Truth is, we all are transients: A perspective on the time-dependent nature of reactions and those who study them

Evgeniy A. Redekop [a],[*],[1], Gregory S. Yablonsky [b],[1], John T. Gleaves [b],[1]

[a] *Centre for Materials Science and Nanotechnology (SMN), University of Oslo, Oslo, Norway*
[b] *Department of Energy, Environmental, and Chemical Engineering, Washington University in Saint Louis, USA*

A R T I C L E   I N F O

A B S T R A C T

Understanding and mastery of Transient Kinetics in the context of multi-scale transport-reaction systems employed in catalysis is one of the ultimate frontiers in chemical science and engineering. In this perspective, we will highlight key results enabled by experiments in the Temporal Analysis of Products (TAP) Reactor Systems spanning several decades of research, several length-scales of space and time, as well as several ensembles of individual (re)actors, ranging from a single 350 μm-sized catalytic particle to a bed fully packed with them. Conclusions are drawn and new horizons are discerned.

Introduction

Discovering new and improving existing heterogeneous catalysts is a formidable research objective, primarily because they offer enormous opportunities for improved chemical processes in industry with major implications for the sustainability of crucial value chains. Catalysis is an inherently kinetic phenomenon of (selective) acceleration of chemical transformation rates, placing the kinetics of catalytic reactions at the core of understanding and controlling catalysis [1]. Kinetic characteristics are not only the sole most decisive criteria by which practical and model catalysts are to be evaluated, compared, and scrutinized, but are also a fertile ground for investigating many fundamental properties of nature, in general (e.g. Astrocatalysis, Enzymology and Biochemistry, Non-equilibrium Thermodynamics, Mathematics, and Physics).

Catalytic surfaces relevant for practical applications are usually vastly complex. They can comprise many chemical elements that are present in various oxidation states, different crystallographic phases, nanoparticles, interfaces, and may feature considerable degree of disorder such as lattice defects, grain boundaries, and extra-framework species. Furthermore, the active (*operando*) states of catalytic surfaces – by which here we refer to configurations of their structural, electronic, and chemical properties giving rise to specific (transient) reaction kinetics – are themselves formed kinetically under non-steady-state conditions. As shown by many examples of industrial and academic relevance, combinations of homogeneous, heterogeneous, and non-

thermally-activated reactions may simultaneously participate in the overall catalytic process. Even when starting with a relatively well-defined initial state, the emerging active state is the product of convoluted processes that depend on many factors, the most relevant of which are listed below:

- the pretreatment history,
- the spatio-temporal distribution of material and surfaces
- the spatio-temporal distribution of species and energy (mechanical and thermal) within the reactor
- the kinetically-dominating sequence of reaction steps occurring on the catalyst surface and in the gas phase,
- time on stream and or residence time in general,
- activation and deactivation of catalysts
- local electro-magnetics fields

Characterizing and understanding the resulting active surface has been a daunting task indeed for several generations of researchers across multiple disciplines. In this perspective, we will reflect on the crucial role of (transient) kinetic characterization in addressing this challenge, with the hope to stimulate wider applications of transient methods in catalytic research.

The scope of Transient Kinetics and of its toolkit is very broad. We particularly focus on experiments conducted with the help of the Temporal Analysis of Products (TAP) Reactor Systems (RS). TAP reactor

---

systems present a particularly potent methodological platform for kinetic experimentation and exploration [2–4]. Methodologically, TAP employs standard non-steady processes as the core concept. First, a standard transport curve, in particular the Knudsen diffusion curve, is used for extracting pure kinetic characteristics of a specific state of the catalytic surface. Second, the standard process, usually – a gas pulse, is used as a perturbation to probe the reaction kinetics, but this perturbation is kept small in intensity in order to perform a state-defining non-steady-state experiment in which he catalyst composition is changed insignificantly. Next, a series of such 'snapshots' inflicts controlled changes of the catalyst state, preferably within a standard scale of some descriptor of the catalyst state (e.g. oxidation or coking degree). Finally, the kinetic characteristics observed at well-defined conditions are systematically compared on the same standard scale of descriptors to those observed under operando conditions. Some of the unique features of the TAP methodology are:

- Extracting the chemical transformation rate from the non-steady-state data with no or very little considerations regarding the mechanism and the kinetic model (i.e. kinetically model-free extraction)
- Determining instantaneous accumulations (i.e. surface storages) of key reactants on the catalyst surface under reaction conditions at multiple time scales, from milliseconds to hours.
- Titrating the number of active sites under reaction conditions.

We also discuss the relevance of reconciling TAP observations with observations provided by other techniques in catalysis as well as other branches of Science as an opportune way forward. Based on these considerations, we outline a systematic program in experimental and theoretical studies of catalytic reactions.

Kinetic characterization objectives

In heterogeneous catalysis, common tactical goals of conducting kinetic experiments, which are measurements of chemical transformation rates of reactants, products, and/or, if Nature permits, surface intermediates, can be summarized as:

1. to better understand the dominant reaction mechanism under certain conditions, including the main catalytic cycle, side reactions, and deactivation,
2. to construct a quantitative model of reaction kinetics, which can be coupled with the mass- and energy-balance models used for reactor design and optimization,
3. as a means of materials characterization (i.e. probe reaction) through different stages of its lifetime, from preparation and pretreatment, through catalytic reaction, to eventual deactivation and regeneration. And last, but not least,
4. to serve as a source of new mysteries, hypotheses, and problems in physical chemistry, mathematical chemistry, and Life in general. Gas-solid catalytic reactions involve non-steady-state and multi-scale process. All these processes create a hierarchy of time scales which is a basis for decoding the complexity. As a result, the complex process becomes a combination of non-steady-state and quasi-steady-state processes.

These goals are, of course, deeply intertwined [5]. Yet reconciling kinetic experiments optimized for these different goals into a consistent view can be challenging, partially due to the diversity of kinetic devices and materials from which relevant data are sourced. Kinetic data for the same reaction may span a diverse range of conditions, from the Molecular Beam Scattering (MBS) under high vacuum conditions [6,7] to various bench-top reactors [8] to pilot plants [9]. Ultimately, it is the cross-examination of the kinetic characteristics across vast ranges of time-scales and operating conditions that is required for achieving forward catalytic engineering and advanced process control.

In order to achieve this methodologically, it is useful to delineate two complimentary aspects of chemical reactions in heterogeneous catalysis: material's state and material's function. Considerable efforts in catalysis are focused on establishing correlations between various descriptors of the material's state and its function at the extremes of either well-defined model or complex industrially-relevant materials and conditions. Transient Kinetics offers crucial descriptors of both, material' state and its function, by applying the main concept of chemical calculus – to separate the history-dependent material's state from its instantaneous kinetic properties (function) – across vastly different scales of kinetic complexity and kinetic uncertainty.

Temporal analysis of products (TAP) Reactor Systems

TAP pulse-response experiments in the Knudsen regime [3,4] must be delineated from TAP Reactor Systems as experimental platforms in general [10]. In these reactor systems, pulse/step-response and steady-state experiments can be combined across different pressure regimes and time scale, including ambient and above ambient pressure-flow experiments. Importantly, this can be achieved in the same device and on the same complex sample, offering a powerful tool to interrogate the kinetic properties within a wide range of experimental conditions. The following few sections exemplify that when kinetics are compared between disparate conditions, a new level of understanding in catalysis emerges, which would not have otherwise been readily achieved by experiments only under industrially-relevant conditions. This, in turn, can provide a firm ground for the design of advanced catalytic materials and technological processes.

