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Advances in dynamically controlled catalytic reaction engineering†

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Transient reaction modulation has found its place in many branches of chemical reaction engineering over the past hundred years. Historically, catalytic reactions have been dominated by the impulse to reduce spatial and temporal perturbations in favor of steady, static systems due to their ease of operation and scalability. Transient reactor operation, however, has seen remarkable growth in the past few decades, where new operating regimes are being revealed to enhance catalytic reaction rates beyond the statically achievable limits classically described by thermodynamics and the Sabatier principle. These theoretical and experimental studies suggest that there exists a resonant frequency which coincides with its catalytic turnover that can be exploited and amplified for a given reaction to overcome classical barriers. This review discusses the evolution of thought from thermostatic (equilibrium), to thermodynamic (dynamic equilibrium), and finally dynamic (non-equilibrium) catalysis. Natural and forced dynamic oscillations are explored with periodic reactor operation of catalytic systems that modulate energetics and local concentrations through a multitude of approaches, and the challenges to unlock this new class of catalytic reaction engineering is discussed.

Introduction

The field of heterogeneous catalysis has undergone a series of major transformations as our understanding of the physical world has evolved to describe the molecular interactions as thermostatic (equilibrium), to thermodynamic (dynamic equilibrium), and now finally truly dynamic (non-equilibrated) catalysis. Dynamic catalysis—the ability of a material to accelerate a reaction under forced periodic input perturbations—promises to fundamentally shift the field of surface catalysis. The concept merges classical catalytic surface kinetics with periodic oscillatory control-theory to unlock a new operating window whereby catalytic activity beyond classically perceived thermodynamic limitations is achievable.

In recent years, this concept of dynamic catalysis has garnered an increasing level of attention from researchers aiming to overcome thermodynamic barriers limiting catalytic turnover rates. The importance has been underscored by Dauenhauer,[1,2] Stolte,[3] and Silveston.[4–7] While we understand catalysts to be inherently dynamic materials that change continuously over the duration of a chemical reaction, we have demonstrated an otherwise humbling inability to describe their transient nature and predict their behaviour *a priori*. Haber and Bosch screened thousands of materials in pursuit of an ammonia synthesis catalyst leading to their Nobel prizes in 1918 and 1931, respectively;[8,136] it was not for nearly another century that Ertl would receive a Nobel for being able to describe the mechanism.[9] Only recently with the onset of supercomputing, high throughput thermodynamic modelling, and machine learning has the predictive nature of static catalytic performance begun to be possible.[10–15]

Notably, both the century-old screening and modern computational approach rely on a single underlying concept: a reaction must occur in a well-controlled, steady, static

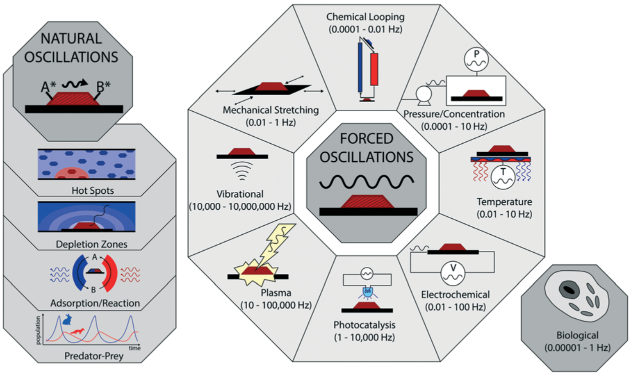

Fig. 1 Schematic overview of naturally occurring oscillations present in catalytic reacting systems and modes for externally engineered forced catalytic oscillations that periodically perturb the reacting surface.

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† Electronic supplementary information (ESI) available: Details on dynamic catalysis in literature used to construct Fig. 7. See DOI: 10.1039/d0re00330a

environment. By operating at such conditions, however, equilibrated surface conditions lead to restrictions on catalytic turnover, often limited by insurmountable constraints such as those described by the linear scaling relationships or volcano plots, despite having global thermodynamically favourable driving forces (*e.g.* ammonia synthesis; C–H activation). This review aims to lay the historical backdrop for reaction engineering approaches that attempt to dynamically tune the surface toward the eventual implementation of truly dynamic catalysis. As outlined in Fig. 1, it will first consider the evolution in our understanding of naturally occurring dynamic reaction oscillations before moving to our ability to achieve stimulated catalytic response through a multitude of engineered forced oscillations.

Evolution of thought: from static to dynamic active sites

The history and evolution of heterogeneous catalysis has been extensively chronicled and reviewed by Robertson,[16] Lindström and Pettersson,[17] and Wisniak,[18] among others. The field was founded upon thermodynamic equilibrium relationships pioneered in the mid-1800's by van't Hoff, Ostwald, and Arrhenius. Our mechanistic understanding became a science with the publication of the first true text on chemical kinetics, *Etudes de dynamique chimique* by van't Hoff in 1884.[19] A rapid period of growth made the first major innovation that is foundational today: chemical reactions are dynamically equilibrated (later extended to surface by Langmuir[20]). This was in contrast to the phenomenological kinetics described by Harcourt and Esson of the same era who described the observable kinetics through differential equations and the law of mass action.[21] The two concepts were reconciled in the unifying theory of Marcelin that introduced standard Gibbs energy to describe a reaction along a potential energy surface. This perspective is combined with several key advances in the 20th century, namely a) statistical and transition state theories of Eyring, b) equilibrated surface kinetics by Langmuir and Hinshelwood, and later c) advanced thermodynamic calculations through density functional theory (DFT). Collectively, this has led us to our current ability to describe in great detail the mechanism, energetics, and kinetics for elementary surface catalysed reactions from first principles.

Notably, however, the above-described progression still relies on approximations to dampen dynamical effects resulting from fast equilibrium steps followed by either slow kinetic steps that require overcoming energetic barriers, reaction transients, or spatial gradients. While approximations such as pseudo-steady state (PSS) or most abundant surface intermediate (MASI) are effectively used to reconcile the stiff sets of differential equations that result from rapidly equilibrated surface phenomena with transient reaction or transport steps, these approaches rely heavily on the existence of static external forces (isothermal, isobaric, potentiostatic, *etc.*). To that end, extreme efforts are often made to remove inhomogeneity in the system such as hot spots or concentration gradients due to channelling or feed disturbances. Despite these macroscopic efforts, natural microscopic perturbations are inevitable, as described in the Nobel lecture by Gerhard Ertl, where the surface is shown to experience local oscillations in response to reaction events.[22] The question then becomes, what might happen if such micro- or macroscopic perturbations are intentionally imposed upon a surface?

Perhaps the earliest mathematical formulation of externally induced reactor transients for catalytic systems dates back to the 1960's out of Rice University, where Horn and Lin laid out the groundwork conceptualizing the field.[23] They were able to derive iterative and optimization expressions for transient systems, though at the time they did not claim they held any practical applications. At the same time, experiments were explored by other groups that began to study catalytic reactions under dynamic conditions, starting largely through the oscillations of pressure or concentration at externally induced frequencies ranging from tens to ten thousandths of a Hertz, as discussed in the *Pressure/Concentration* section below.

Early studies were typically limited to the bench-scale reactor level which lacked the spatial resolution required to induce rapid surface oscillations, as perturbations would typically be dampened. However, with the advent of microtechnology, improved lasers, and controls, studies performing time dependant experiments through various techniques are becoming more common.

Chemical dynamics has been defined differently by scientists over the past hundred and fifty years. According to van't Hoff "[Chemical] dynamics is devoted to the mutual actions of several substances, *i.e.* to chemical change, affinity, velocity of reaction, and chemical equilibrium".[24] Ostwald defined it as "the theory of the progress of chemical reactions and the theory of chemical equilibrium".[25] The most current interpretation considered in the remainder of this review is one in which the surface reaction transiently and periodically changes on the timescale of a elementary surface events (*e.g.* adsorption, diffusion, reaction), opening the door to macroscopically observed mean field events (turnover frequency) and surface resonance theory.

Sabatier's rule and the volcano plot

Catalytic reactions are by their very nature cyclic. In the most simplistic case for a heterogeneous catalyst, this is represented by the periodic cycles of adsorption, surface reaction, and product desorption to regenerate the active site. If any one of these steps is slow—whether due to thermodynamic, kinetic, or transport driving forces—the catalytic turnover will also be slowed. The classical approach for increasing kinetic rates and in turn overcoming activation barriers is achieved by tuning the surface interactions. This can often be done by selecting an active site which stabilizes a transition state, modifying gas-phase pressure, or increasing temperature. While doing so may overcome one barrier, it often inadvertently inhibits a second part of the catalytic cycle. For example, raising temperature may provide enough energy to overcome an activation barrier, but doing so may favour gas phase desorption of reactants, thus depressing the overall kinetics (turnover frequency) by decreasing surface concentrations. This conflicting duality between rate enhancement and inhibition corresponding to the strength of the surface interaction directly gives rise to the multidimensional kinetic optimization function which in its simplest form is linearized as the BEP relations and visualized by way of the volcano plot.[26] This leads catalyst selection to be guided by Sabatier's rule which suggests that for any given reaction, the optimal catalyst exists at a compromise between two competing surface phenomena.

