Elucidating complex catalytic mechanisms based on transient pulse-response kinetic data

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HIGHLIGHTS

- A new strategy was developed for discriminating between catalytic reaction mechanisms.
- This strategy is based on temporal coherency of transient kinetic data.
- Transient kinetic data include the net production rates R and gas concentrations C.
- The R–C data were obtained from thin-zone TAP experiments via the Y-Procedure.

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ABSTRACT

We describe a strategy for discriminating reaction mechanisms based on the non-steady-state coherency of kinetic characteristics including net production rates as well as gas and surface concentrations. The suggested strategy of mechanism discrimination utilizes two novel concepts: instantaneous surface storages and temporal kinetic coherency. The first concept is used to express the catalyst composition during transient experiments through gaseous transformation rates, while the second concept is used to test whether a hypothetical reaction mechanism is consistent with observed kinetic characteristics. In our study, these kinetic characteristics are made available by analyzing exit-flow rate data of Thin-Zone Temporal Analysis of Products (TAP) pulse-response experiments via an algorithm called the Y-Procedure. To illustrate our mechanism discrimination strategy, we used a prototypical multi-route CO oxidation mechanism. The constructed decision tree can be used to distinguish between multiple variations of this mechanism.

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1. Introduction

The kinetic behavior of catalytic reactions remains the primary source of information for establishing their underlying mechanisms. In mean-field microkinetic models, catalytic reaction mechanisms are described by networks of elementary steps which obey the law of mass action (Chorkendorff and Niemantsverdriet, 2007). A reaction network of optimal complexity must adequately represent an observed kinetic behavior without introducing unnecessary or speculative details (Yablonskii et al., 1991; Marin and Yablonsky, 2011). It is essential that optimal reaction mechanisms are established based on kinetic data with as few *a priori* assumptions as possible. The regression of kinetic data with an array of candidate models, which is typically used for mechanism discrimination, relies heavily on such assumptions. Therefore, the recognition of kinetic "fingerprints", i.e. characteristic features of certain mechanistic motifs, within kinetic data before the data are subjected to standard regression procedures plays an important role in mechanism elucidation. The recognition of kinetic "fingerprints" facilitates a more intuitive understanding of reaction pathways, helps to reject some incompatible mechanistic hypotheses at low cost, and constrains the estimation of kinetic parameters.

It is usually problematic to formulate a systematic decision tree for mechanism discrimination based on kinetic "fingerprints". A decision tree suggested in this paper enables systematic discrimination between possible combinations of elementary steps within a comprehensive list by leveraging some elements

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of both top-down and bottom-up approaches to mechanism construction.[1] In each node of this tree, the decisions are based on kinetic "fingerprints" exhibited by the non-steady-state (transient) kinetic data.

Kinetic "fingerprints" exhibited by steady-state data have been studied extensively including the isothermal multiplicity of steady-states for catalytic (Bykov et al., 1981; Kevrekidis et al., 1984; Schwartz and Schmidt, 1988) and general reaction networks (Feinberg, 1988) or the co-planarity of steady-states in a transformed state space for enzymatic reactions (Harrington et al., 2012). Transient phenomena in catalytic kinetics can provide even more kinetic "fingerprints" for elucidating reaction mechanisms (Schwarz, 1968; Berger et al., 2008), although they are usually challenging to observe experimentally. A classical example of transient kinetic "fingerprints" is the passing of a substance concentration through a maximum, which suggests that this substance is an intermediate involved in a consecutive reaction scheme, as opposed to a parallel reaction scheme. Moreover, the intersection points of different concentration curves and the coincidences of such intersections in time have recently been identified as a rich source of previously unknown transient kinetic "fingerprints" (Yablonsky et al., 2010).

Herein we focus on Temporal Analysis of Products (TAP) experiments which provide high-quality non-steady-state kinetic data for reactions mediated by industrial high surface area catalysts (Gleaves et al., 1988; Prez-Ramrez and Kondratenko, 2007; Gleaves et al., 2010). TAP experiments have millisecond temporal resolution and allow for precise control of the catalyst state, making them well suited for a *conversation-like inquiry* into various characteristic features of reaction mechanisms. The latter approach is known as Interrogative Kinetics (IK) (Gleaves et al., 1997). In TAP experiments, the exit-flow rates of individual substances are observed at the outlet of a continuously evacuated microreactor after injecting a very small and short pulse of gas at the microreactor inlet. A catalyst is typically packed in a thin layer between two inert zones inside the TAP microreactor. This packing configuration, known as the Thin-Zone (TZ) configuration, ensures that the spatial non-uniformities of temperature, gas concentration, and surface composition within a catalytic sample remain low even for high per-pulse conversions (Shekhtman et al., 1999; Phanawadee et al., 2003; Shekhtman et al., 2004; Shekhtman and Yablonsky, 2005).

