

Up Up Down Down Left Right Left Right B A Start for the Catalytic Hackers of Programmable Materials

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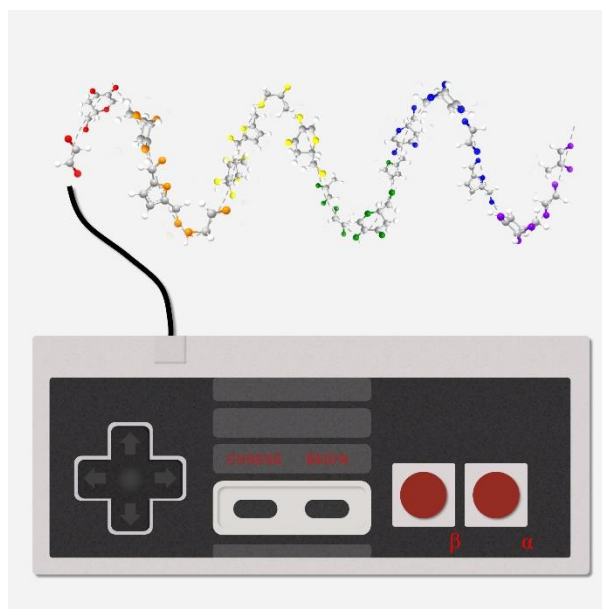
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Abstract. The valuable information of catalysis for the past century has been the composition and structure of high-performing catalytic materials. But a new class of programmable catalysts that change the electronic characteristics of their active sites on the time scale of the surface reaction are changing the catalyst design process by requiring additional information describing the input program that directs the temporal changes in the catalyst surface. Catalyst programs vary in complexity associated with the number of combined waveforms required to optimize surface chemistry rates and selectivity to products. The path forward for writing and optimizing catalyst programs will combine together the methods of parameter screening, rational design based on molecular models, and machine learning. This new approach to catalysis will change the nature of catalysis science, with researchers pursuing dynamic catalytic programs with improved catalytic performance over static catalyst compositions.

Secret codes, passwords, and functional algorithms have been part of human culture since ancient times providing entrance to organizations and buildings, benefits in commerce and competition, and access to information hidden from general society.^[1] Militaries in particular have used passcodes and sounds to identify affiliation and share strategic information; for example, paratroopers of the allied forces invading Normandy in 1941 as part of Operation Overlord (i.e., D-Day) used a simple clicking passcode to identify friend from foe in the dark (two clicks for allied friend).^[2] The complexity of methods of information subterfuge increased significantly with the use of wireless transmission, where cryptography has advanced through various technologies such as mechanical Enigma machines^[3] to modern electronic algorithms to



allow for private communication beyond the power of the advanced computer capabilities.^[4]

The growth and expansion of the internet combined with digital tools and services for entertainment, productivity, and travel have engrained in general society the power of secret information such as passcodes.^[5] Passcodes are ubiquitously used for accessing banking information, uploading social media content, ordering groceries, or sending and receiving electronic mail. In entertainment, the famous Konami code (↑↑↓↓←→←→ B A Start) remains both historically relevant and ubiquitous for providing users significant benefits in multiple video games including the famous *Contra* video game on the Nintendo Entertainment System.^[6] More recently and more seriously, secret security flaws in programming code allowing for breaches in common software such as operating systems are