The concept can be explored through the consideration of a semiempirical derivation of a simple case study, $A \rightarrow B$, where the reaction progresses by serial adsorption to (A^*), first order activated surface reaction ($r = k[A^*]$), and desorption of the product, B. The adsorption equilibrium of A is described as a function of the adsorption energy by the Langmuir isotherm ($K_A = \exp[-\Delta G_{ad}/k_BT]$), and the surface reaction rate constant by an Arrhenius-type relationship ($k = k_0 \exp[-E_a/k_B\mathrm{T}]$). As described by the Brønsted–Evans–Polanyi relationship ($E_a = E_a^0 + \gamma_p\Delta H_r$),[27] the activation barrier (E_a) typically scales linearly with the heat of reaction (ΔH_r).[28,29] Combining the two steps, it is clear that increasing surface interactions (*i.e.* stabilizing surface intermediates/transition states), will certainly favour the adsorption, concentrating the reactants. However, doing so simultaneously increases the energy required for the adsorbed reactant to escape the thermal well, toward the products, hence an increase in activation energy. For this reason, the heat of adsorption of a model compound can typically be taken as a descriptor for catalytic activity, giving rise to linear regions that increase or decrease with the energy—the volcano plot.[27]

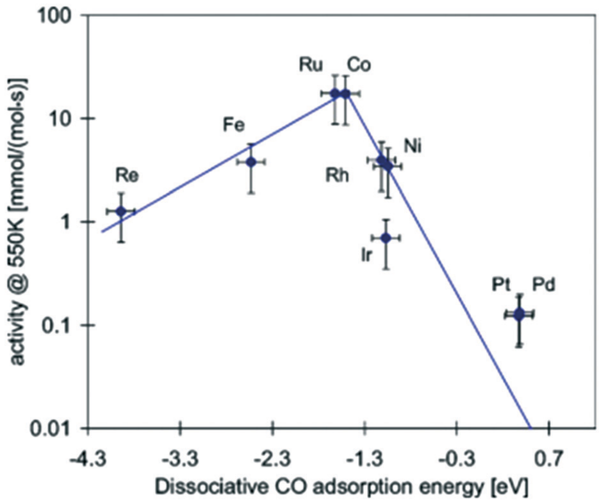


Fig. 2 Classical volcano plot demonstrating how catalytic activity scales linearly with a thermodynamic descriptor with two competing phenomena, leading to an optimum and upper limit on performance (reprinted from Bligaard *et al.*[138] with permission from Elsevier).

Traditionally, Sabatier's rule is used as a guideline in catalyst selection as depicted by a volcano plot such as in Fig. 2, which graphically shows two limiting phenomena as two intersecting lines. The volcano plot practically serves as a predictor of catalytic activity (kinetics) based on a scaling with a thermodynamic descriptor that is readily available (*e.g.*, ΔH_{CO}). It is a simple form of mapping activity to a two-dimensional visualization. It often neglects the intrinsic complexity of the multi-step mechanisms and convoluted transport, leading some to criticize it for vastly simplifying reaction mechansisms.[30] To partially address this concern some have adopted *n*-dimensional volcanos to capture multiple orthogonal descriptors.[31] Notably, however, while the plots are largely reproducible and show clear trends through computational techniques such as DFT, experimental successes to construct the plot are rare.[32]

In recent years, reviews have focused on understanding the linear scaling relationships, specifically with emphasis on predicting catalytic activity *a priori*[33,34] and overcoming the scaling relationships.[35–39] Chemists and engineers have found creative ways to optimize catalysts at cheaper costs, using alloyed materials that mimic desired single component energetics at the apex of the volcano, often using chemical dopants to functionalize catalyst surfaces and modify its properties.[36] The surface interactions are then further manipulated by creating structures with interesting catalytic interactions by studying metal–organic complexes, unique surface faceting and single atom catalyst structures. Importantly, however, these strategies are still found fundamentally bound by these thermodynamic relations and Sabatier's rule. Recently, we have transitioned into a generation of materials and reactor designs attempting to identify performance beyond this theoretical performance limit.

Pérez-Ramírez and López have compiled the most critical ideas and methods for breaking the scaling relations.[36] More narrowly, Kalz and coworkers put together an excellent review describing recent efforts in understanding naturally occurring dynamic behaviour of heterogeneous catalysts.[40] These approaches have been studied to circumvent these kinetic material limitations, including the use of single atom catalysis,[35,41] engineering alloyed metal surfaces,[42] and process dynamics. Each technique has been studied and built up as they are understood to surpass these catalytic barriers.

Natural oscillations

As our understanding of the active site evolved into dynamical considerations, the presence of naturally occurring oscillatory behaviour could be observed. Both seminal and recent works demonstrate the natural tendencies of catalytic systems to experience periodic oscillations.

In Gerhard Ertl's Nobel lecture,[43] he cited the tendency in nature for the population of hares and lynx to directly respond to one another per the Lotka–Volterra model.[44,45]

This theory models the time dependent predator–prey interactions per the simple equation set:

$$\frac{dX}{dt} = \alpha_1 X - \alpha_2 XY$$

$$\frac{dY}{dt} = \beta_1 XY - \beta_2 Y$$

The theory extends to catalysis. To this end, Ertl identifies the oxidation of carbon monoxide over crystalline platinum catalysts, where "X" and "Y" correspond to each chemical surface species (O_2 and CO) competing for binding sites. Specifically, Ertl references the way that each species is able to interact with the catalyst surface while minimizing energy. The periodic saturation and cleaning of the surface is what leads to the observable harmonic rate of carbon dioxide production. This natural oscillation and mathematical solution extends to a multitude of naturally occurring phenomena across varied timescales. Some reactions include CO oxidation over noble metals,[46,47] NO reduction over noble metals,[48] and hydrogenation reactions over various metal catalysts,[49,50] with many specific reactions summarized by Imbihl and Ertl[51] as well as Schwartz and Schmidt.[52]

Perhaps among the most well-studied of these self-oscillating experiments is carbon monoxide oxidation over noble catalysts. When oxygen at sufficient pressures is present in the reaction over palladium, platinum, or even sometimes nickel, the pure metal lattice incorporates the oxygen into its lattice structure to become more thermodynamically stable. These two structurally and energetically different materials transition between one another during the course of the reaction (Fig. 3), all-together changing the reaction mechanism between a Langmuir–Hinshelwood mechanism on the pure metal and a Mars–Van Krevelen mechanism on the oxide surface.[53]

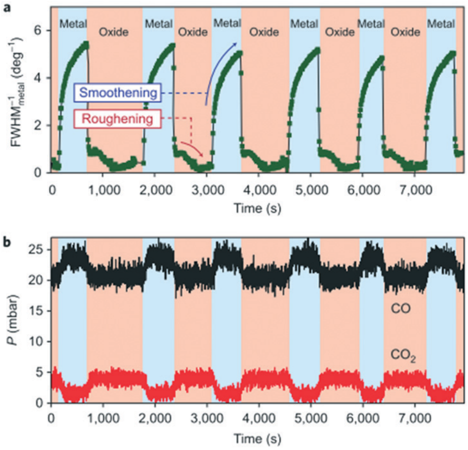


Fig. 3 The spontaneous tendency of a platinum metal surface to oscillate between metal and oxide states during CO oxidation. a) SXRD FWHM^{-1} peaks describing the smoothness of the surface that is alternating between metal and oxide, and b) mass spectrometry of the corresponding reactor pressures (reprinted from Hendriksen *et al.*[53] with permission from Springer Nature).

In the case of the partial oxidation of methane over a NiO/SiO_2 catalyst, redox reactions lead to local temperature oscillations as induced by these endo- and exothermic reactions. The frequency of these oscillations are proportional to the reaction temperature itself, with higher reaction temperatures seemingly leading to higher frequencies and *vice versa*. These reactions initially occur at the top of the catalyst bed, where the reactants first come in contact with the material. These oscillating hot spots propagate downwards in the bed leading to somewhat discrete layers of catalyst which are "hot" at any given time, as observed in Fig. 4.[54]

Additionally, some natural oscillations may be due to micro-depletion zones within the vicinity of a catalytically active site. In a recent computational Monte Carlo study (Fig. 5), kinetic and diffusive phenomena are coupled to observe the effect of a reaction on the microenvironment about a catalyst site. As the ability of products to diffuse away from the active site diminishes due to increased number density of local particles, there is a trapping effect, meaning that products stay more local and reactants struggle to interact with the catalyst. When the magnitude of the kinetic rate is substantially larger than the diffusive rate, strong oscillations occur. This is because product molecules are able to diffuse away from the active site in batches. Reaction occurs instantaneously upon product removal, leading to a back and forth motion in the product/reactant equilibrium.[55]

Interestingly, single reaction events on catalytic surfaces have been directly observed using *operando* techniques imaged at <80 ms.[56] Across all the naturally observable oscillations, however, time scales for the oscillation remain orders of magnitude slower (10–10 000 seconds) than that of catalytic turnover phenomena (<1 second). While it is possible there are secondary, much faster vibrations involved (*e.g.* bond vibrations, steric rearrangements, *etc.*), resonance between the two is not apparent.

Forced oscillations

Forced oscillations, as described here, constitute an approach to externally apply periodic input perturbations to a reacting system to induce an enhancement of some form. While

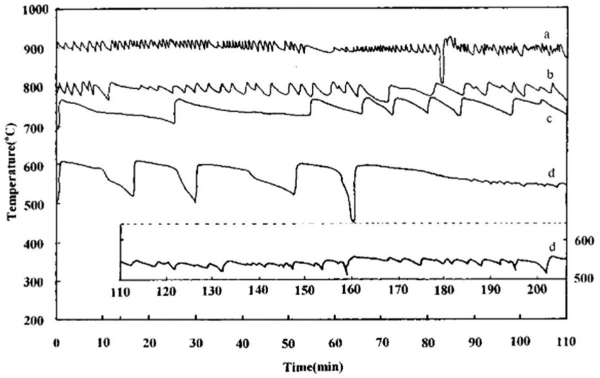
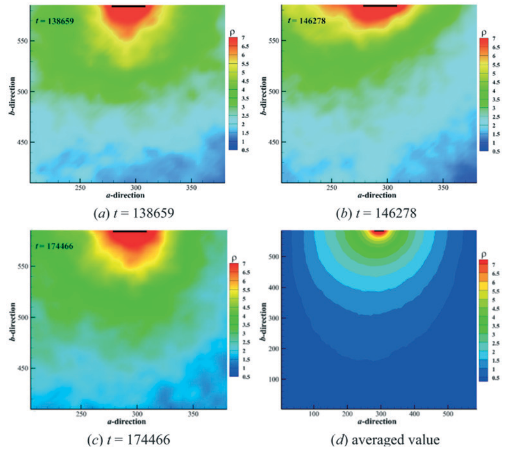


Fig. 4 Natural thermal oscillation of supported nickel catalysts at different inlet gas phase temperatures between 746 °C and 352 °C (a–d) (reprinted from Hu and Ruckenstein[54] with permission from American Chemical Society).



(a) t = 138659

(b) t = 146278

(c) t = 174466

(d) averaged value

Fig. 5 Simulated product density for an arbitrary reaction about a single active site on a catalyst surface, showing local high concentration pockets oscillating in time as described by coupled reaction and diffusion processes (reprinted from Li *et al.*[55] with permission from Elsevier).

