numerical methods can be used for solving the estimation problem involving differential equations. Available optimization methods to carry out this task can be classified into deterministic and stochastic. The first ones correspond to gradient based methods whose major disadvantage is that the quality of the solutions is affected by the initial estimates of the parameters which are essential to ensure that the obtained solution is close to a reasonable minimum. On the other hand, stochastic approaches present better global convergence properties since they perform a parallel exploration of the search space.

Having this framework in mind, a Genetic Algorithm (GA), which belongs to the stochastic family, is adopted to solve the resulting optimization problem. The GA is an adaptive stochastic method originated by laws of nature that outperform classical techniques due to capacity to deal with uncertainty and insufficient information [3].

Usually, kinetic models with nonlinear rate equations suffer of considerable parameter uncertainty which can lead to inaccurate predictions. In nonlinear estimation, after a solution has been found for the estimation problem, an assessment of the parameter values should be performed in order to estimate their uncertainties in rigorous statistical terms. In other words, it is also necessary to estimate the confidence intervals, the joint confidence region, and to examine the correlations between the parameter values.

This work aims at applying a GA technique for estimating the kinetic parameters in the CO-PrOx model systematically tuned with experimental data obtained in our laboratory. Additionally, an identifiability analysis is performed to assess the quality of the model parameters obtained.

2 Experimental

Conventional cordierite monoliths (two pieces, 1.4 cm length and 1.4 cm diameter each) with square cross-section of side *ca.* 0.5 mm (900 cpsi) were selected as support for the catalyst. Titanium isopropoxide (Panreac) was used as precursor to obtain a homogeneous and well-adhered layer of TiO₂ over the cordierite by thermal decomposition at 723 K for 4 h (1 K min⁻¹). Finally, pre-formed gold nanoparticles were grafted onto the TiO₂ support (2% w/w) by calcination at 573 K for 2 h (2 K min⁻¹) [4]. The gold nanoparticles were obtained by the two phase transfer method [5]. Before experiences, samples were activated under reaction mixture at 473 K for 2 h.

Experimental data towards the kinetic fitting were measured in a conventional lab facility. Monolithic samples mentioned above were sealed in a stainless steel housing inside a furnace (Heraeus). A gas mixture resembling the composition exiting a shift reactor (1.41% CO, 24.33% CO₂, balance H₂) was used in combination with air to prepare the reactor feed by using two independent mass flow controllers (Brooks). An absolute operating pressure of 1.2 bar was selected for all tests to mimic conditions in a fuel cell. Table 1 reports the operating conditions covered in the catalytic tests. Reactants and products (CO, CO₂, H₂, and O₂) were analyzed continuously with an HP

4890 gas chromatograph equipped with Carbosieve and Porapak-Q packed columns and TCD. Water contents in the reactor exit were calculated by closing element balances.

Steady-state measurements of the catalyst performance were achieved under isothermal and isobaric conditions in the experimental set up described above. Measurements were replicated 2-4 times with adequate reproducibility. A total of 48 different experiences were performed, collecting 192 experimental points to be used in the kinetic fitting (as exit molar flowrates of CO, CO₂, H₂ and O₂). After *ca.* 45 h of operation no catalyst deactivation was measured.

Table 1. Experimental conditions

Temperature [K]	334 - 473
Pressure [bar]	1.2
Feed load [mmol/(g _{cat} ·min)]	2.1-22.5
Feed concentration [mol _{O2} / mol _{CO}]	0.4 - 4.1

3 Theoretical framework

3.1 The parameter estimation problem

A parameter estimation problem (also known as inverse problem) consists in finding the model parameters of the process under study which give the best fit to a set of experimental data [6]. In order to accomplish this task, the proximity between observations and predictions taken from the model is used as the objective function to be minimized.