Single particle – a catalytic point

Our journey begins with a single point. What constitutes the smallest functionally-representative unit of a technologically-relevant catalyst that could be considered a single spatial point in the complex space of kinetic properties? Recent results in multi-scale theoretical modeling, synthesis, and characterization of catalytic materials suggest that often the answer to this question could be a single 100–1000 μm particle, which encompasses several possible pore systems, crystallographic phases, nano-structures, and diverse types of surface sites. Individual particles have recently been imaged under *operando* conditions using a variety of structural and spectroscopic techniques, e.g. computed X-Ray Diffraction Tomography (CT-XRD) of a single particle of an extruded zeolite catalyst [11] or X-Ray nanotomography of a single FCC catalytic particle [12]. Transport anisotropy within a single zeolite crystal [13] and diffusion inhomogeneity among individual zeolite crystallites within a single batch of material were also measured using microscopic imaging [14]. From the functional perspective, such individual composite catalytic particles are the minimal units that are likely to exhibit the full range of reaction phenomena relevant for the process optimization. However, the aforementioned advanced characterization methods do not readily provide the kinetic information critical for the assessment of catalytic functionality.

Pioneering kinetic experiments on a single catalytic particle were reported by Zheng et al. [15] CO oxidation was investigated on a 400 μm piece of polycrystalline Pt positioned among hundreds of thousands of inert quartz sand particles. This single catalytic particle was able to convert up to 80% of injected CO molecules when experiments were conducted in the Knudsen transport regime. This surprising finding reflects the stochastic nature of Knudsen diffusion as the means of reactor-scale gas transport, which allows previously unreacted CO molecules to attempt multiple approaches towards the reactive Pt surface during the course of a single experiment. Feres et al. [16] have also shown that the position of a single particle within the TAP reactor controls the observed conversion rate by determining the probability of such repeated attempts. It should be emphasized that the kinetic data from a single particle represent the ultimate limit in terms of spatial uniformity with which kinetic characteristics can be associated with a

specific state of the catalytic material in the presence of transport and reaction-induced gradients of composition. Thus, by the analogy with REMI analysis [17], a single active particle can be proposed as a sensitive probe of the local transport conditions within a chemical reactor. Furthermore, results from the Knudsen regime were compared to ambient pressure-flow experiments within the same TAP Reactor system, and clear correlations in kinetic behavior were established between the two regimes, illustrating that kinetic information for a single particle is transferable between disparate conditions.

Mutual influence within a swarm of catalytic particles

Next, question arises how multiple catalytic points influence each other when embedded within a larger, transport-influenced field of reactant concentrations inside a catalytic reactor. The dependency of the combined performance of separate active moieties on their separation distance and spatial distribution has been extensively studied by theoretical and experimental methods since the times of Smolukowski's seminal paper [18]. In catalysis, the now classical contributions from Berger et al. [19] demonstrate that "catalyst dilution should be applied with caution since it may significantly influence the conversion and lead to an erroneous interpretation of data", which the authors attributed to axial dispersion and bypassing. Feres et al. [16] have shown that, under the conditions of TAP experiments in the Knudsen regime, two active macroscopic surfaces can exhibit a combined conversion rate that is lower than expected from simply adding the two together. This is explained by the development of the reactant depletion zone between the two surfaces. The same effect of mutual kinetic "shadowing" was recently described for 100 μm-sized catalytic particles by Mirena et al. [20], and the magnitude of this effect was sensitive to the gas transport regime inside the reactor. We hypothesize that similar effects can also be observed at either larger or smaller spatial scales and expect that transient kinetic experiments with different spatial densities and geometric arrangements of active moieties will guide the optimization of mesoscopic catalyst structures as well as structured chemical reactors. For example, such experiments may aid in the design of next generation hybrid catalytic systems, in which multiple ingredients perform different steps of the overall catalytic process, e.g. CO_2-hydrogenating metal oxides mixed with methanol-converting zeolites [21] or multicomponent materials for super dry reforming of CH_4 [22].

Thin Zone – the golden standard for systematic kinetic characterization

Thin Zone (TZ) experiments [23] encompass the next level of the ensemble size probed in transient kinetic experiments. In TZ, a large number of catalytic particles is packed as a narrow layer that, however, uniformly covers the entire cross-section of a tubular reactor. In the axial direction, the thickness of this layer is minimized with respect to the thickness of the surrounding inert zones. If the local gas transport is fast enough with respect to reaction kinetics, the entire length of the packed bed reactor can now be considered as a one-dimensional system which is radially well mixed. Moreover, the active catalytic zone can maintain high degree of spatial uniformity in axial direction, if certain constrains are satisfied for the relative rates of the axial transport and reaction [24]. For practical and statistical reasons, this essentially zero-dimensional configuration is preferred for catalyst characterization because it is relatively easy to implement (e.g. does not require precise 3D positioning of individual particles) and it yields ensemble-averaged kinetic characteristics representative of the entire batch of a catalytic material. At the ambient pressure-flow conditions, the TZ principle takes the form of differential Plug Flow Reactor (dPFR), but with reduced robustness of the transport regime and (typically) reduced temporal resolution [25].

TZ TAP pulse-response experiments in the Knudsen transport regime are particularly attractive for systematic catalyst characterization because they offer superb control over the catalyst uniformity, while providing very accurate millisecond-resolved kinetic characteristics.

Provided that the amount of molecules injected per pulse is much smaller than the total number of active catalytic sites available within the TZ, the catalyst state can be considered as well-defined in both spatial and temporal sense. Then, a large number of such state-defining pulses can be used to implement a well-defined state-altering experiment, in which the catalyst state is purposefully changed in a step-by-step fashion and the impact of this change on reaction kinetics is monitored [23,26].

The unique spatiotemporal uniformity during TZ TAP experiments drastically simplifies the mathematical treatment of experimental data. A one-dimensional reaction-diffusion model with very narrow active zone can efficiently be integrated for the purposes of parameter estimation via non-linear regression [27]. Under certain conditions, TZ TAP data can even be analyzed in a kinetically "model free" manner [28]. For example, moment analysis of pulse-response transients yields a set of Shekhtman reactivities [29,30] – three quantities per pulse per reactant that can be interpreted in terms of general mechanistic aspects of reaction prior to regressing the data with preconceived rival microkinetic models. Analytical relations for translating Shekhtman reactivities into apparent kinetic coefficients are available for many limiting cases of common microkinetic models, which allows for rapid data evaluation. An even more powerful strategy for kinetically "model free" TZ TAP data analysis is to reconstruct entire time-resolved histories of the transformation rates and gaseous concentrations for each reactant from their experimentally observed exit flow rate transients via an algorithm known as the Y-Procedure [31]. The availability of rate-concentration {R,C}(t) dependencies for a well-defined state of the catalyst with millisecond time resolution unlocks unprecedented avenues for understanding of transient kinetic data. Instantaneous accumulation (surface storage) of molecules, stable molecular motifs, and atoms can be inferred from transient transformation rates of gas substances [32], and these {S}(t) quantities can be used as compositional descriptors of the transient catalyst state. Even straightforward comparison of the absolute values and temporal characteristics of surface descriptors with the rate-concentration transients can offer deep insights into the mechanism of the underlying catalytic reactions [33–37]. Furthermore, these {R,C,S}(t) transients can serve as a basis for high-throughput and highly standardized kinetic characterization of many possible in situ evolving catalyst states for series of materials spanning large compositional and structural spaces. The Rate-Reactivity Model (RRM) [38] was proposed as the mathematical conduit for this purpose.