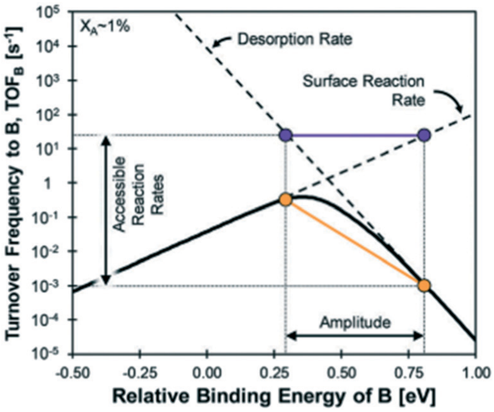


Fig. 6 Modified Sabatier–Balandin volcano plot describing the theoretical rate enhancement under forced dynamic oscillations or the surface binding energy (reprinted from Ardagh *et al.*[1] with permission from The Royal Society of Chemistry).

unique theories for the mechanism of rate enhancement are proposed for each technique discussed below, the mechanism by which rate enhancements can be expected upon periodic external stimuli can be generalized as one of three approaches:

1. Periodic surface loading and cleaning.
2. Overcoming activation barriers.
3. Operation in multiple thermodynamic regimes.

In the first scenario, external pulses cause the surface to experience a different environment (temperature, concentration, voltage, *etc.*), which may cause it to be regenerated or pre-loaded with a desired reactant. The second case considers high surface coverage of a reaction intermediate which can progress to the products if sufficient energy is provided to overcome an activation barrier. The final case considers a cyclic process where one stage is thermodynamically favoured under a particular set of conditions and the second stage of the cycle is favoured under a distinct alternate set of conditions; switching between the two (*e.g.* looping) will allow the surface to turnover.

Process dynamics classically involves using feedback loops to modulate a controllable variable, such as temperature or pressure, among others. By changing a variable, the surface energy or local concentration is changed, which in turn effects the real time kinetics. As such, a standard catalytic volcano plot (which compares kinetics to energetics) can be further interpreted to estimate the corresponding reaction turnover. Ardagh *et al.* determined that if a surface interaction energy can be periodically oscillated in the absence of any other competing phenomena (*e.g.* transport), a corresponding rate enhancement due to energetic oscillations is expected, and furthermore the location of the optimal performance should approach the natural resonance (turnover rate) of the catalysed target reaction. This optimized rate could be magnitudes higher than the static counterpart. This concept is referred to as catalytic resonance theory.[1] Ardagh and coworkers further identify a new interpretation of the static volcano plot to account for this resonance phenomena; they show it to be a powerful tool for making predictions about dynamic reactions using forced oscillations (Fig. 6). Notably, even though the net energy input between static and dynamic operation is identical, increased production is predicted due to the theorized rate enhancements.

There are a multitude of approaches that have been used to modulate inputs in chemical reactions at an expansive range of frequencies. In this review, we will assess some of these techniques, their attainable time scales, and resulting rate enhancements.

Catalytic resonance theory combined with foundational knowledge of natural surface oscillations in kinetic cycles present an exciting new lens through which we can interpret modern dynamic catalysis. By understanding, matching, and amplifying natural surface resonances, it appears to be possible to achieve enhanced catalytic reaction rates. While catalytic resonance theory presents a sound theoretical basis for achieving forced dynamic catalysis, its translation beyond the theoretical landscape has not yet been realized. Notably, reaction dynamics have been applied extensively in experimentally reacting systems: temperature, light, over potential, vibrations, *etcetera*—many of which observe enhancements. Each of these technologies, however, introduce distinct oscillations which may not resonate with intrinsic kinetic phenomena. In Fig. 7, the vertical axis represents the dimensionless frequency which is defined as the timescale for the externally forced oscillation ($\tau_{ext} = f_{ext}{}^{-1}$) divided by the intrinsic kinetic timescale (τ_{rxn} = TOF^{-1}). Resonance between the two is achieved when the external oscillation frequency is identical to the observed response frequency (*i.e.* TOF/f_{ext} = 1). Harmonics occur at integer values, but are beyond the scope of this review. While no literature references to this ratio are known for catalytic resonance, in fluid mechanics the rate of an external pressure

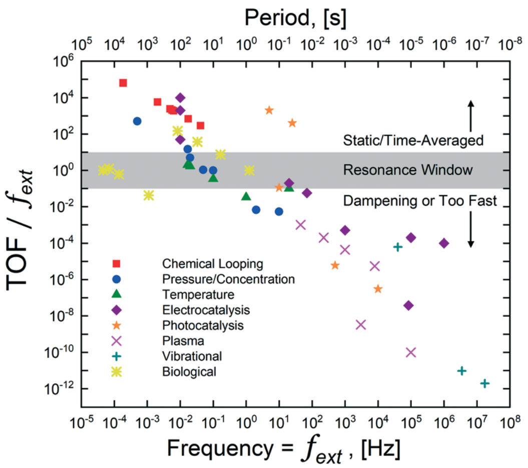


Fig. 7 Typical oscillation ranges found in literature for different pulsing techniques as compared to the resonant frequency for the reaction. For full list of literature citations see.†

perturbation on the dampening fluid velocity is described by the Hodgson number ($Ho = fV\Delta P/\bar{q}\bar{p}$), where f is the frequency, V is the system volume, ΔP is the pressure drop, p is the average static pressure, and q is the average volumetric flowrate.[57] Similarly, in acoustics, the ratio of natural resonance of a material to an externally applied excitation frequency is used in frequency response analyses to identify peak resonance and dampening.[58] The figure summarizes that only a few technologies induce oscillations that resonate with natural kinetic frequencies on the order of the observed reactions (grey box). Question of whether those oscillations are dampened out or truly felt by the surface is even further suspect, especially at higher frequencies. Lower frequencies likely achieve time-averaged responses consistent with the weighted average of the static cases as oscillations occur much slower than the kinetic steps. It is important to note that while resonance may not exist under these situations, several cases described in the forced oscillations section below do still merit further consideration for overcoming other limitations (*e.g.* periodic surface regeneration). Each case will be evaluated individually in the subsequent sections.

Waveforms

Process dynamics are externally controlled by applying waveforms that generally fall into one of four categories: square/pulse, sinusoidal, sawtooth, or triangle. As described in Fig. 8, each waveform consists of an amplitude, frequency, and duty. The amplitude describes the magnitude of the signal, the frequency describes how many full wave cycles are completed per second, and the duty cycle describes how often the signal is "on" relative to the total period, and is most relevant to pulse/square wave functions.

Generally, amplitude is used to define net magnitude of the perturbation. For example, in periodic temperature oscillations, amplitude may correspond to the temperature swing, ΔT. The specific duty, or relative time spent in each phenomenological regime, is adjusted to achieve the correct time in the excited/base states. For example, the part of the cycle corresponding to the high input may be overcoming a rate limiting kinetic steps ($\tau_{on} = 1/k_{rxn}$), while the low input may be necessary for the transport steps of the elementary reactions ($\tau_{off} = 1/k_{ads}P$),[59] making the duty cycle with optimal resonance, $\text{Duty} = \tau_{on}/(\tau_{on} + \tau_{off}) = k_{ads}P/(k_{ads}P + k_{rxn})$. Similarly, the frequency ($f = 1/(\tau_{ON} + \tau_{OFF})$), should be made to match the natural resonance, or turnover, of the reaction itself. Optimizing each of these parameters means having precise knowledge of the reaction kinetics and thermodynamics.

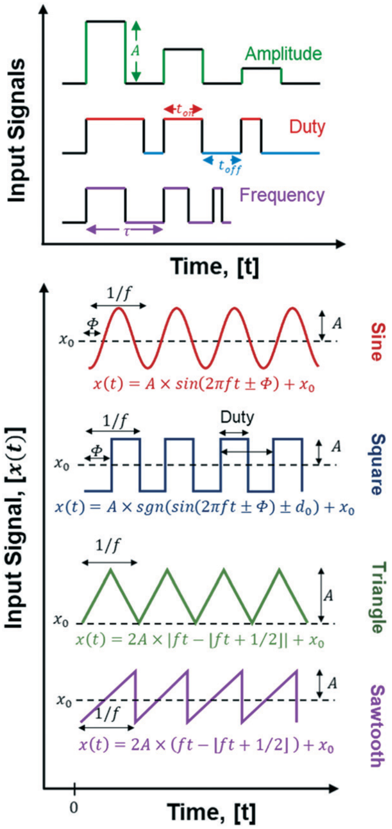


Fig. 8 (Top) Graphical representation of the tuneable variables for pulse waveforms including amplitude, duty, and frequency (inverse of period) (bottom) graphical interpretations input waveforms and their respective equations as a function of time, t, amplitude, A, frequency, f, phase shift, ϕ, offset, x_0 and duty parameter, d_0.

For rapid oscillation-induced rate enhancements, square waves are optimal as they present the sharpest transition between two distinct regimes, whereas the slower transition experienced in other waveforms dampens this switch. It is important to note, however, that some catalytic applications have benefited from controlled ramping. Sawtooth or triangle waves, for example, are used in intermittent temperature programmed desorption (ITPD)[60] or when clean square steps are not achievable due to dampening. Temperature programmed reactions (TPR) are commonly used to characterize weak and strong binding to material surfaces.[61] This technique is, by its very definition, dynamic. Additionally, sawtooth waveforms are commonly used in battery cycle testing, in charge discharge cycles or cyclic voltammetry to probe electrocatalytic mechanisms.

These waveforms can be mathematically described to represent a controllable system variable x, that is periodically perturbed as a function of time, giving rise to the system input function $x(t)$, as represented in Fig. 8.

Increasing the amplitude increases the intensity of the oscillation by extending the bounds (*e.g.* changing your maximum/minimum temperature, pressure, *etc.*). Increasing the frequency involves increasing the number of oscillations per unit time. Shifting the waveform in time involves either offsetting the reference time conditions for an arbitrary wave by a phase shift, ϕ, which shifts the wave left or right at time zero—this becomes relevant when relating an induced frequency to a measure periodic response. Similarly, the output parameter can be shifted in parameter space by an offset of x_0. Duty is the parameter that describes the relative amount of time the wave is above a certain threshold (*i.e.* "on" state), and is characteristic of a square (pulsed) waveform. Duty can be modulated with the relationship $d_0 = -\cos(\pi \times \text{Duty})$ in the respective equation and is some number between 0 and 1. Decreasing the duty means decreasing the relative time spent at the upper limit; as the duty approaches zero, the square wave approaches a periodic pulse input.