In chemical processes, deriving a suitable model for a chemical reaction is usually carried out by using mass balances. They are generally represented by dynamic non-linear systems expressed by a set of differential-algebraic equations (DAEs). By taking into account the steady state in a radial symmetrical flow reactor, the DAEs are expressed with respect to an independent variable z which represents distance. Thus, the associated parameter estimation problem is formulated as the following optimization problem:

$$\min J(\mathbf{p}) = (\mathbf{y}^e - \mathbf{y}^*)^T \mathbf{V}^{-1} (\mathbf{y}^e - \mathbf{y}^*) \quad (1a)$$

subject to

$$\frac{d\mathbf{y}}{dz} = \mathbf{f}(\mathbf{y}, \mathbf{u}, \mathbf{p}, z) \quad (1b)$$

$$\mathbf{h}(\mathbf{y}, \mathbf{u}, \mathbf{p}, z) = \mathbf{0} \quad (1c)$$

$$\mathbf{y}(z_0) = \mathbf{y}_0, \quad z \in [z_0, z_f] \quad (1d)$$

$$\mathbf{y}^L \leq \mathbf{y} \leq \mathbf{y}^U \quad (1e)$$

$$\mathbf{p}^L \leq \mathbf{p} \leq \mathbf{p}^U \quad (1f)$$

The objective function (1a) consists in minimizing the weighted quadratic output error between the experimental values \mathbf{y}^e and model values \mathbf{y}^* at the same sampling distances, i.e. least squares function. The matrix \mathbf{V} is a diagonal matrix with a collection of weighting factors. Equation (1b) represents the evolution of the differential state variable \mathbf{y} along the reactor length z where \mathbf{f} expresses the right-hand-side vector in this differential equation. Here, \mathbf{h} is the algebraic constraint vector, \mathbf{u} is the algebraic state variables that are also functions of distance, and \mathbf{y}_0 is the initial condition vector for state variables \mathbf{y} . Furthermore, the state variables depend on the model parameter vector \mathbf{p} which is distance independent.

3.2 The optimization method: Genetic Algorithms

As mentioned before, several numerical techniques can be used for minimizing the error of estimation in problem (1). Stochastic optimization algorithms have shown a good performance in parameter estimation problems over their deterministic counterparts [7]. In this work, a genetic algorithm (GA) method is used to perform the parameter identification procedure. This optimization technique, like other stochastic ones, has crucial advantages over deterministic algorithms such as it does not require good initial guesses for model parameters, does not require derivative of the objective function, and is able to determine the global minimum through extensive calculation of the objective function in the parameter space.

Genetic algorithm is a metaheuristic optimization method based on the evolution of populations of solutions according to operations that resemble those found in biologic selection process in living beings [8]. It essentially uses a combination of selection, crossover and mutation operations to evolve a solution of a problem. At the beginning of GA a population of random individuals is created. Each individual of the population represents a solution of the optimization problem, in other words, the vector of optimization variables. A subset of them is selected according to their fitness value (objective function) and then are mathematically combined (crossed) by pairs chosen in a random way with the aim of generate a new population of solutions (offspring). The crossover operation emulates the exchange of genetic material between homologous chromosomes that results in recombinant chromosomes. To provide diversity, a mutation process is applied on some individuals in order to introduce modifications in positions randomly chosen. These steps are repeated until some stopping criterion is reached, for instance, when the assigned number of population generations is reached or the difference between the best individuals of two successive iterations reaches a certain threshold value. A detailed description of the methodology involved in GA is beyond the scope of this work. The interested reader is referred to extensive literature on the subject [3, 9].

3.3 Confidence intervals and regions

In nonlinear models, both confidence intervals and regions can be estimated by extending the covariance matrix obtained for a linear case leading to an approximate one as [10]:

$$\mathbf{C}(\mathbf{p}^*) = \frac{J(\mathbf{p}^*)}{N - n_p} \left[\left(\frac{\partial \mathbf{y}}{\partial \mathbf{p}}(\mathbf{p}^*) \right)^T \mathbf{V}^{-1} \left(\frac{\partial \mathbf{y}}{\partial \mathbf{p}}(\mathbf{p}^*) \right) \right]^{-1} \quad (2)$$

where the term $J(\mathbf{p}^*)/N - n_p$ is an unbiased approximation of the residual variance σ^2 and $\frac{\partial \mathbf{y}}{\partial \mathbf{p}}(\mathbf{p}^*)$ is the sensitivity matrix corresponding to sensitivity of model variables \mathbf{y} with respect to the estimated parameters evaluated at \mathbf{p}^* . Parameter N is the total number of measurements while n_p is the number of estimated parameters.