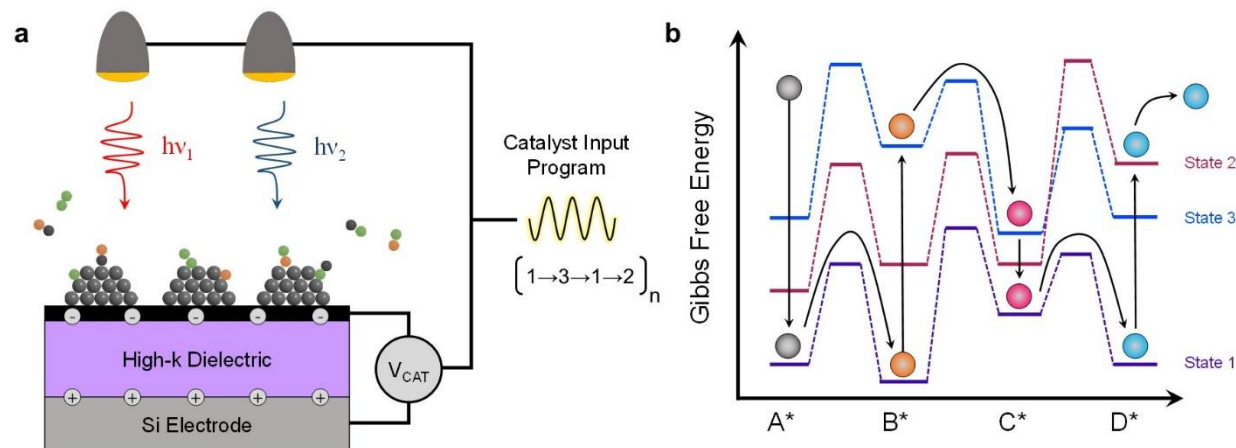


Figure 1. Programmable Catalyst Methods and Mechanism. (a) Programmable catalysts undergo change in active site electronic structure via the application of light of mixed wavelengths, charge via applied potential, V_{CAT} , or physical strain that changes the catalyst between multiple states via an input program. (b) The reaction of $A(g)$ to $D(g)$ via surface intermediates A^* , B^* , C^* , and D^* is optimized for a repeating input program of states $1 \rightarrow 3 \rightarrow 1 \rightarrow 2$ which provides the smallest barrier to elementary reaction or desorption at each step of the reaction sequence.

sufficiently valuable and powerful that governments pay for them.^[7] The capability of passcodes and secret inputs has embedded in society the power of secret information.

Yet the secrets of the materials community have so far been inherently different from passcodes and passwords; the key insight into obtaining high materials performance is composition and structure. Metal-organic frameworks (MOFs) derive their benefit for catalysis and separations from minor variations in precise composition and structure surrounding active binding sites.^[8,9] Zeolites exist in a variety of pore and cavity structures with active sites that can be modified with framework substitutions or active site ion exchange.^[10] And just as Coca-Cola and Kentucky Fried Chicken (KFC) have precise ‘secret’ formulas providing differentiable flavor,^[11,12] catalysts such as silver metal to promote ethylene epoxidation have a precise formula of surface inhibitors and promoters (e.g., chlorine, alkali) that significantly improve reaction selectivity to ethylene oxide.^[13,14] The concept of a secret catalyst composition is so embedded in the zeitgeist that it was the McGuffin of the 1980 film, *The Formula*, starring Marlon Brando and George C. Scott; competing interests from around the world are pursuing a secret coal-derived synthetic fuel formula that could destroy the existing oil economy.^[15]

The introduction of programmable catalysts changes the type of information input required for control of surface chemistry. While conventional heterogeneous catalysts have one or more static active sites for catalysis, a programmable catalyst has an active site that changes throughout a single catalytic cycle (i.e., on the time scale of the reaction itself). As shown in **Figure 1a**, a catalyst can be temporally modulated with light, charge or strain to change the nature of catalyst active sites. The benefit of this approach follows from the sequence of elementary steps on a surface; a multi-step reaction benefits from a catalyst that is optimized in time for each reaction step.^[16] The ‘program’ is therefore the temporal sequence of catalyst inputs that manipulate the catalyst surface to best control catalytic activity and selectivity to desired products. As shown by the example of **Figure 1b**, a specific input sequence (states $1 \rightarrow 3 \rightarrow 1 \rightarrow 2$) provides the clearest benefit in catalytic rate for an $A \rightarrow B \rightarrow C \rightarrow D$ generic reaction. While programmable catalysts have been shown to consist of mundane active sites (e.g., Pt nanoclusters or alumina),^[17,18] the program of catalyst inputs can be as complicated as required to optimize a chemical reaction. A catalytic cycle with 16 surface reaction intermediates benefits from a catalyst active site that switches between 16 different electronic states per turnover. Modeling of these programmable dynamic catalysts indicate substantial new power for catalysis scientists and engineers such that an

effective program essentially becomes a ‘cheat code’ for chemistry. How will these catalytic programs be discovered?

