

Energy Flows in Static and Programmable Catalysts

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Abstract. Programmable catalysts that change on the time scale of a catalytic cycle provide a new opportunity to control the flow of energy to reactants and products to promote faster and more selective chemistry. While traditional chemical manufacturing processes consume energy to achieve favorable reaction conditions, programmable catalysts aim to dynamically add or remove energy to catalytic cycles through perturbations of the catalytic surface via strain, charge, or light. These surface energy flows are quantified by the changes in adsorbate binding energy with time, and the overall efficiency relating energy inputs to catalytic performance are defined by the characteristics of the undulating catalytic surface. Understanding and quantification of energy flows in programmable catalysts provides baseline definitions and metrics for comparing dynamic conditions and identifying optimal catalytic performance for more efficient chemical manufacturing.

Catalytic processing remains the most energy intensive manufacturing sector in the world, consuming power to drive chemical transformations for production of materials, chemicals, and fuels.^[1] The synthesis of ammonia from fossil-fuel-derived hydrogen alone consumes 1-2% of global energy, making it a major source of CO₂ emissions, particularly from the hydrocarbon-derived H₂ consumed in the process.^[2] Other major chemicals including ethylene, propylene, methanol, and a mixture of aromatics comprised of benzene, toluene, and xylenes (BTX), annually consume multiple exajoules of energy in their manufacture.^[1] These massive processes, in addition to their substantial energy requirements, emit a concomitant amount of carbon dioxide, making them key targets for efficiency improvement to meet global sustainability goals.

New opportunities exist with alternative feedstocks such as water, CO₂, or lignocellulosic biomass, but improvements in chemical manufacturing can also derive from the philosophy of chemical process design. The energy consumption associated with chemical manufacturing is directly related to the pathways of energy flows throughout a catalytic reaction. Traditionally, the progression of catalytic turnover

on adjacent individual sites is not synchronized, with distinct elementary steps of a catalytic turnover (adsorption, reaction, desorption) occurring at different moments in time. Energy released in one reaction step can be absorbed in other steps, either in the same catalytic reaction or in a neighboring reaction. Energy via heat, current, or light is applied continuously at a fixed rate to maintain constant conditions required for exothermic or endothermic elementary reactions. An alternative approach would synchronize all reactions to proceed through the same steps in the catalytic cycle at the same time across a catalytic surface; energy could then be provided only when required in the catalytic cycle, potentially leading to reduced energy consumption and overall improved catalytic rates and/or selectivity beyond conventional static methods.

The traditional fixed-condition approach to chemical manufacturing operates reactors at thermodynamically favorable conditions by applying mechanical and thermal energy inputs to control temperature and pressure. As depicted in **Figure 1A**, energy provided to compressors, heaters, or chillers can manipulate reaction conditions and overall reaction thermodynamics.

