Identifiability of Kinetic Parameters of Methanol Synthesis in Plug-Flow Tracing

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The identifiability of the fundamental kinetic parameters of a model of a plug-flow isotope transient tracing of methanol over PdNO/Al was investigated. The values of the parameters were estimated by securing a least-squares fit between the tracer data and the partial differential equations describing the reaction response in a plug-flow mode. The results demonstrate that modeling and identifiability of isotope transient tracing data provide for a meaningful assessment of heterogeneous catalytic reaction systems.

Introduction

Valuable information concerning the concentration of adsorbed intermediates and the step velocities of heterogeneous catalytic reaction systems can be obtained from isotope transient tracing data. Isotope transient tracing of reaction mechanisms involves the superposition of an isotopically labeled but otherwise equivalent feed component, a tracer, on a reaction system running at steady state. The transients of traced species can be modeled to estimate the kinetic parameters of the reaction system. Given the significance of isotope transient tracing in heterogeneous catalysis, addressing the identifiability of the models of chemical reaction kinetics, the possibility of estimating the parameters from experimental data has become an indispensable part of such research endeavors. The investigation of this aspect of kinetic studies is within the scope of model identifiability. A comprehensive treatise on the identifiability of parametric models has been recently presented by Walter and Pronzato (1997). The application of model identifiability to chemical reaction kinetics was initiated by Happel et al. (1986) and Walter et al. (1986). Since then, the application of identifiability in chemical reaction systems has been investigated widely (general reaction systems of arbitrary kinetic order, Vajda and Rabitz, 1994; electrochemistry, Berthier et al., 1993, 1996).

Happel et al.'s (1986) approach to the identifiability of models of isotope transient tracing in gradientless recirculating reactors (CSTR) is as follows. If a heterogeneous catalytic reaction system consists of gas-phase species A, B, ... , and adsorbed intermediates $A_1 \ell$, $A_2 \ell$, ... , then the state space model for CSTR isotope tracing is given by

$$\frac{\tau F^j}{W}\frac{d}{dt}z^j(t) = R_j,\ j = A, B, \dots, \tag{1a}$$

$$C^k\frac{d}{dt}z^k(t) = R_k,\ k = A_1 \ell, A_2 \ell, \dots, \tag{1b}$$

where F^j is the steady-state flow rate of gas-phase species j, ([mol/s](NTP)) and C^k is the steady-state surface concentration of adsorbed species k. z^j, the fractional concentration of gas-phase species j, is equal to the ratio of its instantaneous flow rate after the introduction of the tracer to its steady-state flow rate F^j, and z_k represents the ratio of the surface concentration of k to its steady-state value C^k. R_j and R_k are the overall rates of production or consumption of j and k. They are, in general, functions of the mechanistic step velocities $v_{\pm j}$, $v_{\pm k}$, which represent the steady-state rates of exchange of matter among the species. Thus, the system of differential equations (Eqs. 1a and 1b) depends on $\theta = (v_{\pm j}, v_{\pm k}, C^k)$, a vector of kinetic parameters. If $z^j\ (t, \theta)$ is the solution of the system of differential equations (Eqs. 1a and 1b), then the model is said to be identifiable if only one value of θ corresponds to z^j at any t for all t; or, if z^j is in a

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one-to-one correspondence with respect to θ for all t. Mathematically, the system is said to be identifiable if

$$z^j(t,\bar{\theta}) = z^j(t,\theta), \text{ implies } \bar{\theta} = \theta \text{ for all } t.$$

Except for very simple reaction mechanisms, the above system of differential equations cannot always be solved and thus the identifiability of models with respect to t variable cannot always be investigated. However, they showed that the model identifiability can be equivalently addressed through the Laplace transform of the equations. Thus, a model is said to be identifiable if

$$Z^j(s,\bar{\theta}) = Z^j(s,\theta), \text{implies } \bar{\theta} = \theta \text{ for all } s,$$

where $Z^j\ (s,\theta)$ is the Laplace transform of $z^j\ (t,\theta)$.