Catalysts of the Past. Heterogeneous catalyst formulations of the past frequently have a story associated with their fortuitous discovery. As related by J.M. Berty in 1983, one of the most famous catalyst formulation innovations was the use of specific inhibitors with silver for ethylene epoxidation.^[19] Thirty years prior, these reactors were air blown at a time when process emissions control was limited. Oxidation reactor performance was oddly observed to correlate with local wind conditions, after which it was determined that chlorine-containing air contaminants from the emissions of a nearby ethylene dichloride cracking facility were highly desirable relative to the air coming from the direction of polyethylene manufacturing. Ethyl chloride and vinyl chloride were discovered to more effectively inhibit over-oxidation to CO₂, such that it is now a preferred reaction co-feed over early chlorine-supplying molecules.^[19,20,21] As with many catalysts over the decades, lucky accidents and attentive experimentalists have found formulation breakthroughs that were never considered or predicted.

The writer and historian Horace Walpole (1717 - 1797) recognized the importance of ‘dumb luck’ or chance discovery; he referred to this intellectual method as ‘serendipity’ after the princes of Serendip who made many discoveries in their journeys despite not looking for them in particular.^[22] Yet serendipitous progress in catalysis is inherently unpredictable and unreliable, and new methods have been developed to prompt ‘smart luck’ via the directed search for catalyst formulations with improved reaction performance. High-throughput screening has provided the technological capability to synthesize, characterize, and evaluate hundreds to thousands of catalysts formulations.^[23] While a single catalyst researcher in the past could evaluate ~10-20 catalysts per year, new methods enabled the screening of orders of magnitude larger parameter space of composition and formulation that could first discover and then optimize improved catalysts.^[24] In addition to the instruments and automation required for screening large numbers of materials, parallel efforts have advanced computational methods integrating mathematics, statistics, and machine learning

required for: (i) designing large screening experiments, (ii) analysis of the data, and (iii) iterative decision making for selecting the next set of catalyst compositions for study.^[25,26]

Catalyst engineering has not relied only on good fortune, serendipitous or not, to discover all catalyst breakthroughs; the parameter space of catalyst composition and structure remains too large to stumble upon all of the required amazing catalyst formulations. Catalysts can alternatively be designed based on an understanding of the reaction mechanism and the relationship between surface chemistry with catalyst active site physical and electronic structure. This ‘rational catalyst design’ approach has motivated decades of fundamental effort to decompose our understanding of catalytic mechanisms to their elementary steps and associated energetics. This effort began with vacuum studies of simple reactions on single crystals and has since expanded with additional experimental methods to study multi-step reactions on complex catalyst particles integrating chemical kinetics and spectroscopy. By the 1990s there was significant progress on building detailed surface chemistry models (i.e., ‘microkinetics’) based on independent kinetics of elementary reactions that could connect catalyst model behaviors to experimental observations.^[27,28,29] A building up approach of combining small bits of information on elementary reactions appeared to be the path forward to understanding catalysis.

Progress towards rational design of catalysts accelerated dramatically in the new millennium due to significant advances in computational heterogeneous catalysis.^[30,31,32,33] While the kinetics of individual elementary reactions were previously obtained through expensive, time-consuming fundamental experimental studies, increasing computational power combined with improved methods of density functional theory (DFT) permitted the direct calculation of the energetics of individual molecules on surfaces and their transition states in elementary reactions.^[34,35,36,37] The energies of individual elementary reactions could then be combined within microkinetic models to understand their cumulative impact on reaction pathways and rates.^[38,39,40] When compared with experimental insights derived from tools such as kinetics or spectroscopy, DFT-derived reaction models provided sufficient clarity on surface molecular reaction behavior that catalysts could be

understood and rationally designed. The fastest catalysts could be rationally identified via constructed Sabatier volcanos^[41,42,43], and catalytic pathway control could be rationally understood via molecular selectivity maps with regions of pathway dominance.^[44]

