



Rapid extraction of quantitative kinetic information from variable-temperature reaction profiles



Daniel H. Coller^a, Brian C. Vicente^a, Susannah L. Scott^{a,b,*}

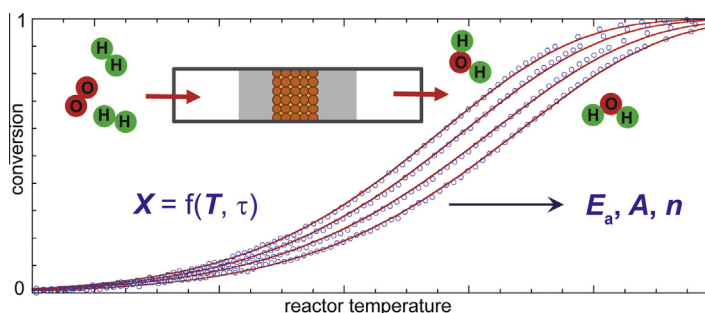
^aDepartment of Chemical Engineering, University of California, Santa Barbara, CA 93106, United States

^bDepartment of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106, United States

HIGHLIGHTS

- Analytical equations describe variable-temperature reaction (activity) profiles in packed-bed reactors (PBR).
- Simulated reaction profiles reproduce key features of experimental profiles that are free of mass and heat transfer effects.
- The influence of individual reaction parameters on the variable-temperature reaction profiles is demonstrated.
- Non-linear curve-fitting of variable-temperature profiles can yield accurate kinetic parameters.
- The method is demonstrated for the oxidation of CO, H₂, and C₃H₈ by O₂ catalyzed by Pd/Al₂O₃.

GRAPHICAL ABSTRACT



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ABSTRACT

Analysis of variable-temperature reaction profiles, measured in an isothermal packed-bed reactor (PBR) whose temperature increases during the experiment, has the potential to yield accurate and precise kinetic parameters quickly for some heterogeneous catalysts. The method is demonstrated here for a typical supported nanoparticle catalyst, 2 wt% Pd/Al₂O₃, in the oxidation of H₂, C₃H₈ and CO by O₂. These reactions do not exhibit major changes in activation energy as a function of conversion over the range of reaction conditions analyzed. Reliable and quantitative information about rate laws was extracted readily from the shapes and positions of the profiles, as an alternative to more laborious conventional kinetic analyses. Temperature and pressure gradients were minimized by the use of sieved catalyst particles and large amounts of inert diluent for both the catalyst and feed gas. Curve-fitting of analytical expressions with as few as two adjustable parameters results in remarkable agreement between models and data. First-order profiles are kinetically-limited, without mass and heat transfer effects, while inverse-first-order profiles deviate from kinetically-controlled behavior at intermediate-to-high conversions. The activation energy and reaction order with respect to the limiting reactant obtained from a single reaction profile (with appropriate data truncation for non-kinetic phenomena, as necessary) are at least as accurate and precise as those obtained from a conventional Arrhenius analysis conducted with data obtained under differential conditions, and can be measured in a fraction of the experimental time. Information about more elaborate rate laws can be obtained by global curve-fitting of a family of such profiles recorded with different volumetric flow rates.

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* Corresponding author at: Department of Chemical Engineering, University of California, Santa Barbara, CA 93106, United States.

E-mail address: sscott@engineering.ucsb.edu (S.L. Scott).

1. Introduction

1.1. Expanding the scope of traditional kinetic analysis in flow reactors

As high-throughput methods for materials synthesis become more versatile and accessible [1], large numbers of heterogeneous catalysts covering a wide range of composition space can be generated quickly [2–4], creating a need for similarly fast and flexible methods to screen for catalytic activity. Comparing performance in a catalyst array at a common temperature has limited usefulness, because the onset of activity can be abrupt for surface-mediated reactions. Comparing temperatures for 50% conversion of a limiting reactant, T_{50} , can also be problematic, because this single-point measurement may be strongly influenced by non-kinetic effects. Even when this is not the case, such comparisons are valid only for measurements made under the same conditions (residence time, feed composition, dispersion of the active phase, etc.), and for catalysts that follow the same rate law. A more robust kinetic assessment requires measurement of reaction orders and activation parameters over a range of operating conditions, which is typically slow and labor-intensive even for a single catalyst. Even more time-consuming is the assembly of a microkinetic model, requiring extensive measurements across a wide range of experimental conditions to identify and quantify the rates of all elementary steps. Nevertheless, acquiring as much of this information as possible for a series of heterogeneous catalysts in a variety of reaction atmospheres is ultimately necessary for properly interpreting reactivity differences, rationalizing the search for and design of new catalysts, benchmarking and optimizing their performance [5].