Tracing can also be conducted in plug-flow regimes (Soong et al., 1986). While the same fundamental concepts apply, the mathematics of modeling and identifiability of transient tracing in plug-flow reactors is more involved. Part of the problem perhaps resides in the complexity associated with the solution of the partial differential equations which describe the concentration profiles in a plug-flow reactor. They involve a space variable in addition to the time variable. The state space models of plug-flow transient tracing (Happel, 1986; Happel et al., 1990) of the above reaction system is given as

$$\frac{\partial}{\partial w}F^j(w)z^j(t,w) + \frac{\tau}{W}\frac{\partial}{\partial t}F^j(w)z^j(t,w) = R_j, \qquad j = A, B, \ldots, \tag{2a}$$

$$C^k\frac{\partial}{\partial t}z^k(t,w) = R_k,\ k = A_1\ell,\ A_2\ell,\ \ldots, \tag{2b}$$

where w, the amount of catalyst swept by the flow ($0 \le w \le W$) from the beginning of the catalyst bed (a suitable variable used in plug-flow isotope transient modeling) represents the axial space variable. In plug-flow tracing, the steady-state flow rates $F^j(w)$ become functions of the amount of catalyst but the concentration of adsorbed intermediates C^k remains independent of w. Obviously, the transient response functions become functions of t, w, and θ. The identifiability of plug-flow models is then addressed via the observable $z^j\ (t,\ W,\ \theta)$, which is the solution of the system of differential equations (Eqs. 2a, 2b) at the end of the reactor at $w = W$, or equally via $Z^j\ (s,\ W,\ \theta)$, its Laplace transform. Thus, in plug-flow tracing, a model is said to be identifiable if

$$z^j(t,W,\bar{\theta}) = z^j(t,W,\theta), \text{ implies } \bar{\theta} = \theta \text{ for all } t, \text{ or,}$$

$$Z^j(s,W,\bar{\theta}) = Z^j(s,W,\theta), \text{ implies } \bar{\theta} = \theta \text{ for all } s.$$

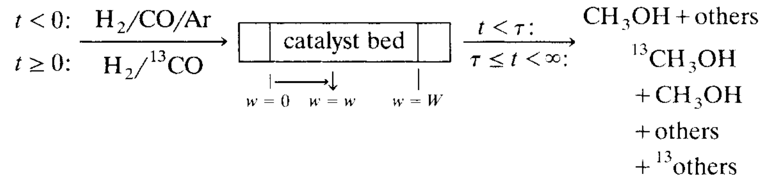
This article is aimed at exemplifying the application of modeling and identifiability to plug-flow ^{13}CO isotope transient tracing of methanol synthesis over PdNO/Al catalyst. The data for this study have been taken from the work of Ali and Goodwin (1998).

Modeling and Identifiability of Methanol Plug-Flow Tracing

Methanol is formed from syngas over Pd catalysts. On PdNO/Al, it proceeds according to the overall balanced equation

$$4CO + 9H_2 = CH_3OH + CH_4 + (CH_3)_2O + 2H_2O$$

Details of the experimental procedure are given by Ali and Goodwin (1998). Following is the experimental process



Briefly, a steady flow of $H_2/CO/Ar$ was continuously passed through a plug-flow microreactor containing $W = 0.05$ g of PdNO/Al until steady state was reached. At steady-state, methanol was produced at the rate $V_{CH_3OH} = 0.07 \times 10^{-6}$, dimethyl ether at $V_{(CH_3)_2O} = 0.095 \times 10^{-6}$ and methane $V_{CH_4} = 0.058 \times 10^{-6}$ mol/g cat/s. The rate of conversion of carbon monoxide was reported to be $V_{CO} = 0.31 \times 10^{-6}$ mol/g cat/s with an overall percentage conversion of 0.57. After steady state was maintained, the feed mixture was instantly switched. at $t = 0$, to one containing $^{13}CO/H_2$ in the original H_2/CO ratio. Transients developed in the rates of methanol, dimethyl ether and methane that were reported in their work. The data on methanol were scanned and are reproduced in Figure 1. Ali and Goodwin did not report a correlation of their transient tracer data, which were reported in Figure 7 of their article.