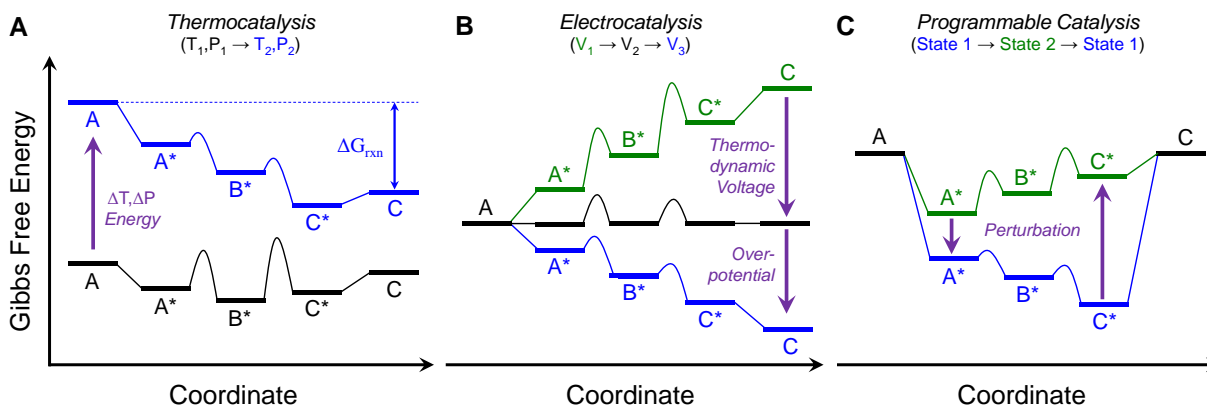


Figure 1. Mechanisms of Catalytic Pathway Control via Energy Inputs. (A) Thermocatalytic reactions are modulated via variation of temperature, T , and pressure, P , to change the overall reaction thermodynamics and intermediate energies. (B) Electrocatalytic reactions are modulated via variation of applied potential, V , to change the overall reaction thermodynamics and intermediate energies. Overpotential is the additional applied potential required to make a reaction overall exergonic. (C) Programmable catalytic reactions exhibit fixed overall reaction thermodynamics but modulate intermediate energies via energy input between multiple states.

New conditions can make reactions more exergonic, which may also reduce the activation free energy of the slowest, rate-limiting catalytic step. But this approach to process design has an important limitation; it binds the selection of reaction conditions to the thermodynamic limits of a reaction, thereby requiring intensive process components for particular chemistries that impose extreme process conditions.

This sequence of design, first identifying exergonic operating conditions and then a catalyst, has resulted in processes to manufacture large volume basic chemicals that are characterized by extreme reaction conditions arising from reaction thermodynamics. Steam reforming of methane to make synthesis gas (H_2 and CO) operates at high temperature above $800\text{ }^\circ C$ to drive the endothermic reaction with favorable entropy generation.^[1] Ammonia is synthesized at pressures above 150 atm to achieve even moderate equilibrium yields (<30%), requiring significant energy input to compress small permanent gases,^[2] and ethane is thermally cracked above $800\text{ }^\circ C$ to produce ethylene and hydrogen.^[3] More efficient, scalable, and cost effective processes would operate at lower temperatures and pressures, but this would require a new approach to catalytic reactor design that decouples process conditions and thermodynamic limits.

The other major limitation of the conventional approach to catalytic process design is its non-

specificity in energy utilization. Consider the reaction of **Figure 1a**; the available thermal energy, RT , might be comparable to the activation energy of the rate-limiting catalytic step, $E_{a,rds}$, but it far exceeds the activation energies required for the other faster catalytic steps in the sequence. Reaction conditions are applied simultaneously to all elementary reaction steps on a catalyst, often providing more energy than needed for low-barrier reaction steps. Thermal energy is delivered equally to all elementary reaction steps, regardless of need. This is particularly problematic in electrocatalytic reactions as depicted in **Figure 1b**: applied voltage decreases the overall Gibbs free energy of reaction but increases power consumption associated with each faradaic elementary reaction. A more exergonic electrocatalytic reaction condition will accelerate the rate-limiting step, but it also suffers the penalty of consuming excess power for other catalytic steps that are already sufficiently fast. This extra use of power to drive reactions that are already fast is inefficient but cannot be avoided when the applied potential is the same during each elementary step.

One of the most important examples of non-specificity in energy utilization is the oxygen evolution reaction (OER) for water splitting. Water is converted to oxygen (O_2) and protons (H^+) within a two-part electrochemical cell, the other half of which converts H^+ to hydrogen (H_2) via the hydrogen evolution reaction (HER). The oxygen