In static systems, process inputs are simply represented as scalar values representing a steady and spatially constant parameter (*e.g.* temperature is 300 K or pressure is 100 bar). Because parameters are constantly changing during dynamic reactions, one value would often leave the system underspecified. Parameterization thus requires specification of parameters such as the amplitude, duty, and frequency or period for dynamic systems. This leaves the challenge of comparing static to dynamic systems side-by-side. To do this end, dynamic variables (input parameters) are commonly reported as time averaged values.

$$\bar{x} = f\int_0^{1/f} x(t)\mathrm{d}t$$

It is important to note that this time-averaging can also be performed on the response ($\bar{y}$).

$$\bar{y} = f\int_0^{1/f} y(t)\mathrm{d}t$$

In the case where the time-averaged response is identical to the weighted average of the static responses, no kinetic resonance or rate enhancement is observed. For example, for a square wave, the time averaged response would be the time-weighted response of the two static systems corresponding to the "on" and "off" states:

$$\bar{y}_{\mathrm{sq}} = \frac{\tau_{\mathrm{ON}} \times y_{\mathrm{ON}} + \tau_{\mathrm{OFF}} \times y_{\mathrm{OFF}}}{\tau_{\mathrm{ON}} + \tau_{\mathrm{OFF}}}$$

In kinetic resonance theory, a corresponding kinetic response specifically deviated from the time-averaged response to the static stimuli. This is owing to the nonlinear nature of the coupled dynamic equations as discussed earlier and the short periods preventing equilibrium of all elementary steps.

It is sometimes beneficial to consider a pulse effectiveness factor.[3] The metric compares the performance (*e.g.* rate or TOF) at steady state $y(\bar{x})$ to pulsed performance $y(x)$:

$$\eta = \frac{y(x) - y(\bar{x})}{y(\bar{x})}$$

For example, if the output measurement is the turnover frequency, $\eta_{\mathrm{TOF}} = (\mathrm{TOF}_{\mathrm{pulsed}} - \mathrm{TOF}_{\mathrm{SS}})/\mathrm{TOF}_{\mathrm{SS}}$. Notably, this effectiveness factor can be calculated on the basis of TOF, conversion, yield, or effluent concentration, underscoring the necessity to explicitly define the basis for calculation.

Frequency response

A common technique for assessing rate enhancements due to periodic input perturbation is the frequency response method. This is a mathematically intensive method, which is nicely outlined by Petrovska and colleagues.[62] In brevity, an input variable, $x(t)$, is oscillated at a wide range of frequencies ($\omega = 2\pi f$) and the periodic response, $y(t)$, is observed in the time domain. These perturbations are added to the steady state values of the input (x_{s}) or output (y_{s}) as denoted by the subscript "s". A mathematical transformation is then used to interpret the real and imaginary parts of the frequency domain (*e.g.* Laplace or Fourier transforms). A frequency that resonates with the characteristic timescale for a physical phenomenon (*e.g.* TOF or diffusional time constant) will show an elevated response (peak) in this transformed domain.

There are two primary types of frequency response, shown here for a sinusoidal input function: linear,

$$x(t) = x_{\mathrm{s}} + A\cos(\omega t) \xrightarrow{t\to\infty} y = y_{\mathrm{s}} + B\cos(\omega t + \phi)$$

and non linear:

$$\begin{aligned} x(t) = x_{\mathrm{s}} + A\cos(\omega t) &\xrightarrow{t\to\infty} y \\ &= y_{\mathrm{s}} + y_{\mathrm{DC}} + B_{\mathrm{I}}\cos(\omega t + \phi_{\mathrm{I}}) + B_{\mathrm{II}}\cos(2\omega t + \phi_{\mathrm{II}}) + \ldots \end{aligned}$$

The output of the linear frequency response is more straightforward and is represented comparably to the input and the output of the nonlinear frequency response is more complex and must be captured by additional terms including the higher order harmonic terms and the "non-periodic" DC term.[62] Linear frequency response is used when the output holds the same shape and frequency of the input and nonlinear frequency response is used for weakly nonlinear systems. It is often useful to transform these functions to the frequency domain such that the response or resonance can be assessed at a particular frequency using Laplace transforms,[59]

$$\hat{x}(\omega) = \mathcal{L}\{x(t)\}$$

$$\hat{y}(\omega) = \mathcal{L}\{y(t)\}$$

And the corresponding impedance caused by the kinetic or transport step is,

$$Z = \frac{\hat{x}(f)}{\hat{y}(f)}$$

Similar analyses can be performed in the frequency domain using Fourier transforms. Reversing the transformation back to the time domain leads to a frequency waveform characterized by the Volterra series,[63] for the nonlinearly related case. This is expanded in the form:

$$y(t) = \sum_{n=1}^{\infty} y_{x,n}(t)$$

Physically, these equations mean that if a time dependent parameter is introduced to a system (such as pulsing temperature), then the form and anticipated time-dependent response (such as observed reaction rate), may be mathematically formulated by using some intermediary function, such as the Arrhenius equation coupled with a rate expression that caused some impedance.

Panic *et al.* performed a study where they compared the experimental and computational results of a frequency response study for ferrocyanide oxidation kinetics while oscillating applied potential and electrode rotation speeds.[64] The study found that using the nonlinear frequency response analysis method was valid for fitting the kinetics of electrochemical reactions. Others have periodically modulated system volume to measure diffusion in microporous materials.[59,65]

Theoretical evaluation of dynamic catalysis

Substantial progress has been made in the computational evaluation of static catalysis, as discussed earlier in this review and by many others.[10,66,67] Similarly, substantial work performed on the dynamics of reactor operation under relatively slow perturbations was performed in the 1960's, as reviewed by Bailey, Amundson, and Lapidus.[68] Computational approaches are also appropriate to make direct predictions relating applied external perturbations to intrinsic rate enhancements using techniques ranging from first principle quantum simulations to continuum calculations. They may also allow for more rapid scanning of a multidimensional parameter space (amplitude, frequency, duty, *etc.*) in the absence of erroneous secondary effects often present in experiments (*e.g.* mixing, dampening, slow *ex situ* measurements). To date, however, few such studies have been performed to directly assess the effect of such perturbations on the intrinsic catalytic mechanism or rate.

Among the most well established theories for dynamic systems is the Lotka–Volterra model.[44,69] This model, also known as the predator–prey model, was famously related by Ertl[22] to compare the dynamic performance of a catalyst to the periodic population of lynx and hares. This model is detailed above under the "Natural Oscillations" section.

López and Albano performed Monte Carlo simulations to test the effect of periodic pressure oscillation specifically in the case of carbon monoxide oxidation.[70] The simulation was based on a model produced by Ziff, Gulari, and Barshad (ZGB), specifically for monomer–dimer reaction systems. It was assumed that the CO oxidation reaction studied followed a Langmuir–Hinshelwood mechanism. Using this model, the authors were able to test a range of applied amplitudes and frequencies to observe the effect on the production rate of carbon dioxide. The authors determined that by oscillating the pressure of CO to a point near the irreversible poisoning of the catalyst surface, a classical Langmuir–Hinshelwood model under periodic input perturbation predicts optimized surface coverage and a subsequent considerable rate enhancement.

Ardagh *et al.* developed an analytical CSTR-kinetic model for describing the resonance of a dynamically changing system.[1,2] In their model, they periodically perturbed the binding energy of bound species and calculated the resulting turnover frequencies. They concluded that as the applied frequency approached the inherent frequency (catalytic turnover), massive rate enhancements of 3 to 4 orders of magnitude were observed. This is the first computational work that explicitly identified catalytic resonance theory.

Challenges. The experimentally observed turnover expected under periodic external oscillations is a complex convolution of a multitude of competing and parallel phenomena. These include: transport (heat, mass, fluid), including boundary layers near the catalytic active sites; dynamic adsorption/desorption and surface diffusion; unsteady coverage-dependent surface kinetics; transient thermodynamic barriers/surface energetics integrated with catalytic cycles that experience multiple microenvironments over the period of a turnover. To this end, substantial strides are required in application of dynamic microkinetic surface models, transport reactor-level models, and first principles energetic simulations under non equilibrated surface conditions. Furthermore, multiscale models are required to assess the true performance under dynamic operation.

Experimental approaches to forced oscillations

Chemical looping

Chemical looping is an industrially adopted technology that physically separates two halves of a catalytic cycle into two independently controlled reactors, passing the catalyst back and forth between. It is most commonly used in combustion applications where the oxidizer (air) and reducing stream (fuel) never come in direct contact, but rather a heterogenous catalyst, often metal oxide, is transported (looped) between these two reactors, as in Fig. 9. This term was coined in 1987,[71] but the technology has grown substantially since the early 2000's due to efforts to reduce carbon emissions by

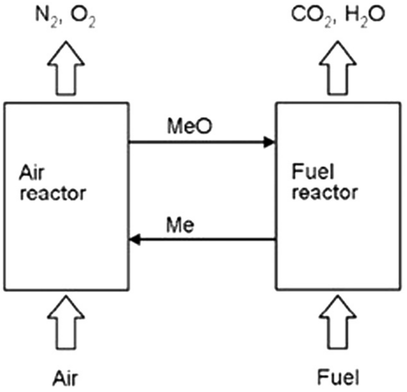


Fig. 9 Standard chemical looping reactor design including both an oxidative air reactor and a reductive fuel reactor. Solid catalyst material is cycled through each reactor to take advantage of the respective oxidative-reductive environments (reprinted from Bolhàr-Nordenkampf *et al.*[77] with permission from Elsevier).

isolating concentrated CO_2 directly. Reviews of developments in chemical looping technology are written by Moghtaderi[72] and Fang.[73]

These reactors currently have many different applications, including chemical looping combustion, gasification reactions, sorbent chemical looping, and chemical looping reforming,[72,74] all of which focus on carbon capture in different forms with solids residence times around 2 to 3 minutes.[75,76]

More recently, ammonia synthesis has been demonstrated through chemical looping-type systems. This proposed process is a high temperature noncatalytic approach to produce ammonia through the reduction of alumina and subsequent hydrolysis of aluminium nitride. This two-step reactor uses a solar driven thermal heater as well as a hydrolysis reactor to yield ammonia yields of up to 84%.[78] The process, however, suffers from classical thermodynamic barriers by requiring extreme temperatures (nearly 1000 °C[79,80]) to form the nitride.

