



Recent advances in dynamic chemical characterization using Temporal Analysis of Products

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The Temporal Analysis of Products (TAP) technique is a pulse response methodology that reveals the time-dependent evolution of chemical processes between a gas phase molecule and a solid surface. By simplifying both the transport and kinetic processes the complexity of a multistep chemical processes can be distilled to where the underlying fundamental steps can be distinguished. Moreover, the technique is applicable to real materials (e. g. industrial catalysts) and hence the complexity of the solid is studied intact; a ‘top-down’ approach. In this short review we discuss key theoretical advancements in the interpretation of pulse response data; though not yet widely implemented, we will highlight the broader impacts of the *Y-Procedure* method [1**], *momentary equilibrium* phenomena [2**] and kinetic coherency discrimination [3**] over more commonly used analysis techniques. The conventional TAP approach for mechanism development is well-laid out in a recent work focused on the upgrading of ethanol to higher hydrocarbons. This includes detailed comparison of the time characteristics of reactant, intermediate and product pulses in both single pulse and pump/probe modes [4**]. This work calls to mind some of the challenges in the conventionally used residual gas analyzer for pulse response detection of homologous products. A new detection method using photoelectron photoion coincidence spectroscopy (PEPICO) was recently demonstrated for a TAP-like setup [5**]. This method presents the exciting opportunity to better resolve complex product spectra and even isomeric species. This enables the mechanistic detail of the TAP technique to be applied to more complex probe molecules as are needed for the study of biomass conversion processes. Finally, we discuss directions for the future development of instrumentation that can directly connect this rich kinetic data to features of catalyst structural and composition.

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Introduction

Observation of the relaxation of a dynamic chemical system in response to a stimulus enables the deconstruction of complexity. When the function of individual parts of a system cannot be readily observed, the working relationships between constituent parts can understood by tracking the evolution of the whole system in response to small perturbations. In this work our focus is on catalytic systems where complex multicomponent metal/metal oxide composites are used to control complex multistep reaction mechanisms. In the study of heterogeneous catalytic reactions a number of temperature, concentration and pressure transient experiments can be employed. Dynamic chemical tests are not only difficult to conduct experimentally but often more challenging is the interpretation of results. For this reason the kinetic evaluation of most chemical systems is conducted under steady-state conditions where instrumentation, experimental methodology and interpretation of data are more straightforward.

The Temporal Analysis of Products (TAP) pressure transient methodology is an evolving kinetic tool that offers certain advantages for the study of industrial materials and the deconstruction of complex reaction mechanisms. One key distinction is the ability to monitor incremental state-by-state changes in the kinetic performance of a material. Catalytic materials are formed kinetically; that is, the steady-state performance derives not only from the operating conditions but also from the history of processes leading to that state. During the initialization period

before achieving steady-state, the transient processes that naturally occur (e.g. desorption of precursor materials, formation of surface structure, change in surface coverage, etc.) may impact the steady-state endpoint that is attained. For this reason, dynamic testing is an essential component of understanding fixed chemical processing but more importantly it can be used to reveal greater information about how the complex system functions.

Context for transient experiments in catalysis

Steady-state kinetic characterization is simple and easy to use for rapid screening of candidate materials and these systems most closely emulate the industrial operating environment. While experimental conditions can be designed to avoid heat and mass transport limitations only the slow reaction step of a complex mechanism is generally observed. The subtlety in the interplay of different reaction steps is missed and often researchers may conduct identical synthesis/characterization only to yield different results.

By implementing dynamic conditions (temperature, concentration, pressure) key features of the complex chemical system can be studied in greater detail. Temperature programmed desorption/reaction is perhaps the most widely used dynamic technique which can be used to indicate the binding strength of reactants, intermediates and products, and often in good correlation to atomistic modeling predictions. Thermogravimetric and differential scanning calorimetry methods are used to measure reaction rates and enthalpies.

Where concentration transients are imposed the frequency response technique may be used but steady-state isotopic transient kinetic analysis (SSITKA) is most common. SSITKA experiments can be used to extract forward and reverse reaction rates of elementary steps as well as surface concentrations of active reaction intermediates under working conditions. A great benefit to interpretation of kinetic data conducted under concentration transients is the incorporation of spectroscopic tools (e.g. IR, Raman, X-ray absorption) that enable observation of the adsorbate and solid structural dynamic response under working conditions of the catalyst; a.k.a. *operando* experiments.

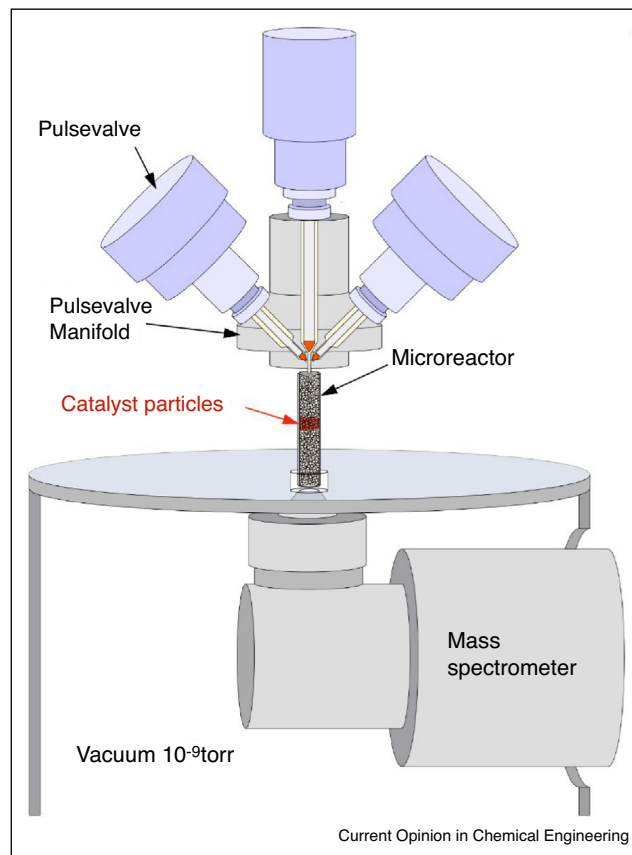
Under working conditions a pressure transient can be pulsed into a reactor flow but in this case the complexity of heat and mass transport can be difficult to separate from kinetic effects. Pressure transients in low pressure (high vacuum) conditions eliminate transport disguises and enable the direct study of the solid material. Molecular beam scattering (MBS) is a primary example where intrinsic kinetic characterization detailing elementary reaction steps can be studied. This technique is conducted on well-defined, model materials and thus a 'bottom-up' approach to material complexity can be

pursued. TAP is an adaptation of MBS where a pressure transient is sent through a packed bed under high vacuum conditions. The distinction is the ability to use industrial catalytic materials where a 'top-down' approach to study the complex material can be conducted. Recent developments in the theory supporting TAP transient response analysis along with significant examples of its use are presented here. This review is not intended to be a comprehensive survey but rather to focus on a few impactful examples that propel the technique forward.

The TAP pulse response technique

Several review articles detail the workings of the TAP instrumentation, experimental methodologies, application examples [6,7,8^{*}] and theoretical tools [9^{*}] for extracting kinetic data; only a brief description will be provided here. The experiment begins with a packed bed, as depicted in Figure 1, where the catalyst material is placed in a thin zone between two inert packed beds (typically SiC or SiO₂); this is the so-called 'thin zone' reactor configuration. The exit of the reactor is open to a high throughput vacuum system where a mass spectrometer is located in close proximity; the pressure is generally

Figure 1



Schematic of the key components of the TAP instrumentation.

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