evolution reaction is energetically uphill, consistent with the formation of a fuel (H_2) from water, by the transfer of four electrons per molecule of generated O_2 . At zero applied potential, the reaction is thermodynamically uphill, and no reaction occurs. At an applied potential of 1.23 V, the modulated electron energy alters the overall reaction thermodynamics to a net zero change in Gibbs free energy; higher potentials are thereafter referred to as overpotential and accelerate the reactions by decreasing the energy level of reaction transition states, consistent with linear scaling relationships of elementary reactions. State of the art oxygen evolution catalysts like iridium oxide require an overpotential of ~ 0.5 V to drive the electrochemical reaction at a viable exchange current density (i.e., rate of reaction).^[4] This extra potential of ~ 0.5 V, required to drive the reaction at reasonable catalytic rates, significantly increases the operating cost of water electrolysis for hydrogen gas.^[5,6] As depicted in **Figure 1B**, the solution to unfavorable or slow reactions has been to use excessive power in the form of overpotential to accelerate the surface chemistry. Similar to faradaic chemistries accelerated in electrocatalytic reactors, non-faradaic chemistries consume thermal power beyond the minimum thermodynamic requirement, in order to proceed at reasonable catalytic rate. Thus, it would be more efficient to only provide excess power for the single rate-limiting step.

While conventional chemical production is limited by thermodynamics and non-specific use of energy, nature has found through evolution an alternative method of controlling energy flows to promote chemistry and motion. In warm blooded animals, temperatures and compositions are precisely controlled to targeted values despite the myriad of chemical processes occurring to maintain life. For example, cells must control internal ion concentrations of potassium (K^+) and sodium (Na^+), independent of the equilibrium compositions between the inside and outside of cells.^[7] Chemical reactions must proceed to maintain life, such as the initial breakdown of six-carbon glucose to smaller molecules^[8,9,10]. Rather than alter local conditions and equilibrium for every individual process in the body, natural systems instead release energy, independently promoting each chemical process.

Energy transfer to chemical processes in living systems occurs via a unique reaction that releases energy to drive a catalyst, molecular pump, or

motor.^[11] For example, part of the lipid bilayer of a cell is comprised of a protein designed to actively move ions between the inside and outside of the cell. The protein structure is described as having a channel with two ‘gates’ comprised of folded protein.^[12] Once an ion is bound to the binding site, the entire protein pump receives energy from dephosphorylation of ATP (adenosine triphosphate) to ADP (adenosine diphosphate), taking on a new structure that closes one ‘gate’ and opens another, allowing diffusion of the ion through the transmembrane domain, followed by a reset of the protein pump via binding of a different counter ion.^[7] The entire sequence relies on the switching of the protein into different conformations and associated energy profiles that ratchet ions from inside to outside the cell.

Energy release to drive molecular events via the ratchet mechanism preferentially directs biological events, with dynamic energy profiles that restrict backwards progression of reactions or molecular motion. In addition to cell wall protein pumps, living systems are full of molecular machinery that contracts muscles, drives reactions, and delivers payloads within the cell. Along microtubule molecular tracks within a cell drive molecular motors called kinesins, which are proteins that move unidirectionally via a ratchet mechanism.^[13] As depicted in **Figure 2A**, a molecular tail connects cargo such as vesicles to a protein molecular motor attached to the microtubule track, where the ATP-to-ADP hydrolysis reaction drives the entire machine preferentially in one direction.^[14,15] While a random walking molecular motor would experience back-and-forth motion, kinesin uses ATP energy combined with a ratchet mechanism for unidirectional net motion as fast as 400 nm s^{-1} .^[16]

The energy associated with dephosphorylation of ATP is liberated via hydrolysis to form ADP yielding $4.6 \cdot 10^{-20}$ to $5.8 \cdot 10^{-20}$ joules (0.29 to 0.36 eV), depending on the local conditions.^[11,17] This substantial energy release is sufficient to progress proteins through an ordered sequence of states throughout living organisms.^[18] The precise mechanism of the biological ratchet as a Brownian ratchet versus a power stroke has been extensively discussed.^[19,20] In the case of kinesin, each ATP-to-ADP reaction releases sufficient energy to advance the molecular motor forward; as shown in **Figure**

