Systems & Control Transactions

Research Article - Peer Reviewed Conference Proceeding
ESCAPE 35 - European Symposium on Computer Aided Process Engineering
Ghent, Belgium. 6-9 July 2025
Jan F.M. Van Impe, Grégoire Léonard, Satyajeet S. Bhonsale,
Monika E. Polańska, Filip Logist (Eds.)

PSE PRESS

A Computational Framework for Cyclic Steady-State Simulation of Dynamic Catalysis Systems: Application to Ammonia Synthesis

Carolina Colombo Tedesco[a], John R. Kitchin[a], and Carl D. Laird[a]*

[a] Carnegie Mellon University, Chemical Engineering Department, Pittsburgh, Pennsylvania, United States of America
* Corresponding Author: claird@andrew.cmu.edu.

ABSTRACT

Dynamic or Programmable Catalysis is an innovative strategy to improve heterogeneous catalysis processes by modulating the binding energies (BE) of adsorbates on a catalytic surface. The technique enables the periodic favoring of different reaction steps, overcoming limitations imposed by the Sabatier Principle and allowing for higher overall reaction rates, otherwise unattainable. Previously, we implemented a simultaneous simulation approach using the algebraic modeling language Pyomo and the solver IPOPT to obtain cyclic steady state results for a unimolecular reactive system with up to four-order of magnitude increases in computational performance compared to the previously reported sequential approach. The flexibility of the method allowed for the investigation of the influence of forcing signal parameters on system behavior and provided a framework for waveform design. In this study, we use a hybrid framework that combines the sequential and the simultaneous simulation approaches to find the cyclic steady state of a more complex system, of ammonia synthesis, comprising 19 reversible elementary reaction steps. The framework allowed us to investigate sine wave parameters with approximately 220 times less computational effort compared to the sequential approach alone. With the parameters studied, our findings indicate that frequencies exceeding 1000 Hz and compressive strains greater than 2% can negatively impact the system performance. Future work will focus on expanding the model to include lateral interactions between molecules, using other waveform as forcing signals, and integrating systematic mathematical optimization approaches. These advancements pave the way to establishing a general framework for identifying optimal waveforms across diverse dynamic catalysis systems.

Keywords: Simulation, Catalysis, Pyomo, Reaction Engineering, Dynamic Modelling, Dynamic Catalysis, Oscillation, Simultaneous

INTRODUCTION

In a world facing pressing environmental challenges, disruptive and interdisciplinary solutions need to be explored. To navigate humanity toward sustainable scientific advancements, it is imperative to reinvent catalytic processes used to produce chemicals that are essential for the modern society. In this context, Dynamic or Programmable Catalysis [1] is a novel concept that has been capturing the attention of scientists in the catalysis field.

Research in heterogeneous catalysis has traditionally focused on selecting the ideal catalyst for a specific reaction, or designing the ideal active site within a catalyst, tied to advances of research in materials science and engineering. At its core, heterogeneous catalysis revolves around an important property of catalytic metals: the adsorption or binding energy (BE). Directly related to this property is the concept of the Sabatier Volcano [2, 3], which states that the ideal catalyst for a specific reaction is the one that binds the substrates with a “just-right” energy. Bindings that are too strong or too weak lead to prominent rate-controlling steps, reducing the efficiency of the catalytic process.

Dynamic Catalysis promotes oscillations of the binding energy throughout the duration of a catalytic

process. These oscillations would allow for faster chemical reactions, due to the periodic favoring of otherwise rate-controlling steps.

Figure 1 shows a representation we call the Extended Sabatier Volcano. The volcano-shaped curve in green represents the dependency of the overall reaction rate, commonly expressed as the Turnover Frequency (TOF), with the binding energy. The peak of this curve marks the balance or the compromise between otherwise rate-controlling steps, leading to the higher TOF value. The main goal of Dynamic Catalysis is to overcome the limitations associated to the volcano curve and obtain overall reaction rates that would be unachievable with conventional, or static, heterogeneous catalysis.