Bridging pressure regimes for deeper understanding of the material and reaction

Having bridged the scales of spatio-temporal uniformity, from a single catalytic particle to ensemble-averaged Thin Zone, we now turn to bridging various operating pressure regimes. The divergence and the need for reconciliation between the fields of applied catalysis and surface science have been at the center of discourse for many decades [39]. The infamous "gaps" have separated the opposite corners of the pressure-materials complexity diagram and, often, the opposite wings of chemistry departments. In the first half of the XXI century, building bridges across the knowledge gaps has rapidly accelerated in the catalytic experiment and theory. A lot of attention have been recently drawn to the advent of *operando* methodologies [40–43] and the achievement of precise control over materials synthesis [44], which now enable comprehensive structural and spectroscopic investigations of even complex materials across wide ranges of operating conditions. However, the role of kinetics in reconciling disparate observations between realistic and model materials and reactions has not been sufficiently emphasized.

From their early days, TAP Reactor Systems enabled the comparison of reaction kinetics for the same sample between different experimental conditions. The case study of n-butane partial oxidation over Vanadium Phosphorous Oxide (VPO) catalysts by Schuurman and Gleaves [45,46] provides an illuminating example of this approach. Industrial selective

oxidation of n-butane into Maleic Anhydride (MA) employed VPO catalysts for many years without the complete understanding of the active phase and intrinsic structure-activity relationships governing their performance. It was noticed in industrial laboratories that hot air treatment of the catalyst after each experimental (steady-state) run, which was apparently conducted for coke removal, improved the catalyst performance in the beginning of subsequent experiment. The origin of this activity improvement remained obscured for a long time, in part because steady-state data do not easily reveal such mechanistic insights. Comparison of the steady-state ambient pressure-flow and the transient Knudsen regime pulse-response experiments, both conducted in a TAP Reactor System, eventually revealed that the average oxidation state of the surface strongly affects the reaction performance. The activation energy decreased from 22 to 12 kkal/mol upon increasing the oxidation state. In combination with Raman spectroscopy, TAP experiments have further demonstrated that high-temperature 530 ºC anaerobic temperature excursions cause the formation of less active $VOPO_4$ phase.

The key role of transient kinetics for successful reconciliation of knowledge across wide ranges of operating conditions can be appreciated with great clarity from a recent study of methanol oxidative coupling on nanoporous Au catalysts by Reece et al. [47]. On pre-oxidized Au surfaces, both on a single crystal under UHV and npAu under ambient pressure-flow conditions, methanol selectively couples into Methyl Formate (MF) with parallel formation of CO_2 as a side product via total combustion. Surprisingly, Knudsen regime TAP pulse-response experiments intermediate-pressure conditions, also revealed the formation of formaldehyde in significant amounts on npAu. Experimental data from all three regimes (UHV, TAP, ambient flow) could be reconciled using the same microkinetic model that could explain the observed differences in reaction selectivity under different conditions by its strong correlation to oxygen surface coverage. This work highlights the importance of systematic comparisons of kinetic characteristics across different conditions as an indispensable tool for establishing a more generally valid understanding of the catalytic chemistry.

One of the factors contributing to successful data reconciliation in methanol oxidative coupling example above is that a technologically-relevant npAu material exhibited a similar microstructure as the model Au single crystal surface [48]. Most materials in applied catalysis do not provide such fortuitous equivalency of microstructure under drastically different reaction environments. Depending on the chemical potential of various species, structural phase changes may lead to the formation of new active sites and/or reaction intermediates at ambient pressure flow conditions which are not readily accessible under lower pressure conditions of TAP and UHV experiments. In these situations, it is especially fruitful to be able to rapidly and reproducibly expose the same sample to different conditions – an advantage offered (nearly uniquely) by the TAP Reactor Systems. For many reactions of industrial importance, the in situ emergent active states of the catalyst are unstable and quickly decay under lower pressures. Examples of such reversible behavior include surface and subsurface oxides, hydrides, and dense adsorbate over-layers. In these challenging cases, transient kinetic experiments under various conditions can be used to map out the range of conditions conducive to the formation of the target active microstructures and help design proper experiments for accessing the required kinetic information.

Another challenge in transient reaction investigations under low pressure conditions that can result in a perceived "pressure gap" in the observed kinetics stems from intrinsically slow rate-determining steps in the catalytic mechanism. The typical sensitivity range of Knudsen pulse-response TAP experiments is determined by the ratio of characteristic time scales of reaction and gas transport. Outside this window of sensitivity, reactions are either too fast, leading to complete conversion, or too slow, resulting in negligible conversion. Many important reactions involved in large-scale industrial processes, unfortunately, fall under this category. CO_2 hydrogenation and NH_3 synthesis are quintessential examples in this category. In this perspective, we would like to highlight several highly motivational studies in which TAP Reactor Systems were utilized to derive useful information even for these challenging reactions. Goguet et al. [49] directly observed CO_2 hydrogenation into CO via the Reverse Water Gas Shift (RWGC) reaction under Knudsen conditions on a highly active Pt/CeO_2 catalyst and were able to infer the lifetimes of surface intermediates in pump-probe experiments with CO_2 and H_2. Behm group have extensively used TAP-like titration sequences to quantify the formation of oxygen vacancies in oxide-supported Au catalysts, which plays an important role in CO_2 hydrogenation to methanol on these materials [50]. TAP experiments under Knudsen conditions have recently been used by Wang et al. [37] to derive new fundamental information about the kinetics and thermodynamics of ammonia synthesis on Fe and Co surfaces.

Low-pressure transient experiments for studies of microporous materials

Transient kinetic studies in the context of catalysis by microporous materials, particularly by acidic zeolites and zeotypes, are distinguished by having to address the strong coupling between chemical reactions, confinement effects, and porous diffusion. A growing body of literature (vide infra) suggests that certain aspects of catalytic kinetics in zeolites can be discerned in much more detail is the measurements are conducted under relatively low pressures ($<10^{-2}$ mbar) in comparison with typical operating conditions (1–10 bar). The advantages of low-pressure regimes for kinetic studies of zeolites stem from the reduced exposure of the catalyst to reactants, which is beneficial for precise quantification of individual reaction pathways and porous diffusion. Reduced exposure to reactants prevents pore crowding and hinders secondary, bimolecular, and deactivation reactions. Furthermore, direct sampling of the reactor effluent into a mass-spectrometry chamber can be more readily implemented for the maximal possible time resolution and sensitivity. Highly specific transient data about individual reactions can be obtained under such low-pressure conditions, which augment the global steady-state kinetics at industrially-relevant conditions to achieve better grasp of structure-activity relationships.

Transient methods trace a prominent history of applications in studies of microporous diffusion in zeolites and zeotypes. More narrowly, TAP pulse-response experiments in the Knudsen regime provide a sensitive probe of adsorption and intracrystalline diffusion kinetics in microporous materials within an adjustable window of operating conditions and materials characteristics. Unlike other state-of-the-art methods for diffusion quantification, like interference IR microscopy [14] and PFG NMR [51], transient kinetic methods with gas-phase quantification are also suitable for measurements of intrinsic catalytic kinetics. Depending on specific combinations of host materials, probe molecules, and catalytic reactions, intracrystalline diffusion may or may not play a role in determining the outcome of such measurements. Under low temperature conditions, TAP data yield quantitative data on diffusion of many probe molecules that can in principle be compared to ab initio calculations and PFG NMR measurements [52]. Under relatively high reaction temperatures typical for the methanol-to-olefins (MTO) and ethanol-to-olefins processes (300–400 C), on the other hand, the kinetics of catalytic transformations of light hydrocarbons in open 3D pore networks, like fresh ZSM-5 materials with MFI structure, do not bare signs of diffusion limitations [53]. However, partially coked MFI materials and more restricted pore systems, like ZSM-22 TON structure [54], can become sensitive to these effects even at reaction temperatures. Therefore, precise time-resolve diffusion quantification under low-pressure conditions is essential for extracting the intrinsic kinetic information. Brogaard et al. [55] and Redekop et al. [54] have successfully demonstrated this approach for the step-wise alkene methylation in ZSM-22, whereby the extracted TAP-derived kinetics was in quantitative agreement with theory. These promising results suggest that TAP and TAP-like experiments can yield unique information about chemistry and chemistry-transport interactions in microporous materials.