Challenges. The underlying challenge for chemical looping is the timescale associated with physically transporting a catalyst or switching the reaction environment. Ultrafast chemical looping (<1 s cycles) of just the temperature or concentration would approach the subsequent temperature or concentration oscillation approaches. Even still, the potential benefits would have to outweigh the extreme energy penalties incurred by switching the large thermal masses. Because temperature and pressure swings are so severe across the dual reactor chemical looping systems, using and stabilizing monodispersed catalysts at the nanoscale is also a substantial challenge.[81]

Pressure/concentration pulsing

Among the first to rigorously study the effect of concentration input transients on catalytic systems were Zhou, Gulari, and Herz who laid the groundwork for this field in the late 70's. Automobile companies such as Toyota and GE were large leaders in the beginning of this research, also in the late-70's to mid-80's.[5] This work had substantial implications to the automotive industry, particularly with transients observed by the three-way catalysts in catalytic converters. At the time, certain vehicles were achieving naturally oscillating behaviour at a frequency of about 1 Hz.[82] Specifically, the enhancement was attributed to dynamic oscillations in composition, inlet flow rate, and temperature of the reactor feed apparent in automotive operating conditions. There have since been many subsequent studies to test if there is a way to exploit this phenomenon to optimize their activity.

Generally, the controlled input oscillation was achieved by using automated electronic switching valves that switches inlet compositions or pressures at a given rate between two or more feed streams. This is used to control the input which is closely monitored using pressure gauges. This technique, in practice, tends to reach oscillation frequencies in the rage of 0.0001 Hz[83] to 10 Hz.[84,85]

The nature of the rate enhancement associated with concentration/pressure pulsing can be found in detail in Silveston's work for the case of carbon monoxide oxidation.[82] To summarize, pressure modulation is proposed to be beneficial for a number of reasons: 1) switching reactant feed streams between pure species allows more fine control of the catalyst surface coverage. In the case of CO oxidation over a precious metal catalysts, CO typically dominates the surface. By allowing only one specie to bind at a time, the composition of each reactant is balanced. 2) Composition modulation has mixing effects of the surface of the catalyst such that the spatial distribution of reactants is ideal for reaction. 3) Pressure modulation can help overcome transport limitations, especially in porous or strongly binding systems which are typically strongly mass transfer limited.[6] Notably, none of these theories directly link the external oscillation to the turnover frequency (resonance) of a particular elementary surface step.

Zhou and colleagues studied carbon monoxide oxidation over a Pd/Al_2O_3 catalyst.[85] They adjusted the concentration of

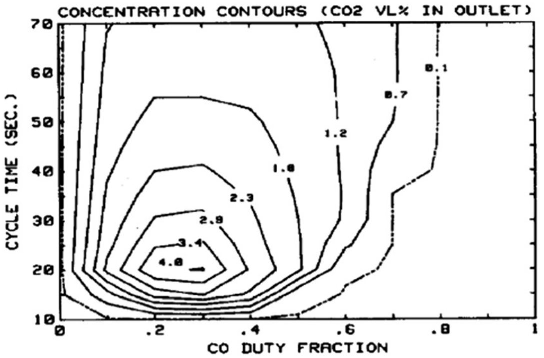


Fig. 10 Contour plot demonstrating rate enhancement for CO oxidation over a palladium catalyst while oscillating feed composition at a range of cycle times and duty fractions. Reaction conditions: temperature 366 K, flow rate 0.7 dm^3 min^{-1}. The dashed, 0.1% line is the steady state optimum CO_2 conversion for the same conditions (reprinted from Zhou *et al.*[85] with permission from Elsevier).

the reactants by switching between a carbon monoxide stream and an oxygen stream, both of which were diluted in nitrogen. They were able to cycle between frequencies of 0.0067 Hz to 0.05 Hz and found that the rate enhancement is up to 44 times higher than respective steady rates. Fig. 10 shows the results of the iterative experimental approach where combinations of cycle time and CO duty were changed to identify point an optimum. Specifically, for this reaction, the authors found that a duty of 0.3 and cycle time of 20 s lead to this large (44 times) rate enhancement. This was attributed to the ability to achieve optimal surface coverages of oxygen on the palladium catalyst.

Oscillating reactant feed concentration consequently leads to catalyst surface changes. This is evident in the work by Hegedus *et al.* where they did just that.[86] They altered the reaction from reducing to oxidizing for a feed stream of NO, CO, and O_2 (which are typical components for the exhaust from an automobile) at 505 °C over an alumina supported platinum catalyst. Fig. 11 shows the concentration of CO bound to the platinum catalyst over a range of concentration switching times, ranging from periods of 0.5 s (2 Hz) to 180 s (0.0056 Hz). Further comparing surface specie concentrations at different oscillation rates, the authors found CO is inhibitive at frequencies slower than 1 s. At frequencies faster than 1 s the time averaged conversion of both CO and NO species increased. Notably, this is the only study reviewed here that directly resolved the transient surface concentration.

In the reduction of nickel oxide, Sohn and Aboukheshem studied the effect of oscillating the pressure of hydrogen gas to regenerate the catalyst at frequencies ranging from 0 to 20 Hz.[87] For this batch type pressure fluctuation reaction, the reduction went to completion in significantly less time when oscillated *versus* when it is left to steady state. The authors justified this observation by describing the increase in pressure as causing a corresponding increase in the ability of reactant gas to transfer through the porous NiO solid. The authors also note that the effect of pulsing is more obvious towards the end of the reaction than it is towards the beginning. This is explained again as mass transfer is enhanced through periodic forcing which is more relevant to reduce the material in the smaller pores which are the last to be reduced.

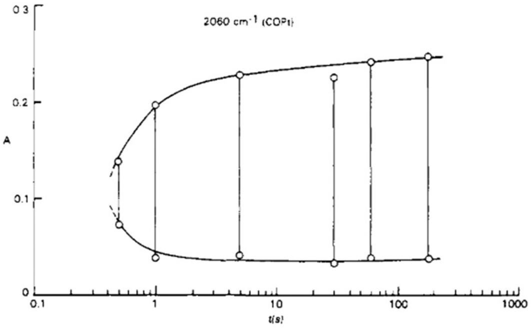


Fig. 11 Shows the maximum and minimum surface coverage of 2060 cm^{-1} band platinum bound CO species at different concentration oscillation rates using infrared spectroscopy (reprinted from Hegedus *et al.*[86] with permission from American Chemical Society).

Special case – sonochemistry. A special consideration of pressure oscillation is sonochemistry.[88] Operating at frequencies between 20 kHz to 2 MHz, this method exploits cavitation effects that lead to rapid localized pressure spikes. While such an effect can be convoluted with induced mixing and locally high temperatures which in turn form reactive radical groups, the resulting potential for elevated conversion due to periodic pressure pulses is nonetheless noted and of interest.[6] Due to the highly energetic nature of this technique, sonochemistry is commonly used in degradation reactions,[89,90] particularly in wastewater treatment. The cavitation bubble is so energetic that it can split water into radical groups which attack and decompose many different types of pollutants.[91]

Challenges. Specific challenges facing pressure/concentration oscillation are primarily centered about achieving forced local perturbations at the catalytically active site that are not dampened out by competing phenomena (mixing, gas phase diffusion, intraparticle diffusion). For example, while pore diffusion is sufficiently fast relative to the perturbation at low frequency, high amplitude/frequency oscillations may be dampened out by relatively slow pore diffusion. Second, the resulting system should also maintain desirable sharp steps in the gas phase switching (minimize axial dispersion), especially in multiscale regions (boundary layers, pore diffusion, packed beds). Even neglecting mass transfer, induced pressure changes >100 Hz approaches the limit due to the speed of sound (*e.g.* ∼343 m s^{-1} through air)—with the exception of local generation as in cavitation. Finally, the ability to describe and account for secondary thermal effects resulting from endothermic/exothermic sorption steps and surface reactions remains understudied. The presence of such effects may convolute the interpretation of rate enhancements, though does not negate the possibility of superior catalytic performance upon forced perturbation.

Temperature oscillations

Dynamic temperature control in reacting systems was studied in the early 2000's by J. J. Brandner and P. L. Silveston. They used their existing backgrounds in microtechnology and pressure oscillations, respectively, to demonstrate the effect of thermal applications in reacting systems.

van't Hoff and Arrhenius demonstrated how the thermodynamic and kinetic rate parameters exhibit an exponential dependence on temperature, later attributed to the activation energy to overcome some transition state energetics. A forced oscillation on temperature, however, causes a perturbation to the elementary process steps which is compounded in multi-step mechanisms. The mathematical propagation of this forced thermal oscillation into the non-linear set of differential equations already exhibiting natural oscillations has not yet been demonstrated from first principle theory or direct experimentation.

The ability to study thermal oscillations on kinetically relevant timescales (>1 Hz) only became a possibility with the advent of microreactor technologies where characteristic heat transfer length scales <10 μm could lead to ultrafast heat transfer. Achieving oscillation frequencies at a magnitude of interest is limited by the heating rate ($\dot{Q}$) of the thermal mass as described by[92] $\dot{Q} = (mc_p\Delta T)/\Delta t$, where m is the thermal mass being heated with a heat capacity of c_p and temperature swing of ΔT over a time period of Δt.

Evidently, if a large change in temperature is desired in a short amount of time, a small thermal mass is necessary. Even so, thermal oscillations have been shown at a wide range of frequencies over the past 20 years, ranging from 0.01[92] to 10's[3] of oscillations per second.

Oscillation temperature is often controlled by using high power cartridge heaters in microreactors with a constant, thermally bound heat sink or by using direct Joule heating of a metal heating component. The small length scales allow very rapid heat transfer through system to local catalyst reaction sites.