Present State of Catalysis. The last four decades of catalysis research have provided a foundation of fundamental molecular understanding of surface chemistry, yet many of the most important challenges for catalysis remain to be addressed.^[45] A major focus of heterogeneous catalysis has been the design of catalysts that could exceed the Sabatier volcano limit via new linear scaling behaviors of molecules on engineered catalyst active sites, yet no catalytic material has yet been experimentally demonstrated to exist beyond a volcano peak.^[46] The Sabatier limit has held back the catalysis of many of the most important reactions for over century; ammonia synthesis via heterogeneous catalysis continues to be operated at high pressure (200 atm) and temperature (~400 °C) due to a Sabatier peak scaling with the binding energy of N* with optimum catalysts of Fe, Ru, Co, and Ni.^[47,48] Similarly, methanol prepared from synthesis gas constitutes a major commodity chemical process important for fuels and chemicals, but it still relies on copper-based catalysts near the reaction Sabatier peak.^[49] The same Sabatier limit also exists for the electrocatalytic synthesis of H₂ from water, where the maximum rate on the best catalyst (IrO_x) remains too slow for low cost energy storage as hydrogen gas.^[50,51] All of these reactions operating at extreme conditions consume massive amounts of energy in the most energy-intensive manufacturing industry, chemical production.^[52]

New catalysts have also not solved some of the most important challenges in reaction selectivity to targeted chemicals. Methane is an abundant one-carbon chemical available throughout the world from natural gas and decomposing organic materials. To upgrade methane to useful chemicals such as methanol, initial catalytic steam reforming creates synthesis gas (CO + H₂), which is then adjusted in H₂/CO ratio and reacted at significant pressure to form methanol, in a capital-intensive energy-demanding process.^[53] Direct synthesis of methanol would instead selectively oxidize from methane without full combustion to CO₂, but the direct process catalysts have struggled to achieve viable selectivity to methanol at any reasonable

conversion (>10%).^[54] Another critical reaction is the epoxidation of propylene to propylene oxide, which is an important large-volume chemical precursor for many three-carbon chemicals (e.g., propylene glycol) as well as a monomer in polyol and polyurethane plastics. While silver catalysts have been improved significantly for ethylene epoxidation, they exhibit lower selectivity for propylene epoxidation; a highly selective catalyst for propylene oxide without significant formation of CO, CO₂, or acrolein remains a major goal of heterogeneous catalysis.^[55] The opportunity to significantly improve the chemical industry still exists with many other major reactions including more selective direct synthesis of H₂O₂,^[56] the conversion of synthesis gas directly to olefins,^[57] and the direct oxidation of benzene to phenol rather than the current industrial cumene process,^[58] among many other important chemistries. Progress in catalyst design for these reactions and many more has not found a method of identifying new catalyst formulations with disruptive increases in performance.

In the past two decades, catalyst have also been designed with new goals for sustainability. As the chemical, fuels, and energy industries transition away from fossil fuels, a focus on low-carbon processes and more sustainable products with new reactions and operating conditions has forced unique thinking about catalyst composition and utilization. This has included catalysts that can operate in liquid water,^[59] solid acids that are weaker than conventional aluminosilicates,^[60,61] and catalysts that can control the chemistry of molecules with significant oxygen.^[62] The strategy has for the most part adapted the catalysts developed for fossil fuel processing to new feedstocks derived from renewable resources such as carbohydrates, natural oils, or lignin.^[63] This adaptability approach to sustainable catalysts has benefited a renewable chemicals industry developing pathways to many key chemicals such as drop-in renewable molecules including p-xylene,^[64] adipic acid,^[65] acrylic acid,^[66] and butadiene^[67] while also inventing entirely new renewable molecules with improved characteristics such as γ -valerolactone,^[68] methyl-caprolactone,^[69] and oleofuran sulfonate (OFS) surfactants.^[70] While catalysts for renewable chemicals have been remarkably effective, they have not fundamentally changed the practices and methods of

heterogeneous catalysis; static catalytic surfaces are still designed to direct the flow of reactions down a fixed free energy gradient, with bias towards the downhill reaction pathways of interest. The fundamental problems that must be solved to overcome the Sabatier limitation and the selectivity challenge of major chemical processes remain to be solved by the next generation of catalyst engineers.