Since an objective of isotope transient tracing is to obtain the rate constants and the concentration of the adsorbed species, one needs to adopt a hypothesis concerning the adsorbed species and the mechanistic steps. Poutsma et al. (1978) suggested that the formation of methanol on Pd involves the addition of adsorbed hydrogen atoms to adsorbed carbon monoxide so that the reaction must proceed through the formation of $CH_xO\,\ell$ complexes. Under carbon monoxide tracing, this hypothesis is sufficient to enable one to estimate the concentration of $CH_xO\,\ell$, because whether $CH_xO\,\ell$ represents a combination of hydrocarbonaceous species or a single molecule is ultimately inconsequential to ^{13}CO tracing. Thus, we decided to employ the following compartmental model to estimate the kinetic parameters of methanol synthesis under ^{13}CO

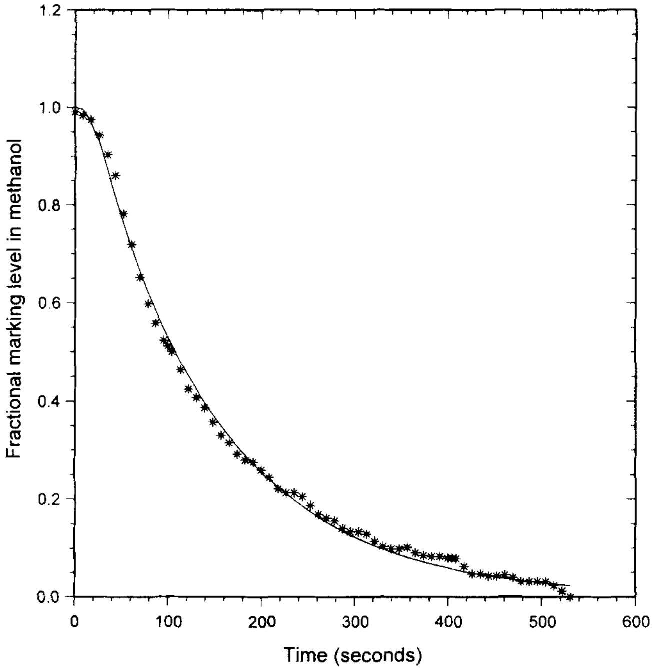
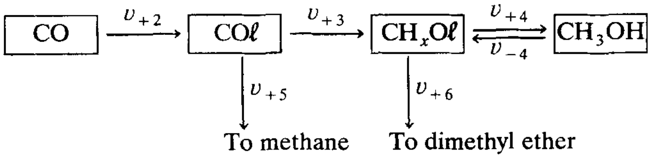


Figure 1. Methanol modeling vs. isotope transient tracing data.

* = Data; = − model.



At steady state

$$\upsilon_{+2} = V_{CO} \quad \upsilon_{+3} = V_{CO} - V_{CH_4} = V_{CH_3OH} + 2V_{(CH_3)_2O}$$

$$\upsilon_{+5} = V_{CH_4}, \qquad \upsilon_{+6} = V_{(CH_3)_2O}, \qquad \upsilon_{+4} - \upsilon_{-4} = V_{CH_3OH}$$

The material balance equations are as follows

$$\frac{\partial}{\partial w} F^{CO}(w) z^{CO}(t,w) + \frac{\tau}{W}\frac{\partial}{\partial t} F^{CO}(w) z^{CO}(t,w) = R_{CO} \tag{3a}$$

$$C^{CO\ell}\frac{\partial}{\partial t} z^{CO\ell}(t,w) = R_{CO\ell} \tag{3b}$$

$$C^{CH_xO\ell}\frac{\partial}{\partial t} z^{CH_xO\ell}(t,w) = R_{CH_xO\ell} \tag{3c}$$

$$\frac{\partial}{\partial w} F^{CH_3OH}(w) z^{CH_3OH}(t,w) + \frac{\tau}{W}\frac{\partial}{\partial t} F^{CH_3OH}(w) z^{CH_3OH}(t,w) = R_{CH_3OH}, \tag{3d}$$