Assuming that measurement noise is uncorrelated, the approximate covariance matrix given in Eq. (2) is also the inverse of the Fisher Information Matrix (FIM) of the estimation problem defined as:

$$\mathbf{FIM} = \sum_{m=1}^N \left(\frac{\partial \mathbf{y}_m}{\partial \mathbf{p}} \right)^T \mathbf{V}^{-2} \left(\frac{\partial \mathbf{y}_m}{\partial \mathbf{p}} \right) \quad (3)$$

Thus, $\mathbf{C}(\mathbf{p}^*) = \mathbf{FIM}^{-1}$ represents the error covariance matrix of the minimum variance unbiased estimator according to the Cramer-Rao theorem. Using this matrix, the approximate confidence ellipsoids in the n_p parameter space can be expressed as [7,8]

$$\{ \mathbf{p}: (\mathbf{p} - \mathbf{p}^*)^T \mathbf{C}^{-1} (\mathbf{p} - \mathbf{p}^*) \leq n_p F_{n_p, N-n_p}^{1-\alpha} \} \quad (4)$$

where $F_{n_p, N-n_p}^{1-\alpha}$ is the value from the F distribution with N observations and $N - n_p$ degrees of freedom and the given confidence level $1 - \alpha$.

The confidence interval of the individual parameters δ_k ($k = 1, 2, \dots, n_p$) at the desired confidence level $1 - \alpha$ can be obtained from the diagonal of the covariance matrix as:

$$\delta_k = \pm t_{N-n_p}^{1-(\alpha/2)} \sqrt{C_{kk}} \quad (5)$$

In Eq. (5) $t_{N-n_p}^{1-(\alpha/2)}$ is the two-tails Student's t-distribution value corresponding to the $\alpha/2$ percentile with $N - n_p$ degrees of freedom and C_{kk} represents the diagonal elements of $\mathbf{C}(\mathbf{p}^*)$.

Correlation is a measure of the strength of relationship between random variables. The correlation matrix, also referred to as the normalized covariance matrix, whose elements are the approximate correlation coefficients between two estimated parameters, is given as follows:

$$Q_{kl} = \frac{C_{kl}}{\sqrt{C_{kk} C_{ll}}} \quad (6)$$

Here, Q_{kl} is the correlation coefficient for parameters k and l . The covariance matrix is symmetric since $Q_{kl} = Q_{lk}$ and it is also positive definite. When $Q_{kl} = 1$ a perfect linear relationship exists between variables k and l whereas a $Q_{kl} = 0$ indicates that the parameters are not correlated. A positive correlation coefficient indicates a direct relationship exists, i.e. if parameter k increases, so does parameter l . The converse is true if the sign of the correlation coefficient is negative. Correlation coefficients greater than 0.99 may lead to a singular FIM, which in turn indicates the presence of unidentifiable parameters.

4 Model Formulation

With the aim of modeling the collected data in the kinetic experiments (see Section 2) a steady state, isothermal, one-dimensional, pseudo-homogeneous reactor model was chosen. This model contains the general mass balance equations around the system boundary in the following form:

$$\frac{dF_j}{dz} = \rho_B A_T S_j \quad \forall j \quad (7)$$

where F_j represents the molar flowrate of species j [mmol min⁻¹], A_T is the cross sectional area of monolith [m²], and ρ_B represents the catalyst loading per unit monolith volume expressed in grams of catalyst per cubic meter [g_{cat} m⁻³].

Furthermore, the mass balance (7) includes the kinetic model developed for a specific catalyst in the form of the overall component conversion rate S_j . It can be obtained by multiplying the stoichiometric coefficient of component j in reaction i , v_{ij} , with the rate of reaction i , r_i .

$$S_j = \sum_{i=1}^M v_{ij} r_i \quad \forall j \quad (8)$$

Specifically, the reaction system representing the measured results from the reaction experiences for CO and H₂ oxidation is given below.