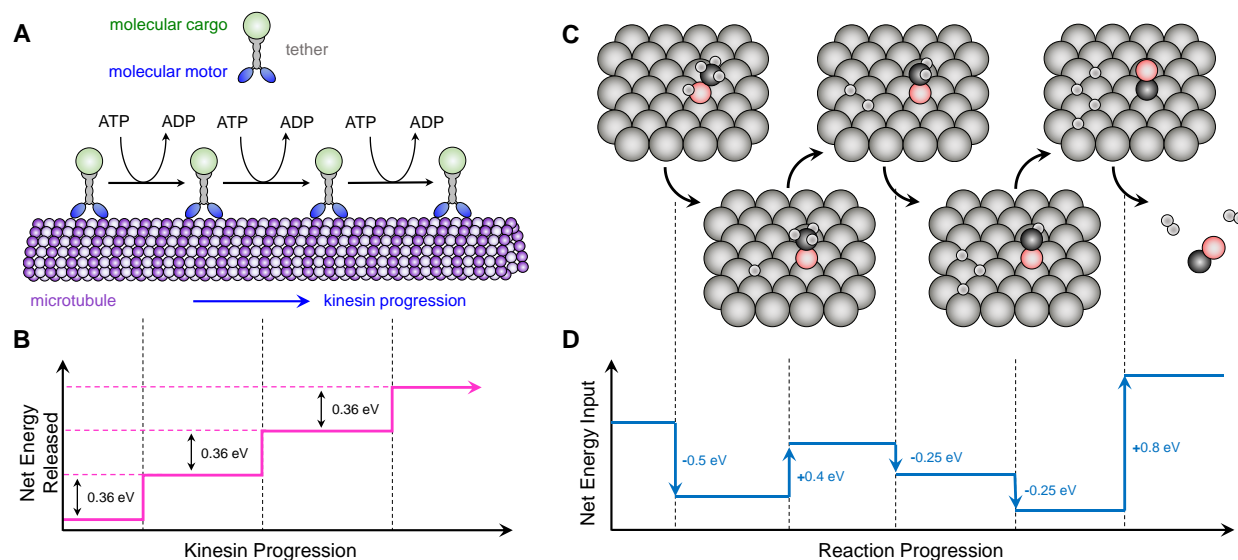


Figure 2. Energy flows in chemical systems. (A) Kinesin progresses unidirectionally along a microtubule within a cell via its molecular motor (blue) tethered to cargo such as a vesicle within a cell. (B) Unidirectional progression occurs instead of random back-and-forth movement due to regular energy release of ~ 0.36 eV from the ATP-to-ADP reaction, which drives the molecular motor in only one direction via a ratchet mechanism. (C) Catalytic reactions such as methanol decomposition on a metal occur via multiple sequential elementary steps. (D) The catalytic mechanism can be tuned via programmed inputs and outputs of energy that are pre-selected to optimize the rate of each elementary action, provided it is possible to precisely control energy flows into and out of a catalyst surface. The blue net energy profile is one example of many possible applied energy programs to control methanol decomposition chemistry.

2B, a series of ATP reactions continue releasing energy to advance the kinesin motor unidirectionally down the microtubule track. Enzymatic reactions have evolved to also use (and make) ATP, including glycolysis of glucose via hexokinase and other enzymes.^[21,22] Biological N_2 reduction for ammonia synthesis from air via nitrogenase enzymes are particularly energy intensive, using up to 16 molecules of ATP to reduce one N_2 molecule.^[23] The energy liberated by the formation of ADP drives these steps forward and when combined with the ratchet mechanism can control the specific sequencing of chemical processes.

Yet natural approaches to release energy via biology's energy transfer agent of ATP have significant drawbacks for chemical and fuel manufacturing. ATP as an energy source used in combination with protein-based biomachinery has a narrow range of temperature, pressure, composition, pH, and applied voltage conditions for which they can operate before denaturation. More robust dynamic surfaces would allow for a broader range of operating conditions favorable for a diverse set of chemistries and conditions. It is also

desirable from a design perspective to apply more variable quantities of energy (different from the 0.29-0.36 eV of ATP hydrolysis), including the ability to remove energy from reactions in any amount. As shown in **Figure 2B**, biological motors have evolved using specific amounts of energy, but more advanced programmable motors, pumps, and catalysts could be designed to allow for any possible energy input or output (positive or negative).