Jensen and colleagues designed a microsystem with an integrated heater deposited inside oscillated at frequencies between 0.002 Hz to 2.5 Hz.[93] In their system they oscillated the temperature of the catalyst bed at amplitudes between 5 °C to 20 °C about an offset of 160 °C. They consistently found that for carbon monoxide oxidation over an alumina supported platinum catalyst, a thermal oscillation rate of 1 Hz lead to time averaged rates up to 70% higher than the quasi steady reaction rates, as shown in Fig. 12. It is important to note that while the enhancement was observed, it was not mathematically related to resonance or intrinsic kinetic barriers. The authors describe that at low frequencies, the reaction rate converges to the individual time averaged response for each temperature regime ($x(t) = T(t)$, $y(t) = \bar{y}$), whereas at high frequencies—faster than the time constants characteristic of the reaction—the rate is that of the averaged temperature of the applied signal ($x(T) = \bar{x} = \bar{T}$, $y(t) = y(\bar{T})$). It is postulated by the authors that the enhancement comes from unique phenomena at an applied frequencies between these two extremes.

Another study was performed by Brandner *et al.* who employed a continuous flow through microreactor with cartridge heaters to control the reaction temperature.[92] Their study showed that when oscillating temperature between 50 °C and 150 °C, their oscillating system notably outperformed the reactor operating at steady state conditions at 100 °C, and they claimed that a steady state temperature somewhere between 100 °C and 150 °C would be necessary to match the oscillatory production. Notably, the kinetics are activated with an exponential dependence on temperature, so it is expected that steady conversions would require an elevated temperature to match elevated conversions achieved for brief operation at 150 °C. Again, resonance theory would apply if the observed rates under dynamic oscillations exceeded even those observed at 150 °C, which was not demonstrated in this study.

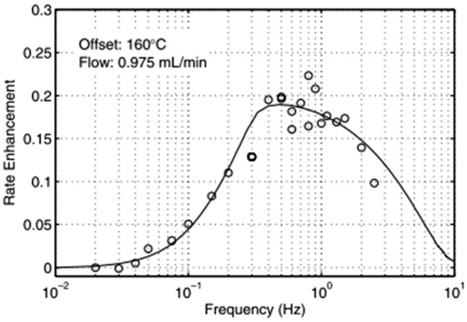


Fig. 12 The rate enhancement for thermally oscillated CO oxidation over Pt/Al_2O_3 *versus* applied frequency for a 10 °C amplitude (reprinted from Jensen *et al.*[93] with permission from Elsevier).

Stolte and colleagues designed their own custom microreactor capable of oscillating temperature from 3.3 Hz to 20 Hz for the reaction of carbon monoxide oxidation over platinum.[3] They altered their base temperatures from 150 °C to 210 °C with amplitudes reported in mJ of energy input, which for various experiments ranged from 50 to 300 mJ. As seen in Fig. 13, they reported a rate enhancement four times greater when normalized to the steady state value at the corresponding conditions as they increased their pulse frequency (or decreased cycle period). Slower cycle times were performed by Luther *et al.* who observed enhanced conversions and additionally have completed microkinetic computational work to model the surface coverages and reaction rates of such systems.[94]

Challenges. Several challenges exist to demonstrate thermally induced dynamic kinetic resonance in catalytic systems. From a theoretical perspective, the complex coupled kinetic and dynamic inputs must be resolved for the multistep mechanism to establish a basis for rate enhancement. This must be then coupled with continuum modelling to resolve transient hotspots due to reaction/

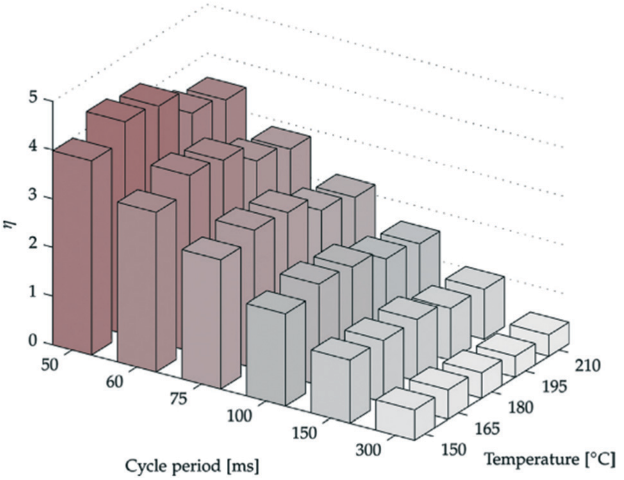


Fig. 13 The effect of cycle period and base temperature on the normalized rate enhancement in the carbon monoxide oxidation reaction over a platinum catalyst in a custom microreactor system (reprinted from Stolte *et al.*[3] with permission from Elsevier).

sorption enthalpy coupled with external heating/cooling. From an experimental perspective, materials need to be developed to withstand the rigor from thermally annealing on the order of 0.1–100 Hz, accounting for mechanical stresses, thermal expansion, and catalyst sintering effects. Careful characterization is also required to characterize the exact temperature of the active site, which has proven challenging to resolve at the stated frequencies and length scales. Similarly, the corresponding analytical tools must be integrated to not only transiently resolve reactor effluents, but also resolve the transient surface composition.

Plasma

Plasma is a highly energetic state of matter made up of charged particles formed upon ionizing gases. It can take a number of different forms, based on its excitation mode, including microwaves, pulsed discharge, and laser produced. A review on plasma activated heterogeneous catalysis was written by Mehta *et al.*[95] with a review on the surface-plasma interactions at the nanoscale was written by Neyts *et al.*[96] The oscillation range in which it has been shown to operate is on the order of 10's[97] to 100 000's[98] of pulses per second.

These types of systems have slight variations in designs, but usually involve a plasma chamber, with their respective induction source connected, and catalyst inside. Induction sources can be microwave excitors with ferroelectric materials,[99] a power supply capable of varying the voltage using a charging system,[100] or nanosecond pulsed power sources controlled by a waveform generator,[98] for example. Reactants pass through this chamber and in line analysis is used for characterization.

A number of possible theories exist for why pulsed plasma leads to rate enhancements. Rousseau *et al.* report that for their reaction of acetylene oxidation, possible reasons for the observed rate and selectivity enhancement included enhanced flux of the highly reactive, short lived species (*e.g.* photons, charged particles) or simply thermal effects.[99]

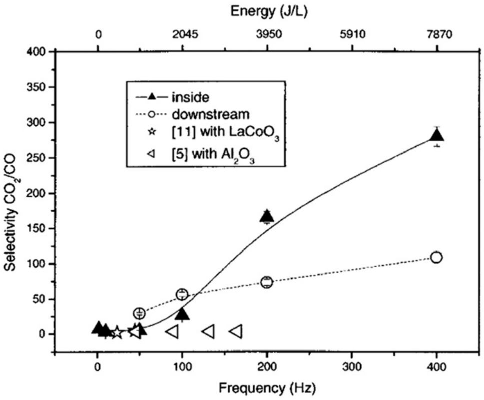


Fig. 14 Selectivity enhancement of acetylene oxidation products for porous alumina catalyst packed inside the plasma discharge region and downstream of the discharge zone showing selectivity enhancement with induced plasma frequency (reprinted from Rousseau *et al.*[99] with permission from AIP Publishing).

In this study, not only did Rousseau *et al.* study the effect of frequency on oxidation enhancement, but they observed how it affected the selectivity of the reaction in total, as shown in Fig. 14. In their experiment, they tested if mixing their alumina catalyst in a ferroelectric $BaTiO_3$ bed or downstream of it had any effect. The ferroelectric material is used to improve reactor energy efficiency as well as enhance the oxidative plasma properties and promotes more desirable reaction pathways. There was a substantial increase in selectivity for this process as the frequency increased to >100 Hz.

Challenges. A recent roadmap has identified that, "the fundamental mechanisms of plasma-catalyst interactions are not yet fully understood. It is a complex environment, as the catalyst may affect the plasma behavior, and *vice versa*, the plasma also affects the catalyst and catalysis mechanisms".[101] Furthermore, the enhancement effect is observed at frequencies many orders of magnitude above the typical catalytic TOFs, so it is unclear what if any benefit is observed due to resonance with the physical surface reaction phenomena. Finally, the physical characteristics of the surface have not been transiently resolved over the period of oscillation to resolve surface transients or perturbation dampening, making mechanism resolution challenging.

Photocatalysis (LED/lasers)

Photocatalysts are able to absorb incident light and use the energy to drive a reaction. Several mechanism are proposed and reviewed by Fujishima *et al.*,[102] Mills and Le Hunte,[103] and Fox and Dulay.[104] A common proposed mechanism is that this light is able to raise electrons from valence to conduction band, leaving holes on the catalyst surface. These holes are highly oxidative reaction sites.[105] There are a number of different ways to drive these reactions, including lasers, lamps, and LEDs.

In the case of semiconductive, photoactive materials, proposed mechanisms tend to involve the interaction of induced electrons or "holes" (electron "voids" formed by incident photons) with reductive or oxidative species.[106] These reactive species facilitate the separation of electrons and holes when the incident light has enough energy to overcome the band gap, or the energy needed to eject the electron to the conductive band.

Beyond the steady catalytic turnover, the possibility for periodic surface irradiation offers an exciting avenue to dynamically control the catalysis. An extensive dynamic analysis of the mechanism for pulsed laser catalysis has also been meticulously derived by Vardi and Shapiro.[107] In it, the authors come to a theory that describes laser induced tunnelling through a potential energy barrier *via* applied high intensity dynamics.

In the case of the reduction of CO_2 over rhenium-based catalysts through photocatalysis, the reaction actually becomes inhibited after a certain amount of exposure to light. The proposed mechanisms for this deactivation include: one-electron-reduced (OER) species react with other radical species which terminates the reaction (radical–radical combination termination) or undesirable side reactions of the OER species at the elevated electron state may terminate the reaction.[108] The authors propose that by only applying very short pulses of light, this can avoid the undesirable reaction of the higher energetic species.

It was found that for lower photon fluxes, the pulsed operation outperformed the continuous LED set up in the reduction of CO_2 to CO, as demonstrated in Fig. 15. It is also interesting to note that the pulsed set ups did not fully deactivate, leading the authors to believe that the photo-deactivation of the catalyst has been reduced.