where

$$R_{CO} = -\upsilon_{+2} z^{CO}$$

$$R_{CO\ell} = \upsilon_{+2} z^{CO} - (\upsilon_{+3} + \upsilon_{+5}) z^{CO\ell}$$

$$R_{CH_xO\ell} = \upsilon_{+3} z^{CO\ell} - (\upsilon_{+4} + \upsilon_{+6}) z^{CH_xO\ell} + \upsilon_{-4} z^{CH_3OH}$$

$$R_{CH_3OH} = \upsilon_{+4} z^{CH_xO\ell} - \upsilon_{-4} z^{CH_3OH}$$

If we replace $\upsilon_{\pm j}$, where possible, with known rates, we will have

$$R_{CO} = -V_{CO} z^{CO} \tag{4a}$$

$$R_{CO\ell} = V_{CO}(z^{CO} - z^{CO\ell}) \tag{4b}$$

$$\begin{aligned} R_{CH_xO\ell} = {} & (V_{CH_3OH} + 2V_{(CH_3)_2O}) z^{CO\ell} \\ & - (2V_{(CH_3)_2O} + \upsilon_{+4}) z^{CH_xO\ell} \\ & + (\upsilon_{+4} - V_{CH_3OH}) z^{CH_3OH} \end{aligned} \tag{4c}$$

$$R_{CH_3OH} = \upsilon_{+4} z^{CH_xO\ell} - (\upsilon_{+4} - V_{CH_3OH}) z^{CH_3OH} \tag{4d}$$

For unmarked species, these differential equations are subject to the initial and boundary conditions

$$\begin{cases} z^{CO}(0,w) & = 1 \\ z^{CO}(t,0) & = 0 \end{cases}, \quad z^{CO\ell}(0,w) = z^{CH_xO\ell}(0,w) = 1,$$

$$\begin{cases} z^{CH_3OH}(0,w) & = 1 \\ z^{CH_3OH}(t,0) & = 0 \end{cases}$$

This system of equations involves three parameters $C^{CO\ell}$, $C^{CH_xO\ell}$, and υ_{+4}. Hence

$$\theta = (C^{CO\ell} \quad C^{CH_xO\ell} \quad \upsilon_{+4}).$$

To estimate θ, we employed a forward finite difference method (Chapra and Canale, 1985) with a partition of size 10 on the reactor bed and obtained a least-squares fit between the data and z^{CH_3OH}. The procedure found a relatively high but statistically poorly determined value for υ_{+4}. This led us to assume that $z^{CH_3OH} \simeq z^{CH_xO\ell}$. Under this hypothesis, we could add Eqs. 3c and 3d, and reduce the system of equations as follows

$$\frac{\partial}{\partial w} F^{CO}(w) z^{CO}(t,w) + \frac{\tau F^{CO}(w)}{W}\frac{\partial}{\partial t} z^{CO}(t,w) = R_{CO} \tag{5a}$$

$$C^{CO\ell}\frac{\partial}{\partial t} z^{CO\ell}(t,w) = R_{CO\ell} \tag{5b}$$

$$\begin{aligned} & \frac{\partial}{\partial w} F^{CH_3OH}(w) z^{CH_3OH}(t,w) \\ & + \left(\frac{\tau F^{CH_3OH}(w)}{W} + C^{CH_xO\ell}\right)\frac{\partial}{\partial t} z^{CH_3OH}(t,w) \\ & = R_{CH_3OH} + R_{CH_xO\ell} \end{aligned} \tag{5c}$$

where

$$R_{\mathrm{CH_3OH}} + R_{\mathrm{CH_xO}\ell} = (V_{\mathrm{CH_3OH}} + 2V_{\mathrm{(CH_3)_2O}})z^{\mathrm{CO}\ell} - 2V_{\mathrm{(CH_3)_2O}}z^{\mathrm{CH_3OH}}.$$

The new model depends on two parameters only, $\theta = (C^{\mathrm{CO}\ell}, C^{\mathrm{CH_xO}\ell})$. The least-squares fit to data is shown in Figure 1. The good agreement between the data and model gives support to the validity of the model as a probable representation of the background kinetics. Also, the fit between Eqs. 5a–5c and data were at least graphically indistinguishable from that for Eqs. 3a–3d giving support to our hypothesis of the equality of fractional marking levels in methanol and $\mathrm{CH_xO}\ell$.