Challenges for Programmable Catalysis. For more than a century the catalysis and reaction engineering community has acknowledged the temporal characteristics of surface chemistry and reactions in general. The rate of a set of elementary reactions that comprise a catalytic cycle is defined as a ‘turnover frequency’ (TOF), and a surface chemistry is comprised of multiple elementary reaction steps each defined with its own characteristic frequency and rate constant (with units of inverse time). Surface reactions can therefore be perceived as a combination of transient events, each with their own characteristic or ‘natural’ frequencies, for which the selected catalyst and conditions will favor some elementary steps over others. The Sabatier limit is therefore a consequence of a many-event process; one event will have a dominant degree of rate control for a fixed catalyst and condition.^[71] And the solution to overcoming kinetic control of any one elementary step is to modulate the catalyst itself during the time period of a single catalytic turnover, thereby shifting the degree of rate control between different elementary steps as the reaction proceeds.^[16,72]

Programmable catalysts are designed to exhibit tunable active sites that can change their electronic or physical interaction with adsorbates and transition states with time (**Figure 1a**).^[73] The mechanisms to modulate catalytic active sites have been developed using light, charge, or physical strain, ultimately changing the nature of the molecule-surface interaction. Pulses of light can weaken the binding of molecules such as carbon monoxide on Pt,^[74] while electrons depleted from Pt nanoclusters within a catalytic condenser device can strengthen CO binding.^[18,75,76] Physical strain in ruthenium surfaces can accelerate N₂ hydrogenation, even on more than one Ru catalytic site.^[77] The many methods of applying light, charge, and strain open up many possibilities for implementing programmable catalysis, but they all have the consistent characteristic of changing the surface energy of reaction intermediates and

transition states rather than the overall thermodynamics of the reaction, as occurs in oscillating temperature or electronic potential (i.e., oscillating voltage electrocatalysis) reactors.^[78]

The benefits of a programmable catalyst that changes over the lifetime of a single catalytic turnover derive from the enhanced level of control of molecules on surfaces. For Sabatier volcanos with two dominant rate-determining elementary steps, oscillation of the surface between two states can promote the overall catalytic rate orders of magnitude beyond the Sabatier limit as the applied frequency of the surface program approaches the natural frequencies ($f \sim k_i$) of the rate-controlling steps.^[16,79] Each change in state of the catalyst surface corresponds to changes in the heat of adsorption of surface molecules, therefore resulting in energy input (strong to weak binding shift) or output (weak to strong binding shift).^[78] The implication is that surface programs, when combined with specific ratchet-shaped dynamic energy profile mechanisms, can push reactions away from equilibrium.^[72,80] For reactions such as ammonia synthesis, energy input via surface-programmed strain oscillations is predicted to accelerate the overall reaction and promote the reaction at lower pressure.^[81] As reactions become more complex, programmed surface oscillations can significantly promote specific reaction pathways over others, providing dramatic potential for control of product selectivity.^[82] Realizing these catalytic benefits will require understanding the new relationships that exist between molecules, surfaces, and complex programmed inputs.

The challenge of programmable catalysis is two-fold: (1) develop the technologies to deliver fast (>100 Hz) and powerful energy oscillations to catalytic active sites, and (2) understand and write the input programs to control surface chemistry. While the techniques to modulate catalytic surfaces have been demonstrated,^[17,73,74] the writing and optimizing of catalytic programs is in its infancy.^[83] With greater control over the chemical events on a surface comes a larger parameter space to explore. While a conventional static thermocatalyst has design parameters of composition and structure along with conditional parameters (temperature, pressure, residence time, and gas composition), programmable catalysts double the number of input parameters for even the simplest program design (e.g., sinusoidal input frequency or pulses of a