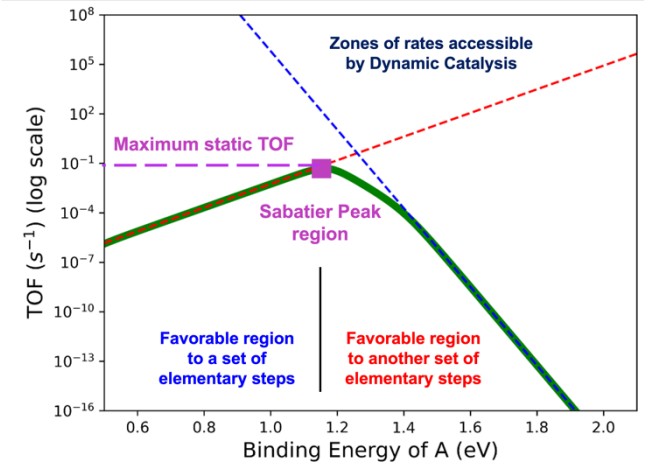

Figure 1. The Extended Sabatier Volcano. This is a conceptual figure; axes values are arbitrary and are used for illustration.

Since its introduction, Dynamic Catalysis has sparked significant research interest. On the computational front, researchers have explored several aspects of the concept: using general model reactions to investigate how binding energy (BE) oscillation parameters relate to activity response [1]; introducing conceptual ideas, such as supervolcanoes and molecular pumps derived from energy diagrams [4]; examining product selectivity and reaction pathways [5]; studying surface modulation through applied electric fields [6]; analyzing negative relationships between the BEs of reactants and products [7]; and applying BE modulation to loop reactions [8].

Other computational studies have focused on different simulation methodologies and optimization of forcing signals, including direct limit cycle solutions [9] and Gaussian kernel-based optimization of square wave parameters [10]. Additionally, rate enhancement and computational analysis of oscillation parameters have been applied to more realistic systems, electrocatalytic oxygen evolution reaction over metal oxides, incorporating both fixed overpotential and an additional arbitrary stimulus source [11]; and methane steam reforming under Ru(211) subjected to applied charge [12].

Experimental implementations of Dynamic Catalysis have also demonstrated rate enhancement due to dynamic oscillations. One study utilized pulsed light to control the rate of elementary steps in methanol decomposition [13], while another employed dynamic electrocatalytic modulation for formic acid decomposition [14]. Ongoing research efforts are dedicated to developing techniques and devices capable of inducing the necessary stimuli on catalytic surfaces to promote energetic fluctuations [15]. An interesting advancement is the “catalytic condenser”, a device that applies voltage to the surface, resulting in BE shifts of up to 0.2 eV [16–18]. We recognize that further experimental exploration is essential to validate the approach. Our goal is to have our computational frameworks leveraged to support experimentalists in developing methodologies for experimenting with real-life and industrially relevant reactive systems.

In this context, the present work builds upon our previous research on the simulation and of a unimolecular (“A-to-B”) dynamic catalytic system and the design of a forcing signal waveform [19]. The goal is to extend the framework to a more complex, intricate and industrially relevant system. Specifically, we draw on the work by Wittreich et al [20], who explored dynamic catalysis simulations for the synthesis of ammonia, one of the most important chemicals for modern society.

We use this broadly complex and detailed system as a case study to test and explore frameworks. Ultimately, our goal is to develop generalizable frameworks and tools for simulating dynamic catalysis processes and optimizing the waveform of the forcing signal. These frameworks would enable the identification of decision variables that yield the best outcomes in dynamic catalysis, paving the way for more effective catalytic systems.

The insights gained from results obtained with these frameworks are intended to guide experimentalists in developing techniques and devices for binding energy oscillations, as well as determining conditions for conducting experiments. We see this line of research as a foundational step toward the full application of dynamic catalysis. It lays the groundwork for extensive physical experimentation, progressing toward research on scaling up processes, and ultimately achieving widespread industrial implementation.

METHODS

Reactive System and Microkinetic Model

The reactive system for ammonia synthesis comprises 19 reversible reactions involving 16 chemical species. These reactions describe the adsorption and desorption of molecules to the catalytic surface, reactions

between adsorbates and their diffusion across the surface. The microkinetic model considers two distinct types of active sites on the surface, step and terrace sites. The compounds involved include the three gas-phase molecules, nitrogen, hydrogen and ammonia (N_2, H_2, NH_3, respectively), as well as six adsorbates on terrace sites and seven adsorbates on step sites.