Challenges. Especially in the case of laser photocatalysis, the stability of the catalyst and sintering of nanoparticles is a concern due to the high energetic nature.[109] As with other approaches, relation back to the fundamental phenomena—kinetic, mass or electronic transport—has not yet been validated experimentally. Similarly, transient resolution of surface species or any periodic response variable ($y(t)$) have not been measured or theorized.

Electrochemistry

Electrocatalysis uses applied voltage to drive a reaction system and is often measured by observing the resultant flow of electrons, or the current passing through the system. Dynamics in electrochemical systems have been well studied since the late 1950's due to an effort to better develop understandings of electrode processes such as the transport and kinetics occurring at the interface of the electrode and surrounding media.[110]

Fedkiw and coworkers studied the anodic oxidation of methanol under pulsed voltage conditions with frequencies ranging from 0.1 Hz to 6 Hz and two amplitudes, either 0.58 V or 0.78 V, as summarized in Fig. 16. They claimed that the limiting portion of this reaction on a platinum catalyst was the build-up of reaction products poisoning the surface.[111] Through their experiments they found that oscillating between a high and low potential, they were able to maintain higher oxidation rates that are not observable under steady conditions. This may have been due to higher applied potentials regenerating the catalyst surface such that the reaction can proceed unobstructed (at the lower applied voltage). In this study, they only tested frequencies between 0.1 to 6 Hz. They noted that a study by Adzic *et al.*[112] tested a wider frequency range, finding an optimal frequency at 2000 Hz, suggesting that while Fedkiw observed improved rates, they may not have been optimal.

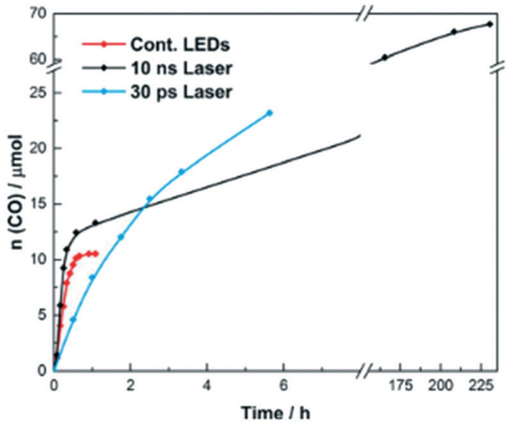


Fig. 15 The effect of laser pulse time on the catalytic reduction of CO_2 to CO over a rhenium-based catalyst. Continuous LED (λ = 365 nm), 10 ns laser (λ = 355 nm, pulse length = 10 ns, frequency = 20 Hz), 30 ps laser (λ = 355 nm, pulse length = 30 ps, frequency = 20 Hz) (reprinted from Pschenitza *et al.*[108] with permission from John Wiley and Sons).

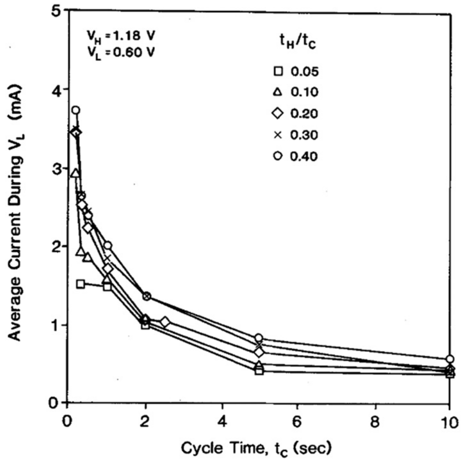


Fig. 16 The observed current (flow of electrons/reaction rate) for the oxidation of methanol over platinum. The upper (V_H) and lower (V_L) applied voltages where 1.18 V and 0.60 V, respectively. The duty (t_H/t_C) was varied over a range from 0.05 to 0.40 while additionally change the cycle time (or frequency) of the experiment (reprinted from Fedkiw *et al.*[111] with permission from IOP Publishing).

Gopeesingh *et al.* studied the oxidation of formic acid over a platinum catalyst.[113] Using a reactor with in-line gas

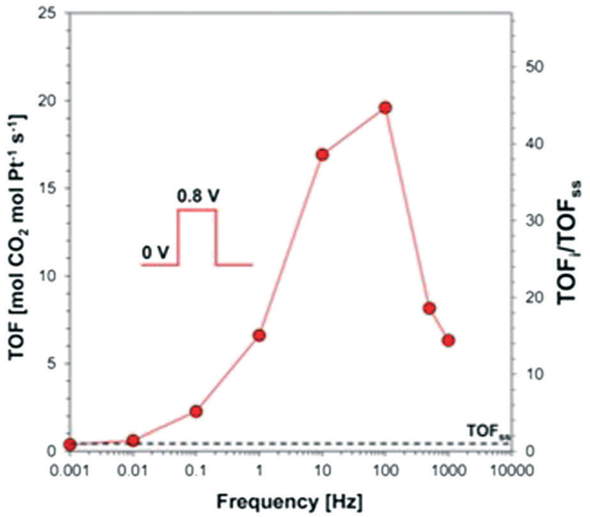


Fig. 17 For the electrocatalytic oxidation of formic acid over platinum under pulsing conditions. The relative rate enhancement is observed at about 100 Hz for 40 times the steady state turnover (reprinted from Gopeesingh *et al.*[113] with permission from Americal Chemical Society).

chromatograph as well as counter, working, and reference electrodes, they were able to obtain turnover frequencies about 45 times that of steady state at 100 Hz applied frequency, as shown in Fig. 17. This is attributed to how the activation energy of the faradaic steps in this reaction significantly decreases with applied potential.

Special case – electrochemical impedance spectroscopy. Electrochemical impedance spectroscopy (EIS) is a special category of frequency response that is used to characterize the physical and reaction phenomena by inducing small variations in applied potential at a range of frequencies and monitoring the corresponding response as a current (reaction flux). This technique can be particularly useful in determining kinetic rate constants in various electrochemical mechanisms[114,115] and measuring various physical and structural properties.[116] The impedance of a system is defined as the Laplace transform of the applied function (voltage) divided by the response function (current), where the voltage is applied and the current is measured and descriptive of electrochemical reaction rates.[117,118] The outputs for such a technique are often in the form of Nyquist or Bode plots which directly relate the imaginary to real portions of impedance or phase to the applied frequency, respectively, as described earlier in the Frequency response section. The practicality to dynamic measurements is especially of use with resonance theories. EIS makes it possible to scan a large range of frequencies to identify those that resonate with the rate controlling kinetics or transport. The Butler–Volmer relationship then allows for understanding the electrochemical kinetic effects by fitting kinetic and transport parameters to the observed EIS.[118,119] This equation describes electrical current through an electrode for more complex reactions with multiple electron transfer.[118,119]

Challenges. Multiple reactions, side reactions, transport steps and competing impeding phenomena may be occurring simultaneously in an electrochemical system. Measuring current response and attributing it properly to the correct impeding phenomena is difficult, and extreme caution should be taken, especially at high frequencies. Furthermore, relation to enhancement from first principles, particularly with kinetic resonance or surface coverages would strongly support future electrochemical approaches, as would the *operando* ability to resolve the transient surface during forced oscillations.

Mechanical (stretching/strain/vibration)

There are a number of modes for mechanically altering the surface structure of a catalyst, including: vibration, piezoelectric induced, reaction induced, and acoustic induced. Each of these methods physically flexes, strains, or otherwise changes the structure of the catalyst for a certain amount of time. This, in turn, leads to altering surface energetics that results in interesting effects on the reaction properties.

Systems range in complexity from beaker atop ultrasonic source[120] to acoustically designed catalytic microreactors controlled by piezoelectric strain inducers. Such a broad technology operates across a very broad frequency range, from 0.01 Hz[121] all the way up to 17.4 MHz.[122]

Piezoelectric materials are solid materials (*e.g.* some crystals and ceramics) that gather charge when some external mechanical stress is applied. Some catalysts such as ZnO nanorods[123] and (Ba, Sr)TiO_3 nanowires[124] serve as piezoelectrically active materials with catalytic activity. For piezoelectric catalysts, any induced vibrations lead to a build-up of surface charge due to the piezoelectric effect (deformations in crystal structure lead to an electric charge and *vice versa*). The accumulation of positive and negative charges induce a dipole, facilitating electrochemical reactions, such as HER and OER reactions to occur on the surface.[123] It is interesting to note that unlike many other techniques that rely on externally induced field change (*e.g.* T or P), this technique homogeneously induces the piezoelectric effect in response to a fast external stimuli (*e.g.* current).

Yukawa *et al.* has experimentally demonstrated that when regions were doped with palladium and gold on either side of a piezoelectrically active z-$LiNbO_3$ material, production rate of ethene from the dehydration of ethanol was increased 16 times in the presence of applied vibration *versus* the absence of it, as shown in Fig. 18.[122] This is especially interesting, because the effect was highly selective towards ethylene, more than doubling the selectivity from 36% to 88%, with little effect on the acetaldehyde pathway.

Oh *et al.* observed the ability to induce pits on the surface of a perovskite during the exsolution of nickel when reduced by hydrogen.[125] Nickel particles began forming in these pits

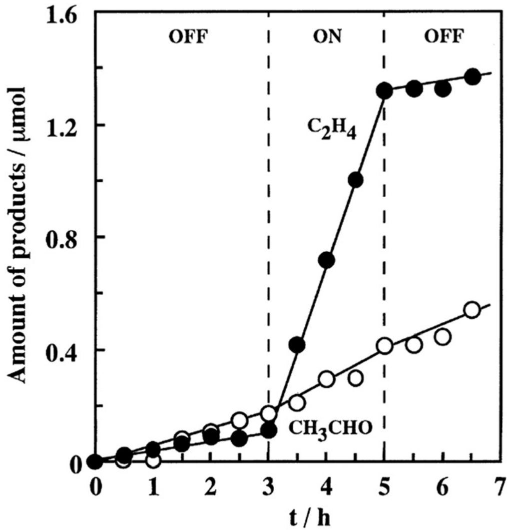


Fig. 18 The effect of applied vibration (3.5 MHz) to the production and selectivity of ethanol decomposition products. There is a sharp increase in ethylene as a direct result of applied vibrations (reprinted from Yukawa *et al.*[122] with permission from Elsevier).