The following mass-action rate equations have been assumed to represent the experimentally observed behavior in the selected operating conditions.

$$r_1 = k_1 p_{\text{CO}}^{n_1} p_{\text{O}_2}^{n_2} \quad (11)$$

$$r_2 = k_2 p_{H_2}^{n_2} p_{O_2}^{n_4} \quad (12)$$

For describing the temperature dependence of the reaction rate constant k_i , an Arrhenius relationship was assumed.

$$k_i = k_i^0 \exp\left(-\frac{E_i}{RT}\right) \quad \forall i \quad (13)$$

Here, k_i^0 is the pre-exponential or frequency factor [$\text{mmol g}_{cat}^{-1} \text{min}^{-1} \text{bar}^{-n}$], E_i the activation energy [kJ mol^{-1}], R the universal gas constant $8.3144 \times 10^{-3} [\text{kJ mol}^{-1} \text{K}^{-1}]$, and T the temperature [K].

The molar flowrates F_j in Eq. (7) are related to partial pressures p_j in Eqs. (11) and (12) through the molar fraction $x_j = F_j/\sum F_j$ and the total pressure $P = 1.2$ [bar] in the system.

$$p_j = \frac{F_j}{\sum_j F_j} P = x_j P \quad \forall j \quad (14)$$

Assuming that measurements follow independent normal distributions with unknown constant variance, minimizing Eq. (1a) is equivalent to minimizing the function:

$$\min J(\mathbf{p}) = \sum_{e=1}^{NE} \sum_{j=1}^{NC} \left(\frac{F_{ej} - F_{ej}^*}{\max(F_{ej})} \right)^2 \quad (15)$$

with the weights $V_j = \max(F_{ej})^{-2}$. Parameters NE and NC correspond to the number of experiments performed under different conditions and the number of components measured, respectively.

In summary, the parameter estimation problem (1) leads to a DAE system with five differential equations (Eqs. (7)) one for each component j , and two algebraic equations, one for each reaction i (Eqs. (11) - (12)). Thus, the model has 5 state variables and contains a total number of 8 kinetic parameters: k_1^0 , k_2^0 , E_1 , E_2 , n_1 , n_2 , n_3 , and n_4 . They were adjusted using the collected experimental data mentioned in Section 2. In these experiments, as no intermediate outputs exist in the tubular reactor, only the flowrate values at the final position z_f are measured.

Figure 1 illustrates a schematic representation of the implemented parameter estimation problem based on a GA. The operations performed on the populations of optimization variables, i.e. selection, crossover and mutation, are implemented in the Genetic Algorithm box and also the termination criterion is checked. The Objective Function Evaluator box computes the corresponding square error value (Eq. (15)).

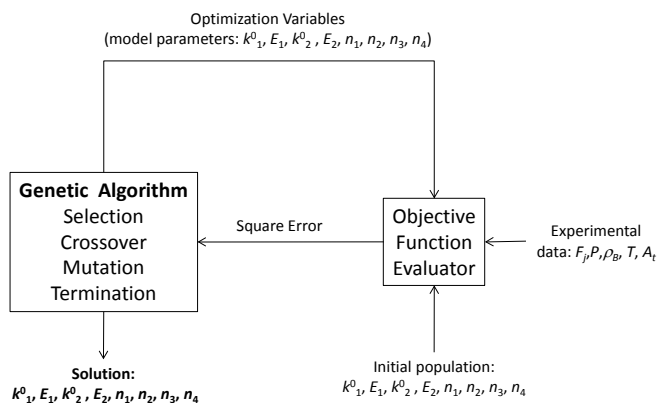


Fig. 1. Genetic algorithm based parameter estimation scheme

5 Results and discussions

The purpose of this study is to obtain a reliable identification of the reaction rate coefficients k^0 's, E 's and n 's in Eqs. (11) - (13) given species molar flowrates F_j in a tubular reactor by making the statistical evaluation of the estimation results.