In our previous work, we directly investigated the wave parameters of binding energy oscillations. In this study, the oscillation is of the stimulus source - compressive and tensile strain applied to the catalytic surface. The strain is represented by variations in the interatomic distances on the surface, which influence the d-band center of the atoms, leading to both physical and electronic rearrangements [21].

We developed our microkinetic model using Python and Pyomo based on the model developed by Wittreich et al [20] in MATLAB, using the data acquired and provided by the authors. This dataset includes results from energy calculations performed with Density Functional Theory (DFT) for a ruthenium-catalyzed system under three conditions: no strain, +4% compressive strain, and -4% tensile strain. The authors established linear scaling relationships with the data, enabling predictions beyond the specific parameters of the DFT calculations. A comprehensive and detailed description of the methodology used to generate the data is available in the Supporting Information of their publication [20].

The microkinetic model consists of thermodynamic and kinetic calculations to obtain a total of 38 rate constant (k) values, corresponding to the forward and reverse rates of each elementary step. Each applied strain value is linked to specific binding energy values, which in turn determine the rate constants. This mechanism explains the periodic favoring of different elementary steps: changes in the applied strain alter the rate constants, thereby influencing the rates at which individual steps occur.

The rate constants are parameters within the coupled system of Ordinary Differential Equations (ODEs) that describe the progression of the reaction over time, with the concentrations of all 16 compounds as the state variables. The complete list of reactions as well as the list of ODEs can be found in the Digital Supplementary Material.

Sequential and simultaneous simulation workflow

By integrating Python and SciPy [22] with Pyomo.DAE [23] and the IPOPT solver [24], we developed a workflow to identify the cyclic steady-state behavior of the system under different forcing signal conditions and parameters. The unimolecular reactive system used in our previous study was small (four state variables) and simple enough that its solving process and run time were not significantly influenced by the initialization of the problem. However, in this ammonia synthesis system, we have observed that proper initialization is critical to the success of the simulation.

To address this, we developed a cascading framework consisting of the following steps: (1) performing a sequential simulation using Scipy's *integrate.solve_ivp* function until cyclic steady state; (2) using this solution as the initialization for a simultaneous simulation approach, employing the same forcing signal as in the sequential simulation; (3) progressively modifying the input conditions, while using the previous solution from the simultaneous simulation as the initialization for the subsequent iteration. Figure 2 presents a workflow block diagram illustrating the framework.

The sequential approach involves a simulation from initial conditions until cyclic steady state behavior for all the state variables, solving therefore an Initial Value Problem (IVP). Successful integration requires low tolerances and a small maximum step size, and the use of a solver that handles stiff problems, like Radau, LSODA or

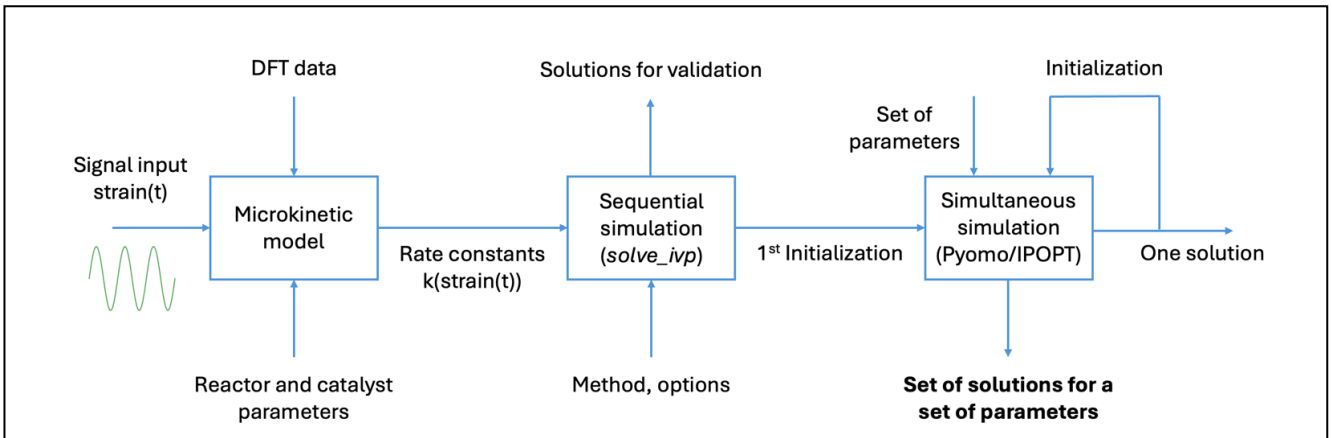

Figure 2: Workflow block diagram and systematic view of the simulation procedure.