Consider the reaction of methanol decomposition on a metal surface in **Figure 2C**, where three bond types (C-H, C-O, and O-H) can decompose through multiple elementary steps in different orders, via unique reaction pathways. With the ability to add or remove energy to a catalyst surface, it becomes possible to imagine a complex program of energy inputs and outputs that change on the time scale of the reaction with favorable conditions for each elementary step. As the example of one possible energy program depicted in **Figure 2D**, these energetic changes can occur in any amount and sequence, ultimately

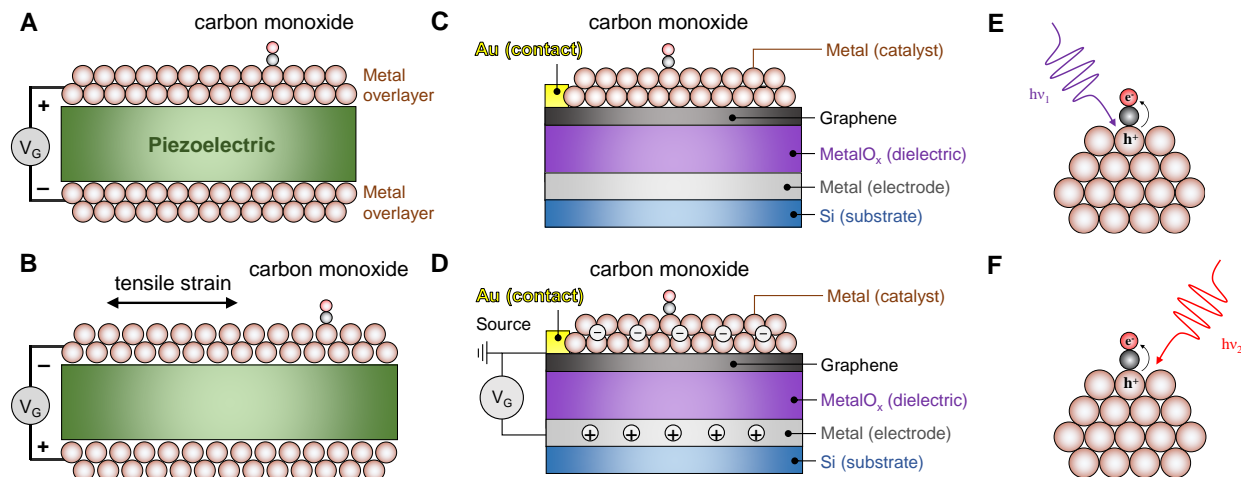


Figure 3. Energy transfer mechanisms of programmable catalysis. (A-B) Carbon monoxide adsorbed to a metal layer will bind stronger when the metal layer experiences tensile strain. (C-D) Carbon monoxide adsorbed on a metal surface binds more weakly to a metal surface in a catalytic condenser with accumulated negative charge. (E-F) Carbon monoxide binding energy to a metal nanocluster varies with imposed light wavelength.

optimized to accelerate the reaction of interest, thereby allowing for less intense reaction conditions.

Finally, energy modulation of catalytic reactions would provide the most benefit if they could be applied with temporal control. Biological systems proceed as molecules, ions, or energy carriers like ATP diffuse to the active sites of motors, pumps, or catalysts. But *programmable* materials can be externally controlled with a preset sequence of energy input/outputs with temporal complexity. A surface reaction such as methanol decomposition on a metal is comprised of multiple time constants associated with each of the elementary reaction steps, and an optimal sequence of energy changes should be sufficiently complex to match the complexity of the multi-step kinetics, thereby controlling catalytic rates and pathway selectivity.^[24]

The methods to deliver energy directly to catalytic surfaces have already been developed via a host of methods that allow for precise control of reactant energies with time.^[24] Of the many possible mechanisms, the energetics of reactions on inorganic surfaces can be continuously modulated via applied light, manipulation of electron density, or physical perturbation (e.g., strain).^[24,25,26] As depicted in **Figure 3A-3B**, one possible method involves the strain of surface catalytic sites. Energy input to a surface can stress or strain the atomic structure, leading to electronic modulation of the

exposed surface where molecules can bind or react. Shifting of the *d*-band of metals under stress has been shown to substantially shift the binding energy of adsorbates,^[27,28] providing a mechanism to input energy to the catalytic surface that can be modulated in extent (more or less strain) and frequency.