The model defined according to Eqs. 5a–5c has an important advantage over the one defined as in Eqs. 3c–3d. While Eqs. 3c–3d could not be solved analytically, the set of Eqs. 5a–5c can be solved by taking their Laplace transforms. Without derivation, if $Z^{\mathrm{CH_3OH}}$ (s, W, θ) represents the Laplace transform of $z^{\mathrm{CH_3OH}}$ (t, W, θ), then

$$Z^{\mathrm{CH_3OH}}(s,W,\theta) = \frac{V_{\mathrm{CO}}C^{\mathrm{CH_xO}\ell}}{V_{\mathrm{CO}}C^{\mathrm{CH_xO}\ell} - VC^{\mathrm{CO}\ell}} \frac{1}{s + \dfrac{V}{C^{\mathrm{CH_xO}\ell}}} - \frac{VC^{\mathrm{CO}\ell}}{V_{\mathrm{CO}}C^{\mathrm{CH_xO}\ell} - VC^{\mathrm{CO}\ell}} \frac{1}{s + \dfrac{V_{\mathrm{CO}}}{C^{\mathrm{CO}\ell}}}$$

where $V = V_{\mathrm{CH_3OH}} + 2V_{\mathrm{(CH_3)_2O}}$. The model is identifiable if

$$Z^{\mathrm{CH_3OH}}(s,W,\bar{\theta}) = Z^{\mathrm{CH_3OH}}(s,W,\theta)$$

implies $\bar{\theta} = \theta$ for all t. It can be easily seen that this identity has an additional solution set

$$\bar{\theta} = \left(\overline{C^{\mathrm{CO}\ell}}\,\overline{C^{\mathrm{CH_xO}\ell}}\right),$$

where

$$\overline{C^{\mathrm{CO}\ell}} = \frac{V_{\mathrm{CO}}}{V} C^{\mathrm{CH_xO}\ell}$$

$$\overline{C^{\mathrm{CH_xO}\ell}} = \frac{V}{V_{\mathrm{CO}}} C^{\mathrm{CO}\ell}$$

The Laplace transform can be inverted to obtain an expression for $z^{\mathrm{CH_3OH}}$ as follows

$$Z^{\mathrm{CH_3OH}}(t,W,\theta) = \left[\frac{V_{\mathrm{CO}}C^{\mathrm{CH_xO}\ell}}{V_{\mathrm{CO}}C^{\mathrm{CH_xO}\ell} - VC^{\mathrm{CO}\ell}} \exp\left(-\frac{V}{C^{\mathrm{CH_xO}\ell}}t\right) - \frac{VC^{\mathrm{CO}\ell}}{V_{\mathrm{CO}}C^{\mathrm{CH_xO}\ell} - VC^{\mathrm{CO}\ell}} \exp\left(-\frac{V_{\mathrm{CO}}}{C^{\mathrm{CO}\ell}}t\right)\right]u(t-\tau) \quad (6)$$

It is always beneficial to model, if available, the exact solution of a system to estimate the value of the parameters (Eq. 6 in this example). However, since Eqs. 3a–3d cannot be solved analytically, to be able to compare the results we used the numerical solutions for all equations.

Results

The value of both solution sets I and II corresponding to θ and $\bar{\theta}$, respectively, are reported in Table 1. $z^{\mathrm{CH_3OH}}$ (t, W, θ) correlates data identically with respect to both sets of parameters. This model is only locally identifiable. Obviously, the interpretation of the rate constants and the choice of a rate-controlling step and the interpretation of the behavior of the catalyst PdNO/Al varies depending on which set of parameters is chosen. It may be possible to reject one of these solutions on the basis of some physical evidence. In the absence of such evidence, both solutions are legitimate and cannot be ruled out.