BDF. Solving a sequence of simulations with this approach involves long computational run times.

The simultaneous simulation approach, in contrast, solves a Boundary Value Problem (BVP), using limit cycle or periodic boundary conditions. These conditions state that the initial and final points of a cycle need to have the same value, which defines the cycle steady state. The ODEs are automatically transcribed into algebraic equations using Pyomo.DAE and IPOPT then solves the square problem for all state variables at all discretized time points simultaneously, outputting a single cycle in the cyclic steady state for all variables [19].

As seen in later figures, the concentrations of the molecules in the reaction medium, which are the state variables, are generally very small, spanning several orders of magnitude - going from around 10^{-4} to 10^{-12} mol/cm^3. These units arise from the many thermodynamic and kinetic calculations that map data to rate constants. Even if the units were converted, the magnitude differences would persist. We explored various manual scaling strategies but found they did not significantly reduce the dependency on initialization or improve solver performance (e.g., reducing memory usage, enabling larger step sizes in the line search, or avoiding the need for restoration mode). However, we observed that scaling the time span (x-axis) had a noticeable impact on solver performance, though it still did not eliminate the dependency to a solid initialization.

In this paper, we focused on the parameters of a sine wave as the forcing signal for the oscillatory system: frequency, amplitude, and offset. The frequency dictates the number of cycles per second, while the amplitude and the offset values define the strain magnitude and its specific values, respectively. The use of strain values beyond those used to obtain the data (+4 and -4%) was done considering the linear scaling relationships can be extrapolated.

RESULTS AND DISCUSSION

Simulation framework outcomes

The simulation workflow, which combines initialization via sequential integration and a loop through parameters using the simultaneous approach, significantly reduced computational time compared to running a sequence of forward integrations for each parameter set. The initial single sequential simulation required 26 minutes to generate cyclic steady state results. Afterwards, the simulations for the almost 300 runs with the simultaneous approach were completed in under 10 minutes. Therefore, the total time required for our hybrid algorithm was of approximately 35 minutes. By comparison, if each of these runs had been performed sequentially, with each taking approximately 36 minutes, the total computational time would have been almost 220 times longer.

To validate the framework, several conditions were also simulated using the sequential approach, and the results were consistent with those obtained through the proposed workflow.

Analysis of wave parameters and responses

The first parameter analyzed was the frequency of the forcing signal. The simulations depicted in Figure 3 were conducted with the default fixed amplitude of 0.04 and offset of 0, corresponding to a strain variation on the catalytic surface from -4% to +4%. From the figure, the average turnover frequency (avTOF) peaks around 500 Hz and declines for higher frequencies. While the absolute changes in values are small, the decrease in avTOF suggests that the rapid transitions between the high and low levels of the wave may not allow sufficient time for an elementary step to be favored in enough extent before the next switch occurs [4]. This result highlights the importance of selecting an appropriate forcing frequency, as operating at excessively high frequencies can also be energy intensive for the process.

Figure 4 was generated by fixing the frequency at 1000 Hz and varying the offset in values of 0.01, 0, and -0.01, individually, while simulating the system across different amplitudes ranging from 0.02 to 0.04. The blue points, representing an offset of 0.01, consistently show the lowest avTOF values for all amplitudes tested, indicating that applying high compressive strain is not favorable. For the default offset of 0, the results reveal an optimal amplitude near 0.024, while the default amplitude of 0.04 results in the lowest avTOF value within this configuration.