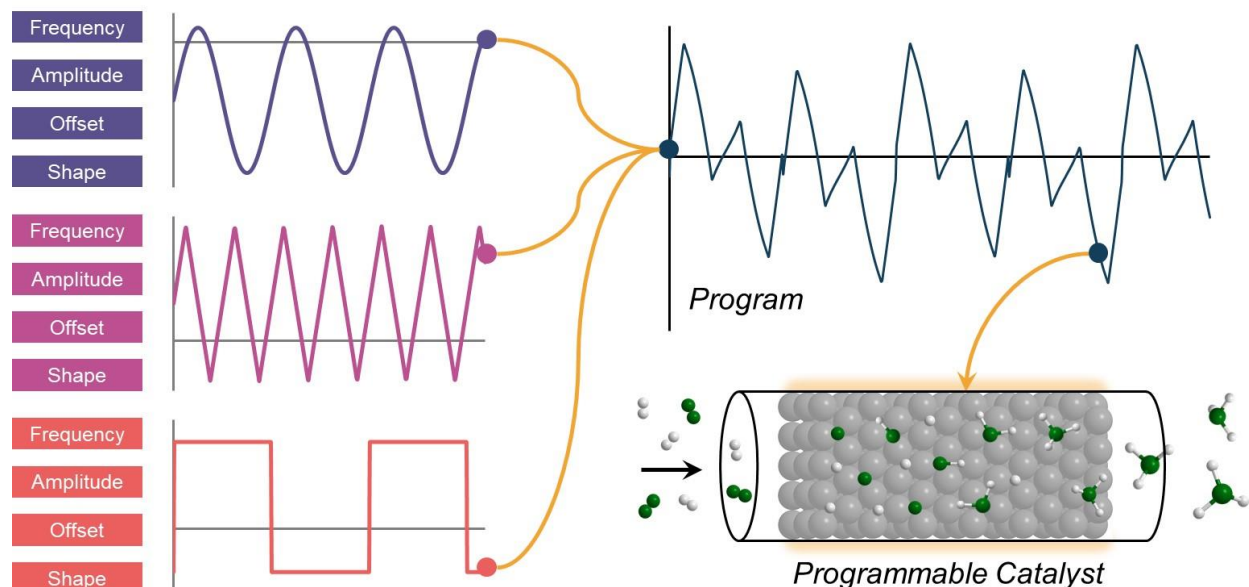


Figure 2. Design of catalyst programs. Three independent input waveforms are combined into a single catalyst program which then modulates the surface of a heterogeneous catalyst to control surface chemistry. The complexity arising from large waveform input parameter space provides the benefits of enhanced control and fine tuning of the catalyst program while also increasing the challenge of identifying the best input program.

single light wavelength). As shown in **Figure 2**, input programs must specify oscillating perturbations with frequency, amplitude, amplitude offset, and waveform type (e.g., square, trigonal), and recent simulations indicate that more complex reaction mechanisms benefit from even more complicated programs.^[84] The dynamic catalytic surface is more like a machine with moving parts (i.e., changing energy landscapes), and understanding the catalytic mechanics of an oscillating free energy profile of a complex reaction network will be one of the core challenges of the 21st century for catalysis science and engineering.

Possibilities and Methods for Developing Catalytic Programs. The composition and structure of effective catalyst input programs remains the great secret of every chemistry and programmable catalyst combination. Like a secret code or proprietary formulation, a small amount of knowledge can unlock capability and performance of dynamic surface chemistry, as demonstrated for even minor variations in simulated catalyst programs.^[85] And like a person that has forgotten their login passcode to their email, guessing a catalyst program input code is unlikely to work; the number of design parameters is likely too great (**Figure 2**). The path forward for designing catalysis programs will benefit from the general

strategies implemented for static thermocatalysis, albeit with a more complicated system; computation, theory, experiment, and characterization working collaboratively can deconstruct dynamic surface chemistries and programmable inputs to understand their mechanics.