While some kinetic descriptors, such as the turnover frequency (TOF), can be obtained relatively quickly [6], direct comparisons are still difficult, especially when a series of catalysts exhibits widely varying activities. A recent proposal [7] to create a “standard” TOF suffers from the need to make long extrapolations, and TOFs can be mis-used in such comparisons [8]. The empirical Arrhenius parameters A (or k_0) and E_a are more generally useful. Ideally, they should be obtained from the temperature dependence of a rate constant, which in turn implies knowledge of the rate law.^a However, even when the form of the rate law is not known, E_a can be extracted from the temperature dependence of the conversion (X) at the outlet of a packed bed reactor (PBR) operated under differential conditions. Obviously, the same information is available from the temperature dependence of the reaction rate ($-r_a$), computed from the product of X and $F_{a,0}$ (the molar flow rate of the limiting reactant **a**, which is proportional to both the inlet concentration of **a** and the volumetric flow rate) and normalized by the catalyst weight W , as in Eq. (1). The ratio W/v_0 is the PBR version of the space-time, τ .

$$-r_a = \frac{F_{a,0}X}{W} = \frac{C_{a,0}v_0X}{W} = \frac{C_{a,0}X}{\tau} \quad (1)$$

In conventional PBR kinetic analysis, the reaction orders are assessed in a series of isothermal, steady-state experiments for which the inlet concentration of each chemical component is varied independently while keeping the conversion very low. The activation parameters are extracted from the response of the outlet conversion to changes in temperature. The need for differential reaction conditions to ensure kinetic control of the rate imposes

important constraints on kinetic experiments: (1) The measurements themselves, made at very low conversions, are often inherently imprecise. (2) Keeping the temperature range small to maintain low conversion contributes to a large (and often unacknowledged) uncertainty in the Eyring and/or Arrhenius parameters. (3) Perhaps most significantly, experiments performed at low conversion over a limited temperature range inevitably exclude the majority of reaction conditions, including those which are likely to be most relevant to practical reactor operation.

Even for a single catalyst, a complete kinetic study requires many experiments over an extended period of time, for which maintaining stable operation of the catalyst and reactor can be challenging. For catalysts that deactivate relatively rapidly [9], the need to conduct lengthy steady-state kinetics experiments is particularly problematic, and would benefit from a faster, variable-temperature approach. For example, the kinetic analysis of CO oxidation by a new, single-site Pd catalyst was limited to a single data point at each reactor condition, and steady-state operation was never achieved, due to rapid catalyst deactivation [10]. Finally, the linearization used in conventional methods of analysis for differential kinetic data alters the weighting of experimental values, and yields parameters that are susceptible to correlations [11–13]. Consequently, distinguishing between kinetic models can be prone to error, and complex behavior can be masked. More accurate and discriminating methods using non-linear analysis of variable-temperature kinetic data (collected by increasing the reactor temperature continuously) have long been available [14,15], although they have yet to be widely adopted.

1.2. Potential benefits of variable-temperature kinetic investigation

Much of the kinetic information one usually seeks (rate law, activation parameters) is contained in the light-off profile. According to one definition, catalyst “light-off” occurs at the transition between the kinetically-controlled low temperature regime and the diffusion-controlled high temperature regime. However, with appropriate choice of reactor conditions, the entire X - T plot can be recorded under predominantly kinetically-controlled conditions, and is still commonly called a light-off profile. Here, we name such data, which are free of transport influences and collected while increasing the reactor temperature at a fixed rate, a reaction profile. Although the full reaction profile constitutes a non-isothermal experiment, the entire catalyst bed remains approximately isothermal for the brief duration of an individual X - T measurement. A flat-bed reactor has also been used to minimize thermal gradients in the catalyst, so that they can be neglected [16].

Such reaction profiles are rarely used to extract kinetic parameters (other than the activation energy, from the leading edge of the curve) even though their analysis could alleviate several of the drawbacks of differential kinetic work. These include differences in feed and catalyst bed characteristics across a series of isothermal runs, and changes in the catalyst that take place while the reactor is being heated to each desired temperature, leaving the material with a complex thermal history. A method for the quantitative analysis of reaction profiles could dramatically reduce the amount of time necessary to assess kinetic parameters for large numbers of heterogeneous catalysts, or for a small number of catalysts under a wide range of reaction conditions. In principle, it allows several kinetic parameters to be measured in a single experiment, minimizing the use of time and material and providing rapid results to guide catalyst synthesis based on performance. This in turn would allow researchers to allocate more resources to their most promising leads, and to reduce time spent on catalysts with inadequate properties.

^a If k is a rate constant for an elementary step, an Eyring plot ($\ln(k/T)$ vs. T^{-1}), is preferred because it gives the physically meaningful activation parameters ΔH^\ddagger and ΔS^\ddagger . However, most measurements in heterogeneous catalysis generate apparent rate constants that contain multiple unresolved contributions from adsorption/desorption and reaction steps. In such cases, the empirical Arrhenius treatment is usually considered satisfactory.

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