This result contradicts the intuitive conclusion drawn in our previous work: that higher amplitudes would lead to higher overall rates by reaching more extreme points of the Sabatier Volcano, where steps would theoretically be highly favorable. As observed for an offset of 0.01, the maximum avTOF occurs when the positive strain reaches the lowest value of 0.02, suggesting that applying excessive compressive strain may be detrimental to the efficacy of the system in achieving high reaction rates.

For an offset of -0.01, represented by the green curve, a maximum avTOF value similar to the one observed with an offset of 0 is achieved, reaching approximately 0.085 1/s for the amplitude of 0.03. The waveform corresponds to a strain oscillation ranging from -0.04 to 0.02. Once again, the analysis suggests that the maximum compressive strain should not exceed 2%. To improve the smoothness of this curve, we ran 100 iterations for this system, instead of 50, as for the others and lowered down the solver's tolerances.

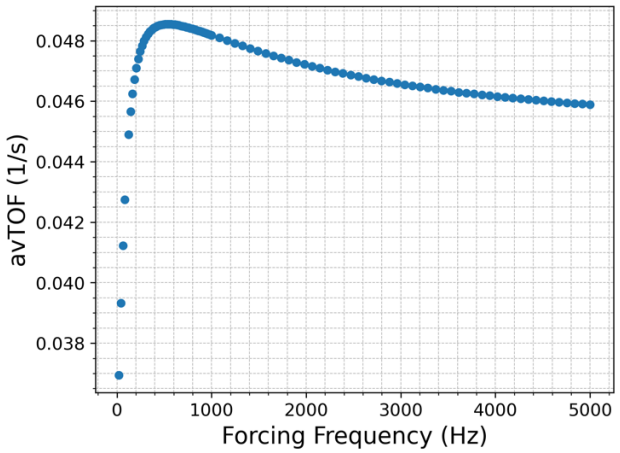

Figure 3: Comparison of avTOF results for different frequencies.

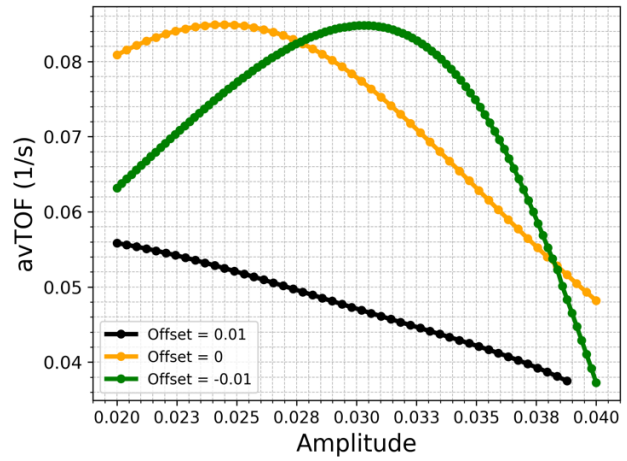

Figure 4: Comparison of avTOF results for different amplitudes and offsets - determining the range of strain oscillation.

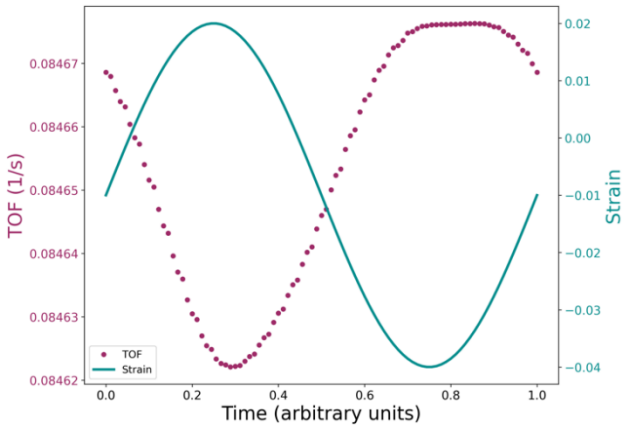

Figure 5: Sine wave forcing signal and turnover frequency response over the span of one cycle in cyclic steady state.

Figure 5 shows the shape of the sine wave and the TOF response for the case with higher avTOF for offset of -0.01, for one cycle in cyclic steady state. For this system, the TOF is calculated based on the concentration of reactants and products in the gas phase at each given moment. It is possible to see the mild delay in TOF response after the changes in direction by the sine wave. The first switch, around 0.3 in relative time, is rounder, and the next switch seems to stabilize in the higher value before going down. The causes for such difference are probably intrinsic to the responses of all the other species involved. Plots of the shapes for the concentration of all adsorbates can be found within the Digital Supplementary Material.