The model implementation and parameter estimation were performed using the GA option of the optimization tool of the MATLAB 7.6.0 platform (The Mathworks, Inc.). The stopping criterion in the GA algorithm corresponds to whatever happens first: (i) maximum number of generations (100) reached or (ii) the cumulative change in the fitness function value over stall generations (50) is less than function tolerance (1×10^{-9}).

The experimental data collected as mentioned in Section 2 are used to estimate the parameters of the model. The optimal values of the estimated parameters as well as the uncertainty of the parameter represented as 95% confidence interval (CI) are shown in Table 2. In addition the correlation matrix, given as an 8×8 lower triangular matrix (the upper triangular matrix is identical to the lower one), is provided in this table. The most pronounced correlations between the parameters are shown in bold with a threshold value of 0.7.

Most of estimated parameters obtained by the GA algorithm have narrow confidence intervals indicating that the number of measurements performed for the parameter estimation were sufficient.

The normalized covariance matrix in Table 2 shows that although a few parameters are quite correlated, most parameters estimated in the optimization are only weakly correlated and thereby suitable for being estimated simultaneously.

The greater correlation coefficients are found between the frequency factors and the activation energies. Likely, any change in one of these parameters could be compensated by a change in the other ones. For example, the coefficient between k_2^0 and E_2 is 0.94 indicating a strong correlation between them and making it difficult to find a unique estimate for these parameters.

Table 2. Estimated kinetic parameters, 95% confidence intervals (CI), and correlation coefficients

p	Value	95% CI	Correlation matrix								
			k_1^0	E_1	k_2^0	E_2	n_1	n_2	n_3	n_4	
k_1^0	2.71×10^6	$\pm 5.06 \times 10^5$	1.00								
E_1	14.82	± 0.508	0.81	1.00							
k_2^0	2.90×10^8	$\pm 2.67 \times 10^7$	0.67	0.90	1.00						
E_2	55.48	± 0.207	0.68	0.86	0.94	1.00					
n_1	1.75	± 0.027	-0.12	-0.60	-0.61	-0.40	1.00				
n_2	1.01	± 0.022	0.77	0.65	0.55	0.38	-0.45	1.00			
n_3	0.00	± 0.017	-0.03	0.41	0.62	0.48	-0.74	0.15	1.00		
n_4	0.70	± 0.008	0.53	0.68	0.77	0.53	-0.67	0.74	0.49	1.00	

Unique parameter estimate means that the parameters shall have an acceptably low correlation to any of the other parameters and a low confidence interval. Thus, in spite of the large covariance above mentioned, a consistent estimation is possible because of the true value of the parameter estimates are located within a very small confidence bands reducing their uncertainty.

The value of activation energies estimated for oxidations of both CO and H₂ are in good agreement with values reported elsewhere for CO-PrOx over Au/TiO₂ catalysts [11, 12]. Moreover, the low value for the activation energy fitted for CO oxidation of *ca.* 15 kJ/mol reflects the outstanding ability of nano-sized gold catalysts towards this reaction at reduced temperatures. A lower adjusted value for E_1 with respect to E_2 confirms the experimentally observed behavior of a selectivity drop with increasing temperature and points special considerations aiming the design of an up-scaled PrOx reactor regarding heat removal from the reaction medium (both CO and H₂ oxidations are highly exothermic). Finally, it is worth mentioning that a fitted value of zero for the hydrogen reaction order (n_3) obeys to the fact that in all experiences a huge excess of hydrogen was present (as in the real situation).

Fig. 2 compares experimental and simulated exit flowrates for all the experiences included in the parameter estimation. The parity plots do not show any systematic deviations, with the points reasonably spread around the diagonal line, indicating that the deviations are due to experimental error.

