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Precise kinetic measurements and spatial uniformity of catalytic beds

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HIGHLIGHTS

- TAP is suitable for characterizing very fast irreversible reactions ($Da_{II} > 100$).
- Uniformity develops when more gas is pulsed than the number of catalyst sites present.
- For 2nd order reactions, uniformity can be achieved for a wider range of states than for 1st order.

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ABSTRACT

Sufficient uniformity of the gas phase and surfaces within a catalytic bed is an essential prerequisite for precise kinetic characterization of heterogeneous catalysts. In addition to uniformity, the gas transport regime must be mathematically well-defined and allow for controlled alterations of the catalyst state. The Thin-Zone Temporal Analysis of Products (TZTR) reactor satisfies these requirements for industrially-relevant powdered catalysts. Numerical simulations of pulse-response experiments were used to chart the conditions of spatial uniformity within the TZTR for very fast (Da_{II} up to 100) irreversible reactions, such as strong chemisorption or oxidation reactions. The simulations demonstrated that even when an initial catalyst state is so reactive that uniformity cannot be readily achieved, a series of reactant pulses eventually creates a catalyst state which is spatially uniform and at the same time reactive enough for kinetic characterization. This point on the scale of possible catalyst states is attained when the total amount of pulsed molecules exceeds the initial number of active sites in the sample, i.e. the theoretical monolayer coverage. Simulations also indicated that the rate at which the catalyst bed becomes more uniform from one pulse to the next is sensitive to reaction order: the desired uniformity is established for a second order adsorption after smaller amount of pulses than for a first order adsorption. Thus, a wider range of spatially uniform, yet kinetically-relevant catalyst states can be characterized for a second order adsorption. These results not only expand the range of validity for the TZTR approach, but also set new bounds for generally achievable precise kinetic measurements.

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1. Introduction

Quantitative kinetic measurements are the basis of practical catalyst evaluation as well as fundamental mechanistic studies of complex catalytic reactions (Marin and Yablonsky, 2011). In

general, an ideal kinetic measurement must satisfy the following criteria: (i) it must not introduce significant macroscopic non-uniformity within the catalytic bed, (ii) it must be state-defining, meaning that the perturbation used to conduct the kinetic measurement (e.g. concentration, temperature) must not alter the catalyst state significantly, and (iii) it must be rapid enough to sample relevant elementary steps of catalytic reactions, which often occur on the millisecond time scale. These demanding requirements typically contradict each other, and suitable compromises must be made on a case-to-case basis.

Temporal resolution, spatial uniformity, and the degree of control over the catalyst state are all strongly dependent on the mode of bulk mass and heat transfer within the reactor device

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(Kapteijn and Moulijn, 2008). In kinetic devices with a convection-dominated transport regime, such as stirred tanks and tubular flow-through reactors, kinetic measurements are typically associated with significant, poorly controlled changes of the catalyst state and essential catalyst non-uniformity. Although they are widely used due to their simplicity, these devices have limited time resolution and are also limited in conversion range ($< 20\%$) in order to maintain catalyst uniformity. These limitations imposed by convective transport motivate the development of alternative reactor types with different modes of transport.

Here we consider an important class of kinetic reactors in which gas transport is dominated by diffusion. For such a reactor, the simplest 1D model is given by

$$\frac{\partial C}{\partial t} = D_{\text{eff}} \frac{\partial^2 C}{\partial x^2} - R(C), \quad (1)$$

where C is the fluid-phase concentration of a chemical species in mol/m^3 , D_{eff} is the effective diffusion coefficient along the spatial direction x in m^2/s , and R is the net production rate in $\text{mol}/(\text{m}^3 \text{ s})$. The solutions of the model Eq. (1) depend on the Damköhler number $\text{Da}_{\text{II}} = \tau_{\text{D}}/\tau_{\text{R}}$ which compares the characteristic time scales of diffusion τ_{D} and chemical rates τ_{R} . This characteristic number governs spatial and compositional changes of the catalyst state during kinetic measurements. In this paper, a Temporal Analysis of Products (TAP) reactor was used to demonstrate that for systems described by Eq. (1) it is possible to kinetically characterize a well-defined, spatially uniform catalyst state without destroying it, even for very fast reaction steps exceeding previously reported rate limits ($\text{Da}_{\text{II}} > 100$).

The methodology and applications of TAP are described in numerous review articles (Gleaves et al., 1988, 1997, 2010; Perez-Ramirez and Kondratenko, 2007; Yablonsky et al., 2003). The primary experimental principle of this kinetic method is to inject very narrow and small pulses of gas with known composition into an evacuated fixed bed reactor containing a catalytic sample. Raw TAP data are comprised of exit flow rates of gases escaping from the reactor into an adjacent vacuum chamber, which are monitored with millisecond time resolution by a calibrated Quadrupole Mass Spectrometer (QMS). Under typical TAP conditions, the transport of injected gas molecules through the reactor packing proceeds via Knudsen diffusion. This mode of gas transport has numerous advantages over conventional flow-driven transport for quantitative kinetic measurements, including the absence of external mass-transfer limitations and a very robust mathematical description given by Eq. (1), i.e. concentration gradients within the bed are well-defined. Moreover, concentration gradients can be reduced in comparison with concentration values by minimizing the length of the catalyst layer sandwiched between two layers of inert packing. This strategy, used previously in Differential Plug-Flow Reactors (Kobayashi and Masayoshikobayashi, 1974), is implemented in the Thin-Zone TAP Reactor (TZTR) by keeping the length of the catalytic bed very small in comparison with the total reactor length (Shekhtman et al., 1999, 2004; Shekhtman and Yablonsky, 2005). Given a high degree of spatial uniformity, temporal variations of nearly-uniform kinetic characteristics related to the specific catalyst state can be extracted from one pulse to the next by the method of moments or within each pulse by the Y-procedure (Yablonsky et al., 2007; Redekop et al., 2011).