For comparison, the TOF of the static system, with no strain applied, is of 0.044 s^{-1}. As seen in figures 3 and 4, for some points the use of the oscillatory stimulus results in a lower overall rate than for the static case. This outcome underscores the importance of identifying the ideal wave parameters and carefully designing the forcing signal for dynamic catalysis systems.

As discussed in our previous work [19], analyzing the Extended Sabatier Volcano reveals important considerations for interpreting wave parameters optimality. According to different Sabatier Volcanoes in the literature [20, 26], ruthenium, the catalyst used in the working system, would be in the Sabatier Peak region, suggesting that oscillating symmetrically between either side of the volcano should be favorable. However, the shape of the volcano, which is highly influenced by the Bronsted-Evans-Polanyi relationship, must also be considered.

For instance, in the volcano shown in Figure 1 for the system discussed in our previous paper, the shape of the volcano led to an optimal range of binding energy values that is not symmetrically positioned on either side of the volcano. This observation highlights once again the need of computational investigations and the development of methods for simulating and optimizing input signals. The behavior of complex reactive systems is often non-intuitive and difficult to predict, emphasizing the importance of systematic exploration.

CONCLUSIONS AND FUTURE WORK

In this work, we expanded on our previous research [19] and the contributions of Wittreich et al [20] to establish a structured and efficient way for simulating ammonia synthesis under Dynamic/Programmable Catalysis. Our approach combines an initialization strategy, based on forward integration results for a default system, with a looped simulation using a simultaneous approach to explore a range of sine wave parameters. The method has shown to improve the efficiency into simulating system with different parameters for forcing signal. Getting the same results solely with the sequential approach would take estimated 220 times more time.

This study represents a foundational step toward further modeling the system and refining the framework.

The next layer of complexity will involve accounting for lateral interactions between adsorbates on the catalytic surface. These interactions affect binding energies and thereby influence the entire dynamic system. With this consideration, the rate constants will depend not only on the applied strain but also on the concentrations of molecules - i.e., the state variables themselves - making the governing ODEs more intricate and their solutions more computationally demanding. To address this, we need to transition the current framework, which integrates Python and Pyomo, into a fully Pyomo-based framework. While this adaptation increases complexity, it will yield a more accurate and reliable microkinetic model by incorporating these essential interactions, which significantly influence the results of the simulations.

We will also extend this workflow to incorporate square wave forcing signals. Square waves, while increasing system stiffness due to their abrupt changes, have the potential for further enhancing the overall reaction rates [1, 4, 19]. From these results, we aim to optimize all wave parameters simultaneously to capture the interdependencies among them. This will require adapting the optimization frameworks from our previous work, particularly in terms of initialization strategies, to ensure convergence.

In parallel, we plan to apply this methodology to a different system, targeting formic acid decomposition (FAD). Like for the ammonia synthesis, the general reaction involves three molecules, but the reaction mechanism is complex and involves many molecules. In the case of FAD, it also involves competing reaction pathways, leading to undesirable products. Leveraging the insights gained from reproducing and adapting the microkinetic model of Wittreich et al [20], we will construct a model for the FAD system. An adjacent part of the work will be using machine learning potentials, trained within the Open Catalyst Project (OCP) [27], to generate input energy data. Our goal is to develop a comprehensive framework that integrates OCP data, microkinetic modeling, simulation, and waveform optimization, not only to enhance reaction rates but also to improve selectivity toward the desired products.

Ultimately, our intention is to develop a general framework for optimizing arbitrary waveforms as forcing signals for general dynamic catalysis reactions. We believe the results from this achievement will provide valuable guidance to experimentalists, enabling them to access the full potential of the promising technique of dynamic catalysis. Such advancements can pave the way for widespread implementation and realization of the benefits of the approach.

DIGITAL SUPPLEMENTARY MATERIAL

Please access the GitHub repository for code used in this work: https://github.com/ccolomb2/dynamic_catalysis_NH3.git. The repository contains three notebooks that generate the figures presented and two csv files with data necessary to run the code.