While complex surface reactions controlled by programmable catalysts are complicated, there still exist general design principles that can guide the development of catalyst input programs. For example, for systems with defined Sabatier volcano kinetics, the catalyst input program likely needs to oscillate between conditions that significantly change the degree of rate control of the two slowest steps of a reaction.^[72,79] The Sabatier volcano therefore provides an approximation for the required amplitude of an input oscillation to the surface required to have a measurable impact on the overall catalytic rate.^[16] Existing simulations also provide insight on the types of surface perturbations that could significantly modify catalytic reactions. As surfaces are modulated with light, charge, or strain, the reaction intermediates linked through a common transition state of relevance to the catalytic rate *need to change* in surface binding energy to differing degrees.^[72] By the BEP linear scaling relationship, the transition state energy

changes linearly with the enthalpy change of an elementary reaction, and the reaction enthalpy of a single step only changes under perturbation if the linear scaling parameter, γ , between surface reactant and product is non-unity ($\gamma \neq 1$).^[72] This simple insight provides guidance on the selection of chemistry-catalyst-perturbation selection; select programmable catalytic systems with $\gamma \neq 1$ for the most important elementary steps as determined by the degree of rate control.

We can also consider possible future design principles and metrics that are still being developed for programmable catalysts. With energy input via the surface resulting from the changing of catalyst electronic states, program design must account for the deviation of each elementary step and the overall reaction from equilibrium. Already, quantitative metrics have been identified for simple surface reactions that have either positive or negative scaling, γ , such that the bias direction away from equilibrium can be predicted.^[72,79] But prediction of the effect of dynamic surfaces on reaction bias away from equilibrium is more complicated for complex reaction networks. For the simple triangle surface reaction ($A \leftrightarrow B \leftrightarrow C \leftrightarrow A$), the influence of three interacting elementary reactions can result in net flow of molecules in either direction (clockwise or counterclockwise) around the reaction loop.^[84] Even more complicated behaviors have been simulated for real chemistries such as ammonia synthesis on ruthenium undergoing dynamic strain; the reaction proceeds to ammonia product compositions that exist either above or below equilibrium dependent on the applied strain frequency.^[77] More detailed understanding and quantitative metrics of these complex dynamic networks are needed to predict the interactions of individual elementary reactions undergoing oscillating transition state energies.

Programmable catalysts and their input programs can also be rationally designed from the ground up via fundamental understanding of the relationships of surface perturbation (charge, light, or strain), surface energies of intermediates and transition states, and the interconnected kinetics of the reaction network. This will begin by understanding the impact of surface perturbation and quantifying the electronic and physical changes occurring on surfaces for varying extent and type of local accumulation of charge, light or strain. These surface modulations will then be evaluated to

quantify their impact on molecular adsorption; similar to periodic linear scaling, we can anticipate the existence of linear scaling over some limited set of perturbation conditions (and likely more complicated scaling behavior at extreme perturbation).^[86,87,88] These intermediate and transition perturbation scaling relationships can then be implemented within a surface reaction model via existing methods (e.g., mean field microkinetic model, kinetic Monte Carlo), such that the time-resolved surface behavior of molecules on a dynamic surface undergoing externally-applied oscillations can be determined. This general approach has already been demonstrated for ammonia synthesis occurring on dynamically strained ruthenium surfaces,^[77] providing a prediction of the extent of surface strain and frequency required to accelerate NH_3 synthesis and promote the reaction beyond equilibrium at reduced pressure. This method of predicting programmable catalysis behavior is challenging due to the difficulty in developing accurate descriptions of surface adsorption enthalpy and entropy with perturbation combined with the existing challenges of describing reaction mechanisms on multiple active sites with additional yet necessary complexities such as surface coverage dependence (i.e., lateral interactions) of molecular energies.^[89,90] However, this approach is based on fundamental understanding of molecular behavior and will continue to advance with time for each programmable catalytic system with improved computational and kinetic modeling methods.

Finally, while the preceding methods involved either rudimentary or detailed understanding of the underlying chemistry and physics of programmable catalysts, there exist additional emerging methods for analyzing and predicting the behavior of complex catalytic systems.^[91,92] The machine learning approach has already been employed to evaluate the structure-function relationships of catalysts of many types (asymmetric, homogeneous, and heterogeneous), with the goal of predicting new catalyst compositions and structures.^[93,94] This general method of pursuing catalysts has many variations, but one common attribute is the generation of a training set of data based on large numbers of catalyst structures and characteristics that serve as the basis for future catalyst predictions. This training set could be derived from the existing literature, a campaign of

high throughput testing experiments, or computational analysis of materials including intensive ab initio calculations or more simple catalyst descriptors.^[95] Applying these methods to programmable catalysis to identify high-performing input programs can operate similarly. A training set of catalyst performance via surface modulation can be generated via the screening of a varied set of parameters distributed around the full parameter space of program design; thereafter iterative prediction and experimental evaluation of catalyst programs can progressively refine the machine learning model and advance towards improved surface control and catalyst performance.