In accordance with the strategy advocated in this perspective, the kinetic at Knudsen conditions must ultimate be reconciled with high

pressure operating conditions. While it is very challenging to observe some reactions below ambient pressure, like CO_2 hydrogenation, other industrially-relevant reactions readily occur even at low pressures. For example, the C-C coupling reactions involved in the Methanol-To-Hydrocarbons (MTH) process have been observed already in the Knudsen transport regime [54], albeit it took thousands of pulses to establish the hydrocarbon pool intermediates and produce ethylene – the first C-C coupling product. Increasing the feed pressure of DME to as low as 10^{-6} mbar resulted in a shorter induction period and considerable production of light alkene MTH products. Importantly, these reactions could be observed separately from the aromatics-forming pathways that required even higher DME partial pressure for gaining prominence. Omojola et al. [56,57] have pursued non-steady-state investigations of MTO reactions on ZSM-5 in the intermediate pressure range (< 10 mbar), and we expect that systematic quantification and comparison of zeolite-mediated kinetics across various pressure regimes will bring about significant breakthroughs in this field [58]. Furthermore, we predict that reconcilable time- and space-resolved kinetic information will in the near future be available from complementary characterization methods, e.g. *operando* IR microscopy [59].

Methodological vision

Having outlined some of the leading trends and persisting challenges faced by the diverse field of transient kinetics, we would like to propose a concise yet far-reaching experimental and theoretical program in kinetics that could be used to harness the power of transient experimentation for revolutionary breakthroughs in catalysis:

- Extract transport-free, non-steady-state kinetic data for catalytic processes, delineating them from data related to mass- and heat transfer.
- Determine the intrinsic parameters of individual steps comprising catalytic cycles (adsorption, desorption, transformations, catalyst deactivation) and the corresponding number of active sites.
- Establish the kinetic fingerprints of structural changes that occur at the catalytic surface under well-defined model and operando conditions.
- Develop the methodology of catalyst design assisted by the no-steady-state kinetic characterization of catalytic reactions themselves and the catalyst restructuring under the influence of reaction conditions.
- Reconcile data obtained using different traditional approaches, i.e. steady-state industrial kinetics and surface science approach, and continuously evolving transient methodologies in reaction kinetics and surface spectroscopy.

This program requires a highly automated, one-device workflow for the comprehensive exploration and mapping of various kinetic states of the same (complex) material, which emerge during standardized pretreatment sequences and reaction conditions. The state-of-the-art TAP Reactor Systems cover most of the relevant pressure regimes for such exploration, ranging from the signature Knudsen flow (10^{-9}-10^{-7} mbar), through the transition region of molecular flow (10^{-7}-10^{-6}) and sub-ambient viscous flow (10^{-6}-10^{3} mbar), to slightly above ambient pressure (1–1.5 bar) flow. At all these conditions, transient (10^{-3}-10^{3} s) and steady-state experiments are enabled by combining high-speed pulse-valves for imposing gas-phase perturbations with time-resolved mass-spectrometry for effluent analytics.
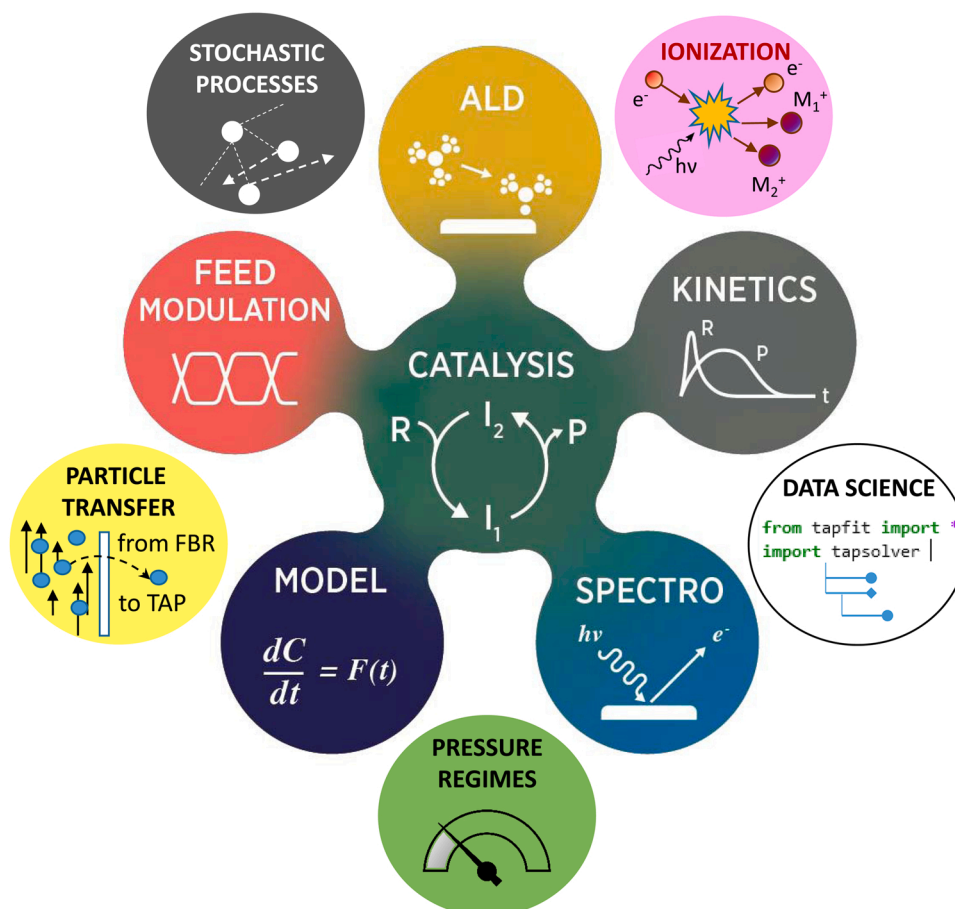
Finally, we would like to briefly outline several concrete research avenues that, in our opinion, will shape the future of transient kinetics in years to come:

- Building on the initial success of single particle TAP experiments [15], stochastic reaction –diffusion modeling [16], and ensemble measurements [20], unexpected discoveries are expected at the limit of studying the kinetics of various ensembles of catalytic points and minimally representative systems. Further progress in this direction will require experimental methods for precise positioning of individual catalytic points within reactor devices and quantitative analysis of the resulting transient reaction-diffusion data accounting for such arrangements.
- Wide-spread use of already available [60,61] and yet to be developed software for transient transport-reaction modeling, coupled with the emerging data science pipelines [62,63] and advanced instrument automation [64] will enable better data integration and knowledge discovery, especially within the framework of tailored mathematical models like the Rate-Reactivity Model (RRM) [38].
- Coupling of transient gaseous kinetics to transient surface spectroscopy, e.g. XAS [65–67] and AP-XPS [68–73], will be used as a means to further reconcile the observed kinetics with the dynamic structural and spectroscopic features of catalytic surface.
- Application of step-response, frequency response, and concentration Modulation Excitation Spectroscopy (cMES) techniques [74] to spectroscopic and kinetic data in the intermediate pressure conditions.
- Tandem use of transient kinetic characterization and incremental (in situ) materials synthesis [75] will allow for exploratory surface synthesis, discovery of structure-performance relationships, and phenomenological catalyst optimization. We expect particularly integration of transient kinetics with the synthesis techniques based on the gas-phase precursor delivery and physical deposition methods that can more readily be automated and integrated within the tandem instruments. The most promising techniques include Atomic Beam Deposition (ABD) [26], magnetron sputtering [76], Atomic Layer Deposition (ALD) [73,77–79], and spark ablation [80].
- Particle extraction from fluidized bed reactors operating under realistic conditions and their transfer into transient, TAP-like kinetic characterization modules will facilitate more systematic comparisons of reaction kinetics between drastically different reactor devices.
- Energy-selective photo- and electron impact ionization mass-spectrometry [81] will achieve quantitative analysis of isomeric distribution in the reactor effluents, including sub-second resolved experiments, and will enable quantification of highly-reactive intermediates like radicals or formaldehyde [82].
- Low-pressure studies of zeolite-catalyzed reactions on technologically-relevant [54,57] and atomically well-defined model [83] materials will unravel unprecedented details the reaction-diffusion coupling in microporous materials and their governing structure-reactivity correlations.
- Finally, systematic exploration of steady-state and non-steady-state regimes in the intermediate pressure range [84] will bring the molecular-scale fundamental discoveries in Transient Kinetics to technological fruition for the benefit of novel, more sustainable chemical technologies. The key technologies required to be perfected for unlocking the full potential of this approach include rapid, highly-repeatable modulation of the reactant feed with reliable and versatile injection devices at intermediate to high pressures and the development of advanced pressure/vacuum interfaces for efficient sampling of the reactor effluents into the ionizing regions of mass-spectrometers (slide-valves and skimmers in differentially-pumped systems).

Broader vision and perspective

Ultimately, precise knowledge and control of Transient Kinetics will enable paradigm-shifting technologies for chemical conversion, whereby kinetics-assisted evolution of the catalyst state in space and time is used to optimize the overall process. Spatio-temporal orchestration of the catalyst state can be used to pursue several strategies including the optimization of.

- steady-state operating conditions
- catalyst lifetime
- industrial safety
- sensing and process control
- non-steady-state operating conditions [85]
- rates of reaction steps on time scales of catalytic cycles (i.e. catalytic resonance [86])
- rates of reaction steps on various length scales, from the nano- and micrometer scale of composite catalytic materials (e.g. multifunctional and hybrid catalysts, including electrodes) through the meso-scale of combined, multi-structural materials used in chemical looping and 3D-rinted or extruded catalytic bodies.

If this goal is to be achieved, a combination of rational design, incremental and exploratory synthesis, advanced spectro-kinetic interrogation, reactor engineering, intricately controlled external stimuli (electro-magnetic fields, flow hydrodynamics, thermal and mechanical energy transfer, chemical feed composition, etc.), and a good deal of creativity must be used in unison.

CRediT authorship contribution statement

Evgeniy A. Redekop: Writing – original draft preparation, Supervision, Project administration. **Gregory S. Yablonsky:** Conceptualization. **John T. Gleaves:** Conceptualization, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

References

[1] G.B. Marin, G.S. Yablonsky, Kinetics of Chemical Reactions: Decoding Complexity, Wiley-VCH, 2011.

[2] J.T. Gleaves, J.R. Ebner, T.C. Kuechler, Temporal analysis of products (TAP) - a unique catalyst evaluation system with submillisecond time resolution, Catal. Rev. 30 (1) (1988) 49–116, https://doi.org/10.1080/01614948808078616.

[3] J.T. Gleaves, G. Yablonsky, X. Zheng, R. Fushimi, P.L. Mills, Temporal analysis of products (TAP) - recent advances in technology for kinetic analysis of multi-component catalysts, J. Mol. Catal. A: Chem. 315 (2) (2010) 108–134, https://doi.org/10.1016/j.molcata.2009.06.017.

[4] K. Morgan, N. Maguire, R. Fushimi, J.T. Gleaves, A. Goguet, M.P. Harold, E. V. Kondratenko, U. Menon, Y. Schuurman, G.S. Yablonsky, Forty years of temporal analysis of products, Catal. Sci. Technol. 7 (12) (2017) 2416–2439, https://doi.org/10.1039/C7CY00678K.

[5] G.B. Marin, V.V. Galvita, G.S. Yablonsky, Kinetics of chemical processes: from molecular to industrial scale, J. Catal. 404 (2021) 745–759, https://doi.org/10.1016/j.jcat.2021.09.014.

[6] M.P. D'Evelyn, R.J. Madix, Reactive scattering from solid surfaces, Surf. Sci. Rep. 3 (8) (1983) 413–495, https://doi.org/10.1016/0167-5729(83)90002-X.

[7] J. Libuda, Reaction kinetics on model catalysts: molecular beam methods and time-resolved vibrational spectroscopy, Surf. Sci. 587 (1–2) (2005) 55–68, https://doi.org/10.1016/j.susc.2005.04.030.

[8] F.M. Dautzenberg, ChemInform Abstract: Quality Principles for Catalyst Testing During Process Development, ChemInform 32 (21) (2001) no–no, https://doi.org/10.1002/chin.200121288.

[9] M.P. Dudukovic, Frontiers in reactor engineering, Science 325 (5941) (2009) 698–701, https://doi.org/10.1126/science.1174274.

[10] J.T. Gleaves, G.S. Yablonskii, P. Phanawadee, Y. Schuurman, TAP-2: an interrogative kinetics approach, Appl. Catal. A: Gen. 160 (1) (1997) 55–88, https://doi.org/10.1016/S0926-860X(97)00124-5.

[11] D.S. Wragg, G.N. Kalantzopoulos, D.K. Pappas, I. Pinilla-Herrero, D. Rojo-Gama, E. Redekop, M. Di Michiel, P. Beato, L.F. Lundegaard, S. Svelle, Mapping the coke formation within a zeolite catalyst extrudate in space and time by operando computed X-ray diffraction tomography, J. Catal. 401 (2021) 1–6, https://doi.org/10.1016/j.jcat.2021.07.001.

[12] Life and death of a single catalytic cracking particle https://www.science.org/doi/10.1126/sciadv.1400199 (accessed 2022 -01 -31).

[13] A. Martinelli, S. Creci, S. Vavra, P.-A. Carlsson, M. Skoglundh, Local anisotropy in single crystals of zeotypes with the MFI framework structure evidenced by polarised Raman spectroscopy, Phys. Chem. Chem. Phys. 22 (3) (2020) 1640–1654, https://doi.org/10.1039/C9CP06199A.

[14] J. Kärger, T. Binder, C. Chmelik, F. Hibbe, H. Krautscheid, R. Krishna, J. Weitkamp, Microimaging of transient guest profiles to monitor mass transfer in nanoporous materials, Nat. Mater. 13 (4) (2014) 333–343, https://doi.org/10.1038/nmat3917.

[15] X. Zheng, J.T. Gleaves, G.S. Yablonsky, T. Brownscombe, A. Gaffney, M. Clark, S. Han, Needle in a haystack catalysis, Appl. Catal. A: Gen. 341 (1–2) (2008) 86–92, https://doi.org/10.1016/j.apcata.2008.02.040.

[16] R. Feres, G.S. Yablonsky, A. Mueller, A. Baernstein, X. Zheng, J.T. Gleaves, Probabilistic analysis of transport–reaction processes over catalytic particles: theory and experimental testing, Chem. Eng. Sci. 64 (3) (2009) 568–581, https://doi.org/10.1016/j.ces.2008.09.033.