ACKNOWLEDGEMENTS

The authors thank Dr. Gerhard Wittreich for sharing MATLAB files used in previous work [28] and for relevant discussions around the concepts. We also thank Dr. Victor Alves and Laurens Lueg for insights into the work.

REFERENCES

1. Ardagh MA, Abdelrahman OA, Dauenhauer PJ. Principles of dynamic heterogeneous catalysis: surface resonance and turnover frequency response. ACS Catal 9:6929–6937 (2019) https://doi.org/10.1021/acscatal.9b01606
2. Sabatier P. La catalyse en chimie organique. Librairie polytechnique, Paris (1920)
3. Bligaard T, Nørskov J, Dahl S, Matthiesen J, Christensen C, Sehested J. The Brønsted–Evans–Polanyi relation and the volcano curve in heterogeneous catalysis. J Catal 224:206–217 (2004) https://doi.org/10.1016/j.jcat.2004.02.034
4. Ardagh MA, Birol T, Zhang Q, Abdelrahman OA, Dauenhauer PJ. Catalytic resonance theory: superVolcanoes, catalytic molecular pumps, and oscillatory steady state. Catal Sci Technol 9:5058–5076 (2019) https://doi.org/10.1039/C9CY01258F
5. Gathmann SR, Ardagh MA, Dauenhauer PJ. Catalytic resonance theory: negative dynamic surfaces for programmable catalysts. Chem Catal 2:140–163 (2022) https://doi.org/10.1016/j.checat.2022.01.001
6. Ardagh MA, Shetty M, Kuznetsov A, Zhang Q, Christopher P, Vlachos DG, Abdelrahman OA, Dauenhauer PJ. Catalytic resonance theory: parallel reaction pathway control. Chem Sci 11:3501–3510 (2020) https://doi.org/10.1039/D0SC00752B
7. Shetty M, Ardagh MA, Pang Y, Abdelrahman OA, Dauenhauer PJ. Electric-field-assisted modulation of surface thermochemistry. ACS Catal 10:12867–12880 (2020) https://doi.org/10.1021/acscatal.0c03575
8. Murphy MA, Gathmann SR, Bartel CJ, Abdelrahman OA, Dauenhauer PJ. Catalytic resonance theory: circumfluence of programmable catalytic loops. J Catal 430:115343 (2024) https://doi.org/10.1016/j.jcat.2023.115343
9. Foley BL, Razdan NK. Clarifying mechanisms and kinetics of programmable catalysis. iScience 27:109543 (2024) https://doi.org/10.1016/j.isci.2024.109543