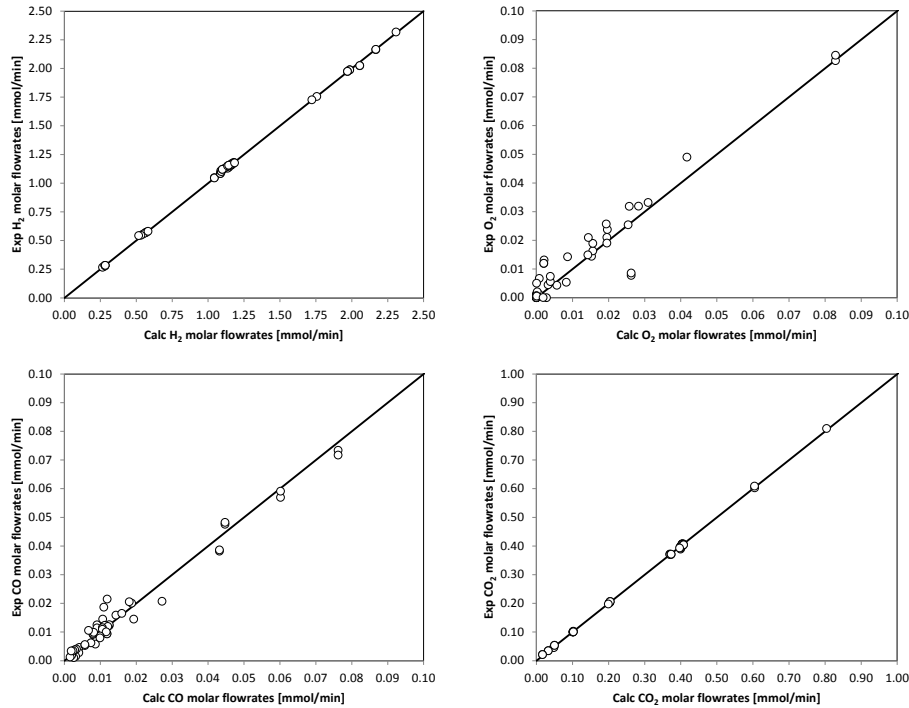


Fig. 2. Parity plots of measured and calculated flowrates using the parameters shown in Table 2

The influence of the operation temperature on both experimental and calculated exit flowrates of the reactants (i.e., CO, H₂ and O₂) is presented in Fig. 3 to show the accuracy of the adjusted parameters in reproducing the measured data. As expected from the Arrhenius expression (Eq. (13)), exit molar flowrates of oxygen descend monotonically with temperature as oxygen represent a reactant for both Eqs. (11) and (12). Hydrogen follows a similar trend. Conversely, a more complex behavior is detected for CO flowrates, with a descend for lower temperatures and decreased conversions for higher temperatures. In fact, this can be explained in terms of the adjusted activation energies (see Eq. (13)) reported in Table 2 for reactions (9) and (10). As the activation energy for CO oxidation is lower than the correspondent to H₂ oxidation, at lower temperatures CO is preferably oxidized while H₂ oxidation is still incipient. On the other hand, as temperature is raised H₂ oxidation becomes dominant, O₂ is depleted and CO leaves the system unreacted. As seen in Fig. 3, a very reasonable match of the model predictions to the observed data was attained.