[17] G.S. Yablonsky, D. Constales, G.B. Marin, A new approach to diagnostics of ideal and non-ideal flow patterns: i. the concept of reactive-mixing index (REMI) analysis, Chem. Eng. Sci. 64 (23) (2009) 4875–4883, https://doi.org/10.1016/j.ces.2009.07.026.

[18] M. v Smoluchowski, Versuch einer mathematischen Theorie der Koagulationskinetik kolloider Lösungen, Z. für Phys. Chem. 92U (1) (1918) 129–168, https://doi.org/10.1515/zpch-1918-9209.

[19] R.J. Berger, J. Perez-Ramirez, F. Kapteijn, J.A. Moulijn, Catalyst performance testing: bed dilution revisited, Chem. Eng. Sci. 57 (22–23) (2002) 4921–4932, https://doi.org/10.1016/S0009-2509(02)00273-7.

[20] J.I. Mirena, E. Redekop, H. Poelman, N.V. Srinath, D. Constales, G.B. Marin, G.S. Yablonsky, J.T. Gleaves, V.V. Galvita, Shadowing effect in catalyst activity: experimental observation, ACS Catal. (2022) 5455–5463, https://doi.org/10.1021/acscatal.2c00818.

[21] P. Ticali, D. Salusso, R. Ahmad, C. Ahoba-Sam, A. Ramirez, G. Shterk, K.A. Lomachenko, E. Borfecchia, S. Morandi, L. Cavallo, J. Gascon, S. Bordiga, U. Olsbye, CO₂ hydrogenation to methanol and hydrocarbons over bifunctional Zn-Doped ZrO2/Zeolite catalysts, Catal. Sci. Technol. 11 (4) (2021) 1249–1268, https://doi.org/10.1039/D0CY01550D.

[22] L.C. Buelens, V.V. Galvita, H. Poelman, C. Detavernier, G.B. Marin, Super-dry reforming of methane intensifies CO2 utilization via Le Chatelier's principle, Science (2016).

[23] S.O. Shekhtman, G.S. Yablonsky, J.T. Gleaves, R.R. Fushimi, Thin-zone TAP reactor as a basis of "state-by-state transient screening, Chem. Eng. Sci. 59 (22–23) (2004) 5493–5500, https://doi.org/10.1016/j.ces.2004.09.015.

[24] S.O. Shekhtman, G.S. Yablonsky, T.A.P. Thin-Zone, Reactor versus differential PFR: analysis of concentration nonuniformity for gas-solid systems, Ind. Eng. Chem. Res. 44 (16) (2005) 6518–6522, https://doi.org/10.1021/ie050554g.

[25] A. Bundhoo, J. Schweicher, A. Frennet, N. Kruse, Chemical transient kinetics applied to CO hydrogenation over a pure nickel catalyst, J. Phys. Chem. C. 113 (24) (2009) 10731–10739, https://doi.org/10.1021/jp902647z.

[26] R. Fushimi, J.T. Gleaves, G. Yablonsky, A. Gaffney, M. Clark, S. Han, Combining TAP-2 experiments with atomic beam deposition of Pd on Quartz particles, Catal. Today 121 (3–4) (2007) 170–186, https://doi.org/10.1016/j.cattod.2006.07.061.

[27] R. Roelant, D. Constales, R. Van Keer, G.B. Marin, Second-order statistical regression and conditioning of replicate transient kinetic data, Chem. Eng. Sci. 63 (7) (2008) 1850–1865, https://doi.org/10.1016/j.ces.2007.12.012.

[28] R. Roelant, D. Constales, R. Van Keer, G.B. Marin, Deduction of connectivity features of pseudomonomolecular reaction networks from thin-zone-TAP-data, Chem. Eng. Sci. 83 (2012) 39–49, https://doi.org/10.1016/j.ces.2011.10.038.

[29] S.O. Shekhtman, N. Maguire, A. Goguet, R. Burch, C. Hardacre, Three primary kinetic characteristics observed in a pulse-response TAP experiment, Catal. Today 121 (3–4) (2007) 255–260, https://doi.org/10.1016/j.cattod.2006.08.068.

[30] D. Constales, G.S. Yablonsky, L. Wang, W. Diao, V.V. Galvita, R. Fushimi, Precise non-steady-state characterization of solid active materials with no preliminary mechanistic assumptions, Catal. Today 298 (2017) 203–208, https://doi.org/10.1016/j.cattod.2017.04.036.

[31] G.S. Yablonsky, D. Constales, S.O. Shekhtman, J.T. Gleaves, The Y-procedure: how to extract the chemical transformation rate from reaction-diffusion data with no

[32] E.A. Redekop, G.S. Yablonsky, D. Constales, P.A. Ramachandran, C. Pherigo, J.T. Gleaves, The Y-procedure methodology for the interpretation of transient kinetic data: analysis of irreversible adsorption, Chem. Eng. Sci. 66 (24) (2011) 6441–6452, https://doi.org/10.1016/j.ces.2011.08.055.

[33] E.A. Redekop, G.S. Yablonsky, D. Constales, P.A. Ramachandran, J.T. Gleaves, G.B. Marin, Elucidating complex catalytic mechanisms based on transient pulse-response kinetic data, Chem. Eng. Sci. 110 (2014) 20–30, https://doi.org/10.1016/j.ces.2013.11.050.

[34] E.A. Redekop, G.S. Yablonsky, V.V. Galvita, D. Constales, R. Fushimi, J.T. Gleaves, G.B. Marin, Momentary equilibrium in transient kinetics and its application for estimating the concentration of catalytic sites, Ind. Eng. Chem. Res. 52 (44) (2013) 15417–15427, https://doi.org/10.1021/ie400677b.

[35] Y. Wang, M.R. Kunz, Z. Fang, G. Yablonsky, R. Fushimi, Accumulation dynamics as a new tool for catalyst discrimination: an example from ammonia decomposition, Ind. Eng. Chem. Res. 58 (24) (2019) 10238–10248, https://doi.org/10.1021/acs.iecr.9b01470.

[36] Y. Wang, M.R. Kunz, D. Constales, G. Yablonsky, R. Fushimi, Rate/concentration kinetic petals: a transient method to examine the interplay of surface reaction processes, J. Phys. Chem. A 123 (40) (2019) 8717–8725, https://doi.org/10.1021/acs.jpca.9b05911.

[37] Y. Wang, J. Qian, Z. Fang, M.R. Kunz, G. Yablonsky, A. Fortunelli, W.A. Goddard III, R.R. Fushimi, Understanding reaction networks through controlled approach to equilibrium experiments using transient methods, J. Am. Chem. Soc. 143 (29) (2021) 10998–11006, https://doi.org/10.1021/jacs.1c03158.

[38] G.S. Yablonsky, E.A. Redekop, D. Constales, J.T. Gleaves, G.B. Marin, Rate-reactivity model: a new theoretical basis for systematic kinetic characterization of heterogeneous catalysts, Int. J. Chem. Kinet. 48 (6) (2016) 304–317, https://doi.org/10.1002/kin.20988.

[39] H.-J. Freund, H. Kuhlenbeck, J. Libuda, G. Rupprechter, M. Bäumer, H. Hamann, Bridging the pressure and materials gaps between catalysis and surface science: clean and modified oxide surfaces, Top. Catal. 15 (2) (2001) 201–209, https://doi.org/10.1023/A:1016686322301.

[40] M.A. Banares, Operando methodology: combination of in situ spectroscopy and simultaneous activity measurements under catalytic reaction conditions, Catal. Today 100 (1–2) (2005) 71–77, https://doi.org/10.1016/j.cattod.2004.12.017.