An important consequence of catalyst uniformity is that the observed kinetics can be related to a specific catalyst state rather than to a spatial distribution of catalyst states. This property is not only advantageous for parameter estimation via the standard model regression, but it also facilitates data interpretation based on kinetic "fingerprints" which do not require the detailed reaction mechanism to be assumed in advance. More recently, an algorithm called the Y-Procedure was developed for translating exit-flow rates into the net production rates and gas concentrations inside the uniform catalyst zone (Yablonsky et al., 2007). This algorithm is based on the Fourier-domain analysis of reaction–diffusion equations which are used to describe TAP experiments (Constales et al., 2001). The Y-Procedure is kinetically "model-free" in that it does not require prior kinetic assumptions

about the reaction mechanism to reconstruct the net production rates and gas concentrations. The reconstructed rate–concentration transients have been used to study the adsorption steps of catalytic reactions (Redekop et al., 2011, submitted for publication) and to determine connectivity features of pseudo-monomolecular reaction networks (Roelant et al., 2012). In this paper we provide the first theoretical and methodological framework for systematic interpretation of "model-free" rate–concentration transients. This framework is applicable to both linear and non-linear catalytic mechanisms and is not limited to pseudo-monomolecular reactions.

The framework for TAP data interpretation suggested here is based on temporal kinetic coherency between the reconstructed "model-free" rates and concentrations. Temporal coherency can be defined as synchronization of kinetic characteristics during a transient experiment such as their coincidence in time or time-independence of their ratios. Given that rate–concentration characteristics can be reliably reconstructed from primary TAP data via the Y-Procedure, their temporal kinetic coherency or decoherency is an observable kinetically "model-free" property which is rooted in the underlying "true" mechanism. Thus, the property of temporal kinetic coherency is not only useful for discriminating between several predefined reaction mechanisms, but can also provide insights for formulating reaction mechanisms *de novo*.

In order to develop a mechanism discrimination strategy, we have employed numerical TAP experiments with catalytic *CO* oxidation, as described in the Methodology section. The main theoretical results are presented in Sections 3 and 4. First, we discuss the calculation of surface storages from transient gas transformation rates as a way to characterize the catalyst composition during TAP pulse-response experiments. Then, we develop a general mechanism discrimination strategy which employs rate–concentration data extended by calculated surface storages. After demonstrating our model discrimination strategy with numerical experiments concerning the model reaction of *CO* oxidation, we discuss the scope of applications which can benefit from these suggested concepts.

2. Methodology

2.1. Model mechanism of CO oxidation

CO oxidation was chosen as a model reaction because of its numerous applications as well as its importance for fundamental studies in catalysis. Catalytic *CO* oxidation is an important way of removing *CO* from exhaust gases (Boaro et al., 2000) or from hydrogen streams intended for use in fuel cells (Ko et al., 2007). Elementary steps comprising *CO* oxidation are also involved in other industrially relevant catalytic reactions including the Water–Gas Shift (Ovesen et al., 1996). Although the mechanism of *CO* oxidation is relatively simple, this reaction often exhibits surprisingly complex kinetic behavior, providing a valuable model for exploring relationships between the structures of reaction mechanisms and their kinetic behavior, e.g. Yablonskii et al. (1991), Slinko et al. (1999), and Kim et al. (2001). Because the mechanism of *CO* oxidation may involve several alternative routes, it is a prototypical case of the mechanism discrimination problem (Freund et al., 2011).

In order to set up a model problem of mechanism discrimination, we considered the elementary steps (listed in Table 1) which may comprise several possible mechanisms of *CO* oxidation. For example, a sub-network of elementary steps 1, 2, and 4 constitutes the Langmuir–Hinshelwood (LH) mechanism, whereby CO_2 is produced in the reaction between preadsorbed *CO* and dissociated oxygen. Another classical mechanism of *CO* oxidation, the

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[1] Typically, top-down and bottom-up approaches are described as follows. The top-down approach begins by suggesting a minimal formal mechanism which reconciles existing data followed by expansion of the model by addition of elementary steps only if this minimal mechanism is insufficient to describe the results of further experiments. The bottom-up approach begins by compiling an exhaustive network of elementary steps which are generated combinatorially, assembled from the literature, or suggested by a deeper layer of modeling hierarchy, e.g. Aghalayam et al. (2000). This network is used to regress available experimental data, and a dominant pathway is adopted as the optimal mechanism.