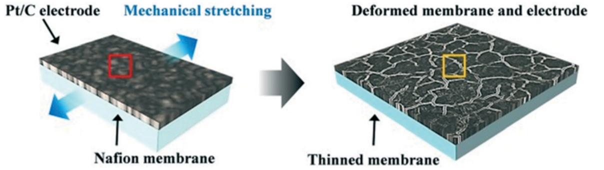


Fig. 19 Mechanical support stretching of a polymeric Nafion membrane coated with Pt/C induces structural changes that enhance catalytic performance (reprinted from Kim *et al.*[127] with permission from Springer Nature).

resulting in strongly bound catalytic sites after the 15 minute reduction cycle. Similar pitting is observed with potential-induced pitting.[126] This development is attributed to the relationship between strain energy and surface free energy which drives exsolution towards the unique structure. Approaches like this can induce structural rearrangements or stresses to a catalytic surface, inducing a response in catalytic activity.

Kim and coworkers have recently demonstrated the ability to deposit a catalyst on a stretchable polymeric surface then apply shear to the support to modify the performance of the catalyst,[127,128] as shown in Fig. 19. In that study, they propose that defects are introduced upon stretching which enhances the catalytic performance. Others have demonstrated reversible or periodic stretching of catalyst pellets.[129]

Challenges. As with other techniques, the mechanical stability of a material exposed to constant periodic strain is always a concern. Furthermore, applied strain to surfaces may affect many different physical properties such as thermal conductivity or diffusivities and phenomena such as the formation, diffusion, and energy of vacant sites or erroneous hot spots. It is difficult to deconvolute these affects from one another to identify the full, complex mechanism, which also lacks physical derivation from first principles.[130] As the field of flexible electronics progress, there is substantial room for advancement toward heterogeneous catalysis that remains to be explored.

Bioreactors

It is important to note the presence and importance of natural and forced oscillations in biological systems. Biological oscillations have been studied for decades and have been reviewed by Silveston *et al.*[4] as well as Hess and Boiteux.[131] Typically in these studies, biological systems are observed under oscillating nutrient or oxygen conditions in order to observe their response. Because the species are living and need to adapt to their new environment, forced oscillation frequencies are typically slower, ranging from 10^{-5} to 10^{-3} Hz.

In the case of the nutrient oscillation of glucose for a sample of *Escherichia coli* in a highly controlled reactor vessel, modulation was achieved by using a solenoid valve to switch between two stock solutions at periodic intervals. The oscillations periods tested were between 0 to 6 hours, with corresponding responses shown in Fig. 20. Because these biological species are living, fast oscillations are not necessary and would result in a dampened mean response. This study observed not only the rate of growth of the cells, but also the change in macromolecular species (proteins, RNA, and DNA) within the cell itself.

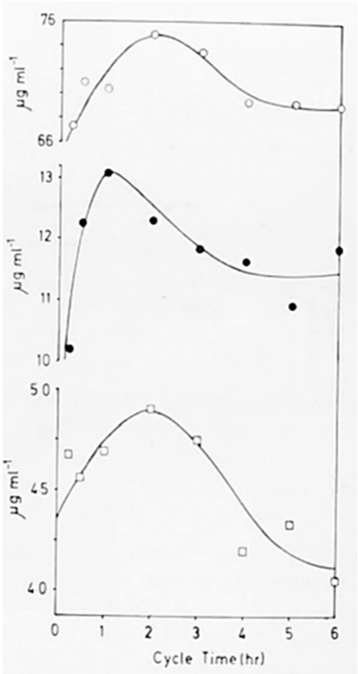


Fig. 20 The observed concentration of macromolecules: protein, RNA, and DNA (from top to bottom) at different glucose modulation rates (reprinted from Pickett *et al.*[137] with permission from John Wiley and Sons).

It was proposed that the reason there is an optimum in production of these macromolecules is due to the presence of "active" and "inactive" ribosomes which become activated, for example, when there is a shift towards more beneficial nutrients available.[132] These ribosomes are free to activate and deactivate based on the available nutrients. It was found that the response to the high concentration (or activation) was notably quicker than the response to the low concentration (or deactivation). This would lead to an overall higher rate at higher frequencies of nutrient supply.

Another study tested the effect of aerobic/anaerobic oscillations on fermentation using *Propionibacterium freudenreichii*.[133] In these experiments it was found that as the oscillations continued, the rate of degradation of the propionate species increased from 0.1 g L^{-1} h^{-1} to 0.32 g L^{-1} h^{-1}. It was claimed that this may be due to the increase in cell concentration in the sample. Oxygen is used in these experiments to adjust the metabolic pathways at given times. While cells are able to grow more quickly under oxygen rich conditions for short periods of time, the presence of oxygen will start to inhibit cell growth at longer times due to the inhibition of cytochrome synthesis. Anaerobic conditions are also beneficial for the decomposition of propionate species which inhibit cell growth.

Special case – polymerase chain reaction (PCR). PCR was invented by Kary Mullis in 1985 as a technique to rapidly multiply DNA through a series of periodic temperature steps. A review by Kricka and Wilding in 2003 outlines the microchip technology and thermocycling.[134] The process typically includes denaturing, annealing, and extending steps. These steps occur at approximately 95 °C, 55 °C, and 72 °C, respectively and are cycled a total of 30 times. PCR cycling originally took hours to complete, but modern microtechnology has been able to reduce that time to under a minute.[135]

Challenges. Biological systems are living organisms that need to evolve or adapt to external changes, leading to long time scales associated with changing conditions. Furthermore, the complexity of the system requires consideration of thousands of unique pathways, through which a standard frequency response may be difficult to prove. Additionally, because these are living organisms, they thrive in a narrow window of conditions. Oscillation temperature or chemical environment to extreme conditions will lead to inevitable cell death. In short, strong parallels can be made between catalytic reaction networks and biological or metabolic pathways; if mechanisms for enhancement can be mathematically proven in biological systems, it would offer promise for translation to similarly complex catalytic systems.

Progress towards achieving truly dynamic catalysis

Despite over half a century of dynamic and periodic catalytic reaction theory, resonance theory had only recently emerged as a potential pathway to operate beyond classical coupled thermodynamic/kinetic limitations. To this end, our progress must be examined both on a theoretical and experimental basis.

From the perspective of theory, the groundwork has only recently been laid for how a periodic perturbation to the catalytic microenvironment might cause an amplified response beyond the time averaged steady state. However, a rigorous analytical model has not yet explored the theoretical solution to such a problem. Similarly, the effect of such a switch on the microstates has not been explored on the quantum scale. Finally, real systems experience impedances from a multitude of kinetic and transport steps at the bulk states, through boundary layers, and at the active site—multiscale models have not been explored for resolving the dampening or amplifying effect of such phenomena.

From an experimental perspective, progress has been made to understand reactor dynamics under slow periodic input perturbations, with time averaged rate enhancements being attributed to: periodic surface cleaning that optimize surface coverage, catalyst regeneration, or enhanced mass and thermal transport removing pore diffusion and hot spot limitations, respectively. Experimental work with microreactors have shown that pulsed energy inputs allow for periods of conversion, attributed to periodic excitation of the surface. However, the vast majority of these techniques are shown to apply enhancements on timescales that do not resonate with the intrinsic kinetics (Fig. 7), leading to the conclusion that the enhancement is on the steady state performance, not the intrinsic catalytic turnover mechanism. Due to the fact that some techniques may inherently be too slow (*e.g.* biological, chemical looping), or too fast (*e.g.* plasma, vibration), truly resonant dynamic catalysis may never be observed through these techniques and enhancements may instead be due to secondary effects (non-linearity of response, the presence of highly unstable and reactive molecules, *etc.*). Finally, the first experimental evidence of catalytic resonance has just recently been shown by Abdelrahman and co-workers[113] who used an electrochemical system to demonstrate the enhancement. Despite these strides, substantial efforts are required to develop systems to induce external periodic forced oscillations that are sensed at the surface without having been damped by the external environment. Furthermore, the effect on the catalytic site should be examined *operando* to prove the existence of surface resonance.

Conclusions

Dynamic catalytic reaction engineering offers an exciting new avenue to explore and further push the limits of heterogeneous catalysis. Natural oscillations are known to exist in reacting systems; exploiting and amplifying those oscillations through externally engineered forced periodic stimuli is a new approach that has recently shown great promise to overcome classical barriers. Theoretical approaches have hinted at the ability to externally tune surface energetics to oscillate at frequencies that resonate with intrinsic reaction barriers, thus introducing catalytic resonance theory. A multitude of experimental approaches have been reviewed for their ability to induce rate enhancements. While each one faces its own challenges, our overarching assessment is that forced periodic oscillations have the potential to induce substantial rate enhancements in catalytic systems. However, substantial efforts remain to bridge the gap between the theoretical rate enhancements, kinetic resonance, and reaction engineering with the experimentally observed forced oscillation responses. Furthermore, substantial efforts remain to achieve *a priori* prediction of catalytic rate enhancement and predictive operating windows for forced oscillations.

From a fundamental perspective, particular efforts are required to precisely describe rate enhancements from first principles. Analytical dynamical models that describe the active site and stiff equations governing the predator–prey resonance and corresponding enhancements would motivate the drive to resolve reactor models capable of achieving such environments. Multiscale models are required that are able to resolve the continuum scale from the induced perturbation/transport dampening all the way down to the microkinetics of surface coverage without applying mean field assumptions (PSS or MASI).

Experimentally, kinetic resonance theory remains to be demonstrated and related back to the kinetic turnover phenomena. Techniques must be refined to measure rate enhancements, 1) *operando* at the active site, 2) in the absence of dampening effects, and 3) in the absence of inadvertent thermal or transport effects.

From an applied perspective, creative ideas are needed to translate these micro-engineered techniques to an industrial scale without losing the critical spatiotemporal resolution necessary for pulsed operation. Catalysts and kinetic expressions are designed with static reaction conditions in mind. To further the advancement of the field, catalysts must be synthesized and kinetic expressions derived that are specific to transients.[40] Furthermore, the economics of operating under dynamically pulsed conditions should be explored, particularly when energy must be rapidly applied then removed from the system.

It is our opinion that if these considerations can be made, the dynamic catalysis concepts reviewed here have the potential to radically transform our knowledge of heterogenous catalysis and more broadly, the chemical manufacturing landscape.

Conflicts of interest

There are no conflicts to declare.

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