[41] S. Alayoglu, J.M. Krier, W.D. Michalak, Z. Zhu, E. Gross, G.A. Somorjai, In situ surface and reaction probe studies with model nanoparticle catalysts, ACS Catal. 2 (11) (2012) 2250–2258, https://doi.org/10.1021/cs3004903.

[42] S. Bordiga, E. Groppo, G. Agostini, J.A. van Bokhoven, C. Lamberti, Reactivity of surface species in heterogeneous catalysts probed by in situ x-ray absorption techniques, Chem. Rev. 113 (3) (2013) 1736–1850, https://doi.org/10.1021/cr2000898.

[43] A.M. Beale, S.D.M. Jacques, B.M. Weckhuysen, Chemical imaging of catalytic solids with synchrotron radiation, Chem. Soc. Rev. 39 (12) (2010) 4656–4672, https://doi.org/10.1039/C0CS00089B.

[44] H. Freund, J. Libuda, M. Baumer, T. Risse, A. Carlsson, Cluster, facets, and edges: site-dependent selective chemistry on model catalysts, Chem. Rec. 3 (3) (2003) 181–201, https://doi.org/10.1002/tcr.10060.

[45] Y. Schuurman, J.T. Gleaves, Activation of vanadium phosphorus oxide catalysts for alkane oxidation. the influence of the oxidation state on catalyst selectivity, Ind. Eng. Chem. Res. 33 (12) (1994) 2935–2941, https://doi.org/10.1021/ie00036a007.

[46] Y. Schuurman, J.T. Gleaves, A comparison of steady-state and unsteady-state reaction kinetics of n-butane oxidation over VPO catalysts using a TAP-2 reactor system, Catal. Today 33 (1) (1997) 25–37, https://doi.org/10.1016/S0920-5861(96)00115-0.

[47] C. Reece, E.A. Redekop, S. Karakalos, C.M. Friend, R.J. Madix, Crossing the great divide between single-crystal reactivity and actual catalyst selectivity with pressure transients, Nat. Catal. 1 (11) (2018) 852–859, https://doi.org/10.1038/s41929-018-0167-5.

[48] K.J. Stowers, R.J. Madix, C.M. Friend, From model studies on Au(1 1 1) to working conditions with unsupported nanoporous gold catalysts: oxygen-assisted coupling reactions, J. Catal. 308 (2013) 131–141, https://doi.org/10.1016/j.jcat.2013.05.033.

[49] A. Goguet, S.O. Shekhtman, R. Burch, C. Hardacre, F.C. Meunier, G.S. Yablonsky, Pulse-response TAP studies of the reverse water–gas shift reaction over a Pt/CeO2 catalyst, J. Catal. 237 (1) (2006) 102–110, https://doi.org/10.1016/j.jcat.2005.10.020.

[50] A.M. Abdel-Mageed, M. Büsselmann, K. Wiese, C. Fauth, R.J. Behm, Influence of water vapor on the performance of Au/ZnO catalysts in methanol synthesis from CO2 and H2: a high-pressure kinetic and TAP reactor study, Appl. Catal. B: Environ. 297 (2021), 120416, https://doi.org/10.1016/j.apcatb.2021.120416.

[51] J. Kärger, M. Avramovska, D. Freude, J. Haase, S. Hwang, R. Valiullin, Pulsed field gradient nmr diffusion measurement in nanoporous materials, Adsorption 27 (3) (2021) 453–484, https://doi.org/10.1007/s10450-020-00290-9.

[52] P. Cnudde, E.A. Redekop, W. Dai, N.G. Porcaro, M. Waroquier, S. Bordiga, M. Hunger, L. Li, U. Olsbye, V. Van Speybroeck, Experimental and theoretical evidence for the promotional effect of acid sites on the diffusion of alkenes through small-pore zeolites, Angew. Chem. Int. Ed. 60 (18) (2021) 10016–10022, https://doi.org/10.1002/anie.202017025.

[53] R. Batchu, V.V. Galvita, K. Alexopoulos, Glazneva, S. Tatyana, H. Poelman, M.-F. Reyniers, G.B. Marin, Ethanol dehydration pathways in H-ZSM-5: insights from temporal analysis of products, Catal. Today (2019), https://doi.org/10.1016/j.cattod.2019.04.018.

[54] E.A. Redekop, A. Lazzarini, S. Bordiga, U. Olsbye, A temporal analysis of products (TAP) study of C2-C4 alkene reactions with a well-defined pool of methylating species on ZSM-22 zeolite, J. Catal. 385 (2020) 300–312, https://doi.org/10.1016/j.jcat.2020.03.020.

[55] R.Y. Brogaard, R. Henry, Y. Schuurman, A.J. Medford, P.G. Moses, P. Beato, S. Svelle, J.K. Nørskov, U. Olsbye, Methanol-to-hydrocarbons conversion: the alkene methylation pathway, J. Catal. 314 (2014) 159–169, https://doi.org/10.1016/j.jcat.2014.04.006.

[56] T. Omojola, N. Cherkasov, A.I. McNab, D.B. Lukyanov, J.A. Anderson, E.V. Rebrov, A.C. van Veen, Mechanistic insights into the desorption of methanol and dimethyl ether over ZSM-5 catalysts, Catal. Lett. 148 (1) (2018) 474–488, https://doi.org/10.1007/s10562-017-2249-4.

[57] T. Omojola, D.B. Lukyanov, A.C. Veen, van. Transient kinetic studies and microkinetic modeling of primary olefin formation from dimethyl ether over ZSM-5 catalysts, Int. J. Chem. Kinet. 51 (7) (2019) 528–537, https://doi.org/10.1002/kin.21275.

[58] T. Omojola, A.J. Logsdail, A.C. van Veen, S.A.F. Nastase, A quantitative multiscale perspective on primary olefin formation from methanol, Phys. Chem. Chem. Phys. 23 (38) (2021) 21437–21469, https://doi.org/10.1039/D1CP02551A.

[59] I.B. Minova, S.K. Matam, A. Greenaway, C.R.A. Catlow, M.D. Frogley, G. Cinque, P.A. Wright, R.F. Howe, Elementary steps in the formation of hydrocarbons from surface methoxy groups in HZSM-5 seen by synchrotron infrared microspectroscopy, ACS Catal. 9 (7) (2019) 6564–6570, https://doi.org/10.1021/acscatal.9b01820.

[60] A. Yonge, M.R. Kunz, R. Batchu, Z. Fang, T. Issac, R. Fushimi, A.J. Medford, TAPsolver: a python package for the simulation and analysis of TAP reactor experiments, Chem. Eng. J. 420 (2021), 129377, https://doi.org/10.1016/j.cej.2021.129377.

[61] Roelant, R. Isothermal Characterization of Linear Catalytic Reaction Networks from Transient Experiments, 2009.

[62] M.R. Kunz, A. Yonge, Z. Fang, R. Batchu, A.J. Medford, D. Constales, G. Yablonsky, R. Fushimi, Data driven reaction mechanism estimation via transient kinetics and machine learning, Chem. Eng. J. 420 (2021), 129610, https://doi.org/10.1016/j.cej.2021.129610.

[63] A.J. Medford, M.R. Kunz, S.M. Ewing, T. Borders, R. Fushimi, Extracting knowledge from data through catalysis informatics, ACS Catal. 8 (8) (2018) 7403–7429, https://doi.org/10.1021/acscatal.8b01708.

[64] Fushimi, R.; Xiaolin, Z.; Patrick, M.; Gregory S., Y.; John T., G. Internet Kinetics: Remote Control of Temporal Analysis of Products (TAP) Reactor System. 2011.