From the concentrations of CO ℓ and $\mathrm{CH_xO}$ ℓ, we evaluated the value of the pseudo-first-order rate constants based on the conditions at the end of the catalyst bed by using

$$\upsilon_{+2} = V_{\mathrm{CO}} = k_{+2}p_{\mathrm{CO}},$$

$$\upsilon_{+3} = V_{\mathrm{CO}} - V_{\mathrm{CH_4}} = k_{+3}C^{\mathrm{CO}\ell},$$

$$\upsilon_{+4} = k_{+4}C^{\mathrm{CH_xO}\ell},\ \upsilon_{-4} = k_{-4}p_{\mathrm{CH_3OH}}.$$

υ_{+4} and υ_{-4} were not estimated. However, it was found that υ_{+4} and, therefore, υ_{-4} were very large compared to $V_{\mathrm{CH_3OH}}$ so that $\upsilon_{+4}/\upsilon_{-4} \simeq 1$, then K_m was computed as the ratio of pseudo-first-order rate constants k_{+4} and k_{-4}. These are reported in Table 2 for both solution sets.

The overall surface coverage can be obtained from the area under the transients of all product species (called the average residence times) and the steady-state rates. For example, if $\tau_{\mathrm{CH_3OH}}$ represents the area under the transient curve of methanol in Figure 1 minus τ, the space time of the reactor, then $V_{\mathrm{CH_3OH}}\tau_{\mathrm{CH_3OH}}$ gives the amount of surface coverage titrated by methanol. Therefore, if C^t represents the overall surface coverage of traceable species, in moles of adsorbed carbon, then

$$C^t = V_{\mathrm{CH_3OH}}\tau_{\mathrm{CH_3OH}} + V_{\mathrm{CH_4}}\tau_{\mathrm{CH_4}} + 2V_{\mathrm{(CH_3)_2O}}\tau_{\mathrm{(CH_3)_2O}} + \tau_{\mathrm{CO}}V_{\mathrm{CO}}. \quad (7)$$

$\tau_{\mathrm{CO}}V_{\mathrm{CO}}$ represents the amount of CO reversibly adsorbed. While reversibly adsorbed CO did not seem to contribute to methanol formation, it could still be present on the surface under the reaction conditions. The transient of CO was not reported by Ali and Goodwin. However, they reported the surface coverages based on the transients of methane, methanol, and dimethyl ether which added up to 41.7×10^{-6}

Table 1. Kinetic Parameters of Methanol Synthesis

Solution Set	$C^{\mathrm{CO}\ell}$ [10^6 mol/g cat./s]	$C^{\mathrm{CH_xO}\ell}$ [10^6 mol/g cat./s]
I: θ	43.04	3.70
II: $\bar{\theta}$	4.53	35.19

Table 2. Pseudo First-Order Rate Constants

Sol. Set	k_{+2} $\left[\frac{\text{g cat. s atm}}{\text{mol}}\right]$	k_{+3} $[\text{s}^{-1}]$	K_M $\left[\frac{\text{g cat atm}}{\text{mol}}\right]$	k_{+5} $[\text{s}^{-1}]$	k_{+6} $[\text{s}^{-1}]$
I	1.56×10^{-6}	5.9×10^{-3}	69.3	1.35×10^{-3}	5.14×10^{-2}
II	1.56×10^{-6}	5.7×10^{-2}	7.3	1.28×10^{-2}	5.39×10^{-3}

mol C/g catalyst. This figure is in good agreement with our estimates of the surface concentrations. Given our results (Table 1), it is clear that the overall concentration of the other adsorbed species leading to methane and dimethyl ether must be small. It should be remembered though that, as the model clearly shows, while C^t corresponds to the overall surface coverage, the individual items in Eq. 7 do not correspond to the surface coverage of any individual species. For instance, $V_{CH_3OH}\tau_{CH_3OH}$ is equal to the combined concentration of a fraction of $C^{CO\ell}$ and a fraction of $C^{CH_xO\ell}$. This is true because at $t \geq 0$ some of the adsorbed CO ℓ still reacts to form methane, and some to form methanol. Obviously, without employing a modeling procedure which is based on rates of production or consumption of species it is not always possible to estimate the value of these parameters. If the paths to methane, methanol and dimethyl ether were independent and did not share a common intermediate species, it would then be possible to use the area under each transient curve to estimate the overall concentrations of adsorbed species in an individual path. The excellent agreement between the data and our model indicates that such is not the case in methanol synthesis over PdNO/Al. Thus, in general, rigorous modeling, similar to that employed in this article, is needed for an assessment of the kinetic parameters of a reaction system.