Another viable strategy for eliminating macroscopic uniformity is to drastically decrease the catalyst loading. For example, Zheng et al. (2008) have used a single Pt particle for CO oxidation and still obtained significant CO conversion. Unfortunately, data interpretation of this elegant experiment is not straightforward, because the 1D model no longer applies in this case. At present, the thin-zone configuration is the configuration of choice for typical TAP measurements. It should be mentioned, however, that efforts are underway to develop an appropriate modeling framework for single-particle experiments (Feres

et al., 2009), which may eventually lead to the change of this status quo and widespread application of single-particle experiments.

The validity of the uniformity hypothesis depends on the magnitude of specific transformation rates which can vary dramatically within the range of possible catalyst states, for example, between empty and fully covered surfaces. These considerations are particularly important for TAP applications in which a catalyst is exposed to a very long series of identical pulses containing either a gas that is irreversibly adsorbed by the catalyst or a gas that irreversibly consumes pre-adsorbed surface intermediate. Such multi-pulse experiments are typically continued until the catalyst is fully saturated (depleted), when the amount of adsorbing (reacting) gas exiting the reactor becomes equal to the injected amount (Redekop et al., 2011; Wang et al., 2013; Shekhtman et al., 2008). Since the catalyst composition changes significantly between the beginning and the end of a multi-pulse experiment, it is important to consider spatial catalyst uniformity at the different stages of compositional change within the multi-pulse sequence.

For an irreversible adsorption or a reaction involving non-porous catalyst, the governing characteristic number is typically defined as

$$\text{Da}_{\text{II}} = \frac{\varepsilon_{\text{cat}} l_{\text{cat}}^2 k_{\text{app}}}{D_{\text{cat}}}, \quad (2)$$

where the apparent reaction rate constant k_{app} , $1/\text{s}$ is given by Phanawadee et al. (2003)

$$k_{\text{app}} = \frac{a_s S_v (1 - \varepsilon_{\text{cat}}) k_a}{\varepsilon_{\text{cat}}}. \quad (3)$$

The Thiele modulus, the square root of the right-hand side of expression (2), is sometimes used instead (Yablonsky et al., 2001), but the former definition (no square root) is employed here. In Eq. (3), k_a is the reaction (adsorption) rate constant in $\text{m}^3/(\text{mol s})$, S_v is the specific surface area of the catalyst in $\text{m}^2/\text{m}_{\text{particles}}^3$, ε_{cat} is the void fraction of the catalyst, and a_s is the surface concentration of active sites in mol/m^2 . It is the latter quantity, a_s , which changes during a multi-pulse experiment and alters the degree of uniformity. Simulations of the gas phase concentrations and surface coverages in the catalyst layer were performed by Phanawadee et al. (2003) for a low, but not unreasonable value of $\text{Da}_{\text{II}} = 0.5$. For this value of Da_{II} and a length ratio $l_{\text{cat}}/l_{\text{total}}$ of $1/30$, the difference between the inlet and outlet concentrations of any reacting gas was shown to be lower than 12% of the inlet concentration, and the maximum difference of corresponding coverages was shown to be lower than 0.08. However, many chemisorption processes have much higher characteristic number values. For example, it was estimated that Da_{II} can be as high as ~ 100 for oxygen chemisorption on the empty surface of polycrystalline Pt (Redekop et al., 2011).

This analysis suggests that assumptions about catalyst uniformity within a TZTR must be re-examined for higher values of the characteristic number Da_{II} . A computational approach (Phanawadee et al., 2003) was adopted in this paper for this purpose and to better define the generally valid range of the uniformity approximation. Multi-pulse TAP experiments with irreversible chemisorption were simulated beginning with an empty catalyst surface until it was completely saturated with adsorbed species. Simulation results demonstrated that the uniformity approximation for the thin-zone is justified even for very high adsorption rate constants (initial Da_{II} of at least up to 100), but only after the total amount of gas pulsed into the microreactor exceeds the number of initially available catalytic sites. This condition implies that a certain number of pulses at the beginning of the sequence must be excluded from kinetic analysis. Importantly, the spatial distribution of coverage along the catalytic bed depends only on the total amount of injected gas and does not depend on the number of pulses used to deliver this total amount (Phanawadee and Boonwatharapunsakun, 2010). Therefore, the minimum coverage necessary to satisfy the uniformity requirement can be prepared either

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