[65] A.M. Abdel-Mageed, S. Chen, C. Fauth, T. Häring, J. Bansmann, Fundamental aspects of ceria supported Au catalysts probed by in situ/operando spectroscopy and TAP reactor studies, ChemPhysChem 22 (13) (2021) 1302–1315, https://doi.org/10.1002/cphc.202100027.

[66] A.I. Frenkel, J.A. Rodriguez, J.G. Chen, Synchrotron techniques for in situ catalytic studies: capabilities, challenges, and opportunities, ACS Catal. 2 (11) (2012) 2269–2280, https://doi.org/10.1021/cs3004006.

[67] D. Ferri, M.A. Newton, M. Nachtegaal, Modulation excitation X-ray absorption spectroscopy to probe surface species on heterogeneous catalysts, Top. Catal. 54 (16–18) (2011) 1070–1078, https://doi.org/10.1007/s11244-011-9727-5.

[68] J. Knudsen, T. Gallo, V. Boix, M.D. Strømsheim, G. D'Acunto, C. Goodwin, H. Wallander, S. Zhu, M. Soldemo, P. Lömker, F. Cavalca, M. Scardamaglia, D. Degerman, A. Nilsson, P. Amann, A. Shavorskiy, J. Schnadt, Stroboscopic operando spectroscopy of the dynamics in heterogeneous catalysis by event-averaging, Nat. Commun. 12 (1) (2021) 6117, https://doi.org/10.1038/s41467-021-26372-y.

[69] L. Artiglia, F. Orlando, K. Roy, R. Kopelent, O. Safonova, M. Nachtegaal, T. Huthwelker, J.A. van Bokhoven, Introducing time resolution to detect Ce3+ catalytically active sites at the Pt/CeO2 interface through ambient pressure X-ray photoelectron spectroscopy, J. Phys. Chem. Lett. 8 (1) (2017) 102–108, https://doi.org/10.1021/acs.jpclett.6b02314.

[70] K. Roy, L. Artiglia, J.A. van Bokhoven, Ambient pressure photoelectron spectroscopy: opportunities in catalysis from solids to liquids and introducing time

resolution, ChemCatChem 10 (4) (2018) 666–682, https://doi.org/10.1002/cctc.201701522.

[71] A. Shavorskiy, G. D'Acunto, V. Boix de la Cruz, M. Scardamaglia, S. Zhu, R.H. Temperton, J. Schnadt, J. Knudsen, Gas pulse–X-ray probe ambient pressure photoelectron spectroscopy with submillisecond time resolution, ACS Appl. Mater. Interfaces 13 (40) (2021) 47629–47641, https://doi.org/10.1021/acsami.1c13590.

[72] E.A. Redekop, N. Johansson, E. Kokkonen, S. Urpelainen, F. Lopes da Silva, M. Kaipio, H.-E. Nieminen, F. Rehman, V. Miikkulainen, M. Ritala, U. Olsbye, Synchronizing gas injections and time-resolved data acquisition for perturbation-enhanced APXPS experiments, Rev. Sci. Instrum. 92 (4) (2021), 044101, https://doi.org/10.1063/5.0039957.

[73] Redekop, E. Aligning Time-Resolved Kinetics (TAP) and Surface Spectroscopy (AP-XPS) for a More Comprehensive Understanding of ALD-Derived 2D and 3D Model Catalysts.

[74] A. Urakawa, T. Bürgi, A. Baiker, Kinetic analysis using square-wave stimulation in modulation excitation spectroscopy: mixing property of a flow-through PM-IRRAS cell, Chem. Phys. 324 (2–3) (2006) 653–658, https://doi.org/10.1016/j.chemphys.2005.12.009.

[75] R. Fushimi, X. Zheng, J.T. Gleaves, G.S. Yablonsky, A. Gaffney, M. Clark, S. Han, Techniques for fabricating nanoscale catalytic circuits, Top. Catal. 49 (3–4) (2008) 167–177, https://doi.org/10.1007/s11244-008-9090-3.

[76] X. Zheng, G.M. Veith, E. Redekop, C.S. Lo, G.S. Yablonsky, J.T. Gleaves, Oxygen and CO adsorption on Au/SiO2 catalysts prepared by magnetron sputtering: the role of oxygen storage, Ind. Eng. Chem. Res. 49 (21) (2010) 10428–10437, https://doi.org/10.1021/ie100547f.

[77] C. Detavernier, J. Dendooven, S.P. Sree, K.F. Ludwig, J.A. Martens, Tailoring nanoporous materials by atomic layer deposition, Chem. Soc. Rev. 40 (11) (2011) 5242–5253, https://doi.org/10.1039/C1CS15091J.

[78] M. Filez, E.A. Redekop, H. Poelman, V.V. Galvita, R.K. Ramachandran, J. Dendooven, C. Detavernier, G.B. Marin, Unravelling the formation of Pt–Ga alloyed nanoparticles on calcined Ga-modified hydrotalcites by in situ XAS, Chem. Mater. 26 (20) (2014) 5936–5949, https://doi.org/10.1021/cm502658d.

[79] J. Camacho-Bunquin, H. Shou, P. Aich, D.R. Beaulieu, H. Klotzsch, S. Bachman, C.L. Marshall, A. Hock, P. Stair, Catalyst synthesis and evaluation using an integrated atomic layer deposition synthesis–catalysis testing tool, Rev. Sci. Instrum. 86 (8) (2015), 084103, https://doi.org/10.1063/1.4928614.

[80] T.V. Pfeiffer, J. Feng, A. Schmidt-Ott, New developments in spark production of nanoparticles, Adv. Powder Technol. 25 (1) (2014) 56–70, https://doi.org/10.1016/j.apt.2013.12.005.

[81] P. Hemberger, J.A. Bokhoven, J. van; Pérez-Ramírez, A. Bodi, New analytical tools for advanced mechanistic studies in catalysis: photoionization and photoelectron photoion coincidence spectroscopy, Catal. Sci. Technol. 10 (7) (2020) 1975–1990, https://doi.org/10.1039/C9CY02587A.

[82] W. Wen, S. Yu, C. Zhou, H. Ma, Z. Zhou, C. Cao, J. Yang, M. Xu, F. Qi, G. Zhang, Y. Pan, Formation and fate of formaldehyde in methanol-to-hydrocarbon reaction: in situ synchrotron radiation photoionization mass spectrometry study, Angew. Chem. Int. Ed. 59 (12) (2020) 4873–4878, https://doi.org/10.1002/anie.201914953.

[83] J.A. Boscoboinik, X. Yu, B. Yang, F.D. Fischer, R. Włodarczyk, M. Sierka, S. Shaikhutdinov, J. Sauer, H.-J. Freund, Modeling zeolites with metal-supported two-dimensional aluminosilicate films, Angew. Chem. Int. Ed. 51 (24) (2012) 6005–6008, https://doi.org/10.1002/anie.201201319.

[84] K.L. Gering, C. Baroi, R.R. Fushimi, Transport modeling and mapping of pulsed reactor dynamics near and beyond the onset of viscid flow, Chem. Eng. Sci. 192 (2018) 576–590, https://doi.org/10.1016/j.ces.2018.07.060.

[85] Y.Sh Matros, Forced unsteady-state processes in heterogeneous catalytic reactors, Can. J. Chem. Eng. 74 (5) (1996) 566–579, https://doi.org/10.1002/cjce.5450740504.

[86] M.A. Ardagh, M. Shetty, A. Kuznetsov, Q. Zhang, P. Christopher, D.G. Vlachos, O.A. Abdelrahman, P.J. Dauenhauer, Catalytic resonance theory: parallel reaction pathway control, Chem. Sci. 11 (13) (2020) 3501–3510, https://doi.org/10.1039/C9SC06140A.