Concluding Remarks. The potential impact of programmable catalysts will ultimately be determined by the evolution of catalytic materials and their ability to modulate surfaces with high amplitude and frequency in molecular binding energy. But since these experimental methods already exist and will continue to improve,^[18,73] it becomes possible to envision a future of heterogeneous catalysis that radically differs from our conventional approach. Catalysis scientists and engineers of the future might conduct laboratory work that feels more similar to computer programming or catalytic hacking. Consider the following scene depicted in **Figure 3**:

A graduate student, fully protected from chemicals by a laboratory jacket, gloves and goggles, unwinds the heating jacket of a glass tube reactor, carefully setting it aside before breaking the reactor seal and lowering the glass reactor tube. A bundle of metal wires from inside the reactor spill out, after which the student carefully assesses and places the wire ends in contact with a thin metallic-looking wafer, the programmable catalyst. After placing all wires and the shiny device back within the reactor and sealing it up, she sits down at the computer desk and begins typing into the potentiostat control software; “now let’s see what this catalyst can really do!” she says.

She starts out her experiments simply by flowing gases over the programmable catalyst, periodically looking over at the output of the mass spectrometer, which clicks away establishing a baseline catalyst performance. She then leans forward with a determined look on her face, ready to explore the different programmable settings of her new catalyst. Every five minutes, she applies a new fixed voltage to the catalyst, each time



Figure 3. Catalyst Hacking. The catalyst hacker examines catalyst input programs to understand the relationship between program structure and catalyst performance, ultimately identifying the catalyst program that maximizes catalytic rate and/or selectivity to targeted chemical products.

watching the mass spectrometer rapidly change and then stabilize at a new reactor output composition. After each change she types the catalyst output concentration into a spreadsheet and notes its calculated rate in the laboratory notebook, after which she sits back and thinks about where to go next with the catalyst input.

After a cup of coffee, she consults her simulation results and writes down a few predicted waveforms of frequencies and amplitudes before loading into the computer the dynamic catalyst conditions of interest. For the next six hours, her computer directs the potentiostat to send the catalyst a new voltage oscillation, ultimately changing the performance of the catalyst and pushing the mass spectrometer detector signal up to higher measured catalytic rates. A few times, a new oscillation leads to a quick increase in mass spectrometer output, ultimately giving a brief moment of excitement, before the catalyst stabilizes about rates about an order of magnitude lower than the target performance. For brief periods of time, there are moments of frustration where the number of input variables of multiple overlapping input frequencies seems too large, and the whole pursuit

of improved catalyst performance feels like finding a needle in a haystack. But she presses on.

At this point, she begins entering her catalyst performance data into a machine learning algorithm, which predicts the next best catalyst input program. With every prediction of a new catalyst program, she dutifully sends the new voltage signal to the catalyst and reports back to the algorithm the catalyst performance. After about two hours, a new trend slowly emerges; with each new catalyst program prediction, the mass spectrometer signal (and the catalyst rate) begins to climb. Every new program iteration is accelerating the reaction, and every five minutes the rate climbs a bit higher. Students in the laboratory begin to gather around the reactor; the excitement is palpable, and researchers start predicting how many more algorithm iterations will be required to break the catalyst rate record. Click and tap on the keyboard; the rate increases moving closer to the new catalytic rate record. Finally, after an hour, she programs into the potentiostat the most complicated program predicted so far by the machine learning algorithm consisting of five overlapping waveforms; loud clicks on the keyboard are heard before a single loud clack of the ‘enter’ key. She sits back in her chair and sips her coffee as the mass spectrometer signal climbs again, now passing the dashed line on her computer screen for a record catalytic rate. The students around the computer desk clap and cheer. Under her breath, the catalyst hacker whispers, “I’m in.”

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Keywords. Catalyst, heterogeneous, program, frequency, dynamic

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