10. Psarellis YM, Kavousanakis ME, Dauenhauer PJ, Kevrekidis IG. Writing the programs of programmable catalysis. ACS Catal 13:7457–7471 (2023) https://doi.org/10.1021/acscatal.3c00864
11. Gathmann SR, Bartel CJ, Grabow LC, Abdelrahman OA, Frisbie CD, Dauenhauer PJ. Dynamic promotion of the oxygen evolution reaction via programmable metal oxides. ACS Energy Lett 9:2013–2023 (2024) https://doi.org/10.1021/acsenergylett.4c00312
12. Vempatti VVR, Wang S, Abdelrahman OA, Dauenhauer PJ, Grabow LC. Catalytic resonance of methane steam reforming by dynamically applied charges. ChemRxiv (2024) https://doi.org/10.26434/chemrxiv-2024-8sxpx
13. Qi J, Resasco J, Robatjazi H, Alvarez IB, Abdelrahman O, Dauenhauer P, Christopher P. Dynamic control of elementary step energetics via pulsed illumination enhances photocatalysis on metal nanoparticles. ACS Energy Lett 5:3518–3525 (2020) https://doi.org/10.1021/acsenergylett.0c01978
14. Gopeesingh J, Ardagh MA, Shetty M, Burke ST, Dauenhauer PJ, Abdelrahman OA. Resonance-promoted formic acid oxidation via dynamic electrocatalytic modulation. ACS Catal 10:9932–9942 (2020) https://doi.org/10.1021/acscatal.0c02201
15. Shetty M, Walton A, Gathmann SR, Ardagh MA, Gopeesingh J, Resasco J, Birol T, Zhang Q, Tsapatsis M, Vlachos DG, et al. The catalytic mechanics of dynamic surfaces: stimulating methods for promoting catalytic resonance. ACS Catal 10:12666–12679 (2020) https://doi.org/10.1021/acscatal.0c03589
16. Onn TM, Gathmann SR, Guo S, Solanki SPS, Walton A, Page BJ, Rojas G, Neurock M, Grabow LC, Mkhoyan KA, et al. Platinum graphene catalytic condenser for millisecond programmable metal surfaces. J Am Chem Soc 144:22113–22127 (2022) https://doi.org/10.1021/jacs.2c09544
17. Onn TM, Gathmann SR, Wang Y, Patel R, Guo S, Chen H, Soeherman JK, Christopher P, Rojas G, Mkhoyan KA, et al. Alumina graphene catalytic condenser for programmable solid acids. JACS Au 2:1123–1133 (2022) https://doi.org/10.1021/jacsau.2c00159
18. Oh K-R, Onn TM, Walton A, Odlyzko ML, Frisbie CD, Dauenhauer PJ. Fabrication of large-area metal-on-carbon catalytic condensers for programmable catalysis. ACS Appl Mater Interfaces 16:684–694 (2023) https://doi.org/10.1021/acsami.3c14623
19. Colombo Tedesco C, Kitchin JR, Laird CD. Cyclic steady-state simulation and waveform design for dynamic/programmable catalysis. J Phys Chem C 128:8993–9002 (2024) https://doi.org/10.1021/acs.jpcc.4c01543
20. Wittreich GR, Liu S, Dauenhauer PJ, Vlachos DG. Catalytic resonance of ammonia synthesis by simulated dynamic ruthenium crystal strain. Sci Adv 8:eabl6576 (2022) https://doi.org/10.1126/sciadv.abl6576
21. Mavrikakis M, Hammer B, Nørskov JK. Effect of strain on the reactivity of metal surfaces. Phys Rev Lett 81:2819–2822 (1998)
22. Virtanen P, Gommers R, Oliphant TE, Haberland M, Reddy T, Cournapeau D, Burovski E, Peterson P, Weckesser W, Bright J. SciPy 1.0: fundamental algorithms for scientific computing in Python. Nat Methods 17:261–272 (2020) https://doi.org/10.1038/s41592-019-0686-2
23. Nicholson B, Siirola JD, Watson JP, Zavala VM, Biegler LT. pyomo.dae: a modeling and automatic discretization framework for optimization with differential and algebraic equations. Math Program Comput 10:187–223 (2018) https://doi.org/10.1007/s12532-017-0127-0
24. Wächter A, Biegler LT. On the implementation of an interior-point filter line-search algorithm for large-scale nonlinear programming. Math Program 106:25–57 (2006) https://doi.org/10.1007/s10107-004-0559-y
25. Ardagh MA, Birol T, Zhang Q, Abdelrahman OA, Dauenhauer PJ. Catalytic resonance theory: superVolcanoes, catalytic molecular pumps, and oscillatory steady state. Catal Sci Technol 9:5058–5076 (2019) https://doi.org/10.1039/C9CY01543D
26. Medford AJ, Vojvodic A, Hummelshøj JS, Voss J, Abild-Pedersen F, Studt F, Bligaard T, Nilsson A, Nørskov JK. From the Sabatier principle to a predictive theory of transition-metal heterogeneous catalysis. J Catal 328:36–42 (2015) https://doi.org/10.1016/j.jcat.2014.12.033
27. Tran R, Lan J, Shuaibi M, Wood BM, Goyal S, Das A, Heras-Domingo J, Kolluru A, Rizvi A, Shoghi N, Sriram A, Therrien F, Abed J, Voznyy O, Sargent EH, Ulissi Z, Zitnick CL. The Open Catalyst 2022 (OC22) Dataset and Challenges for Oxide Electrocatalysts. ACS Catal 13:7457–7471 (2023) https://doi.org/10.1021/acscatal.2c05456
28. Wittreich, G., Vlachos, D. https://github.com/VlachosGroup/NH3-Dynamic-MKM/tree/main