Discussion

Modeling and identifiability play important roles in the interpretation of isotope transient tracing data. To estimate the kinetic parameters of a heterogeneous reaction system from isotope transient tracing data, a most likely mechanism is selected from among a number of possible candidates and the model equations are written. By a least-squares fit procedure, the parameters of the model are estimated. If such a model is not identifiable, multiple sets of parameters exist which equally well correlate experimental data. Where there is more than one identifiable model, the distinguishability characters of models should be addressed as well (Happel et al., 1986). The results from the identifiability and distinguishability properties of a model can and do have a great impact on the way the function of a catalyst is perceived. Since under Langmuir's hypothesis the rate constants of the elementary mechanistic steps become proportional to the step velocities and the concentration of the adsorbed species, for a locally identifiable model the choice of a solution of kinetic parameters will directly influence the choice of a rate-controlling step and ultimately the formulation of LHHW-type rate equations.

Our work resulted in two sets of parameters, both of which equally well correlate the experimental data, indicating that under carbon monoxide tracing our model is only locally identifiable. When a model is locally identifiable, results from modeling and identifiability of isotope transient tracing should be combined with the findings of other independent methods of studies of catalytic reactions to identify the model. These include the spectroscopic methods, measurement of adsorption and desorption characteristics of species involved, and the utilization of other tracers. In the case of methanol synthesis over PdNO/Al, independent measurement of carbon monoxide adsorption on PdNO/Al (Ali and Goodwin, 1998) showed that a total of 104×10^{-6} moles of carbon monoxide was adsorbed on the catalyst of which 16×10^{-6} was reversibly held. Although this amount is not under methanol synthesis condition, it indicates that carbon monoxide can adsorb appreciably on the surface. This result plus the value of the total surface coverage of all traceable adsorbed species, which is about 41.7×10^{-6} mol C/g catalyst, indicate that the solution set I seems to give the more probable value of the parameters describing the distribution of adsorbed species on PdNO/Al. Under these restrictions, the model becomes identifiable.

Since in plug-flow tracing the material balance equations are partial differential equations, the estimation of parameters often requires a numerical approach to obtain a least-squares fit to data. With the help of advanced computer software, this can always be accomplished. When these equations can be solved analytically, at least in the Laplace domain, the identifiability of the plug-flow model can be addressed. The determination of the identifiability characteristics of a model is independent of the numerical values of the parameters and is a mathematical feature of the model itself. For locally identifiable models, if the value of one set of parameters is known, other possible values of parameters can be computed as was shown here and as was earlier discussed by Walter et al. (1986).

Unless the characteristics of the kinetic background of a reaction system are known *a priori*, a modeling approach, as the one employed here, is essential to interpret the tracer data. The method of correlation presented here should serve as a useful adjunct in processing plug-flow isotope transient tracing data in order to estimate the kinetic parameters of heterogeneous reaction systems and elucidate their mechanisms. As is clearly shown, the intricacy of the interplay between the adsorbed intermediates and the branching reaction pathways makes the utilization of mechanistic modeling in such studies almost indispensable. For complex reaction systems, as the one addressed here, additional information may be needed to fully assess the kinetic background of the surface reaction steps. Finally, it is hoped that the findings of this article demonstrate the importance of mechanistic modeling and identifiability in isotope transient tracing studies of chemical reaction kinetics.

Notation

C^i = concentration of the adsorbed species i [mol/g] (NTP)
ℓ = indicator of an active catalyst site

t = time variable
$u(t)$ = Heaviside step function
V_i = steady state overall rate of a species i [mol/g cat./s]
W = weight of catalyst
z^i = fractional marking level in i
$\underline{Z}^i$ = Laplace transform of fractional marking level in i
θ, $\bar{\theta}$ = vectors of kinetic parameters

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