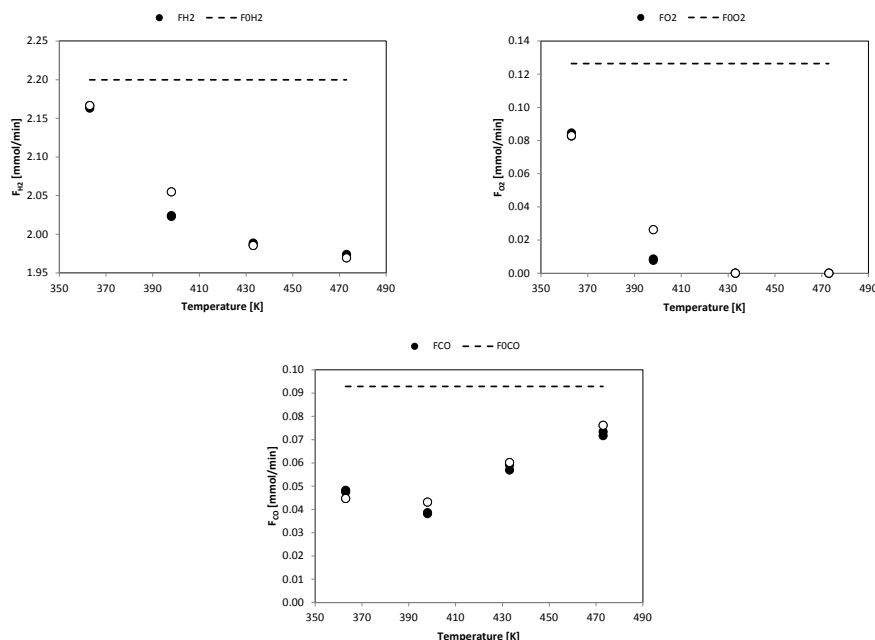


Fig. 3. Experimental (fill symbols) and calculated (open symbols) exit molar flowrates of reactants as influenced by temperature for a total inlet flowrate of 22.1 mmol/(g_{cat}·min) at mol_{O₂}/mol_{CO}=1.35. Dotted lines represent the inlet flowrate of each component.

For illustration purposes only a few confidence regions for some parameter pairs estimated using a GA are shown in Fig. 4. Here, the contours correspond to a confidence level of 95%. In other words, there is a probability of 95% that the true values of the parameter pair fall within this ellipsoidal confidence region that is centered in the parameter estimates. The narrow shapes of the joint confidence regions given in Fig. 4 indicate a reliable estimation of the parameters.

6 Conclusions

In this work, the kinetic parameter estimation of the CO-PrOx system over a novel Au/TiO₂ catalyst is addressed using a power-law model to describe the reaction rates.

Model calibration is accomplished by minimizing a weighted least squares objective function subject to kinetic constraints represented by nonlinear differential equations. Due to the pitfalls in deterministic approaches, a GA based optimization approach was adopted for solving the multimodal estimation problem.

The kinetic parameters have been estimated using experimental data obtained in our laboratory. The goodness of the model fits is quite remarkable considering the wide range of experimental conditions used.

Once the parameter estimations were found, an assessment of the model calibration was performed for checking the accuracy of the estimated parameters.

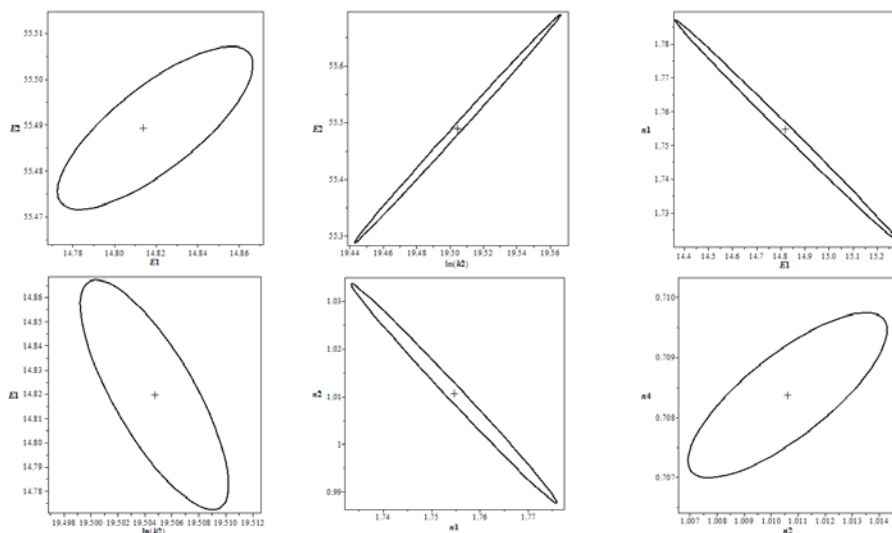


Fig. 4. Ellipsoidal confidence regions corresponding to 95% confidence level. The least squared estimates are indicated by +

7 References

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