Alternatively, the electron density of a solid catalyst can be directly modulated by stabilizing more electrons or holes in the active exposed surface. One recent method to stabilize charge in metals and metal oxides is the ‘catalytic condenser’ depicted in **Figure 3C-3D**. This device consists of a conductive electrode below an insulating high-*k* dielectric layer such as SiO₂, HfO₂, or TiO₂; on top of this is placed a continuous sheet of graphene, on top of which is placed the catalytic active surface (such as a metal or metal oxide).^[26] With an active layer of ~4 nm of amorphous alumina on graphene, condensation of holes at the surface increased the binding energy of isopropanol by ~20 kJ/mole.^[26] Alternatively, when ~4 nm Pt nanoparticles on graphene were the active layer atop a catalytic condenser, variable application of -6V to +6V altered the binding of carbon monoxide by ~20 kJ/mole.^[29] The catalytic condenser can be oscillated as fast as ~3,000 Hz, switching between +/-6V without any loss in maximum accumulated charge in the catalyst layer.^[29] By this platform approach, energy flowing to the active layer through current can be tuned in voltage to rapidly

change the binding behavior of molecules over a broad range of materials and large changes in the heat of adsorption.

A third method of inputting energy into catalyst surfaces occurs via the application of light. As shown in **Figure 3E-3F**, photoexcitation of a catalytic surface yields non-thermal energy exchange between the adsorbate and the metal catalyst. Transient charge perturbation to or from the adsorbate can then promote surface reactions, including desorption, dissociation, or bond formation.^[30,31] Photon illumination provides unique capability for applying energy to a catalytic reaction; variation in applied wavelength yields varying extent of charge manipulation, depending on the adsorbate, binding site, and metal catalyst structure, suggesting the potential to control the energetics of individual steps in a catalytic cycle.^[32] Since photoexcited metals rapidly equilibrate (100s of ps) back to the ground state, a large range of possible application frequencies can be evaluated for controlling surface chemistry.^[33]

With multiple methods to deliver energy to a catalyst surface, the catalytic design process aims to understand the flows of energy into and out of the catalyst and optimize them for maximum catalytic performance or efficiency. A combination of reaction steps consume and release energy, but the net combination of these steps comprise the overall energy requirement of the catalytic reaction. As such, energy consumption in reactors with static catalysts is provided by the unit operations of the process. Ammonia synthesis requires electrical power to compress reactant gases, and steam reforming of methane requires heat transfer through a tube wall; both of these can be quantified by measuring current or flow of reactant gases. For the past century, reactors and processes have been optimized in part by minimizing these energy flows, using more complex reactor, separation, and heat transfer innovations.^[34,35,36]

In contrast to the energy transfer in unit operations required to achieve viable conditions for static catalysts, energy transfer with a programmable catalyst is a molecular phenomenon, where tracking and quantifying energy flows requires understanding of atomistic behavior on surfaces. The energy of the catalyst surface changes with the absorption of light or the rearrangement of adsorbates with variable electron density. By one of the programmable catalyst mechanisms (strain,

charge, or light), energy is directed to the catalyst which then alters the binding strength and transition state energies of surface molecules. The ‘program’ is the sequence of energy inputs and outputs that are selected to modulate the catalyst throughout the catalytic cycle. Characterization of the efficiency of these systems can be divided into two categories: (i) efficiency for delivering energy to the catalyst surface, and (ii) efficiency of the ideal ratchet mechanism. These efficiencies combine to determine the overall energy efficiency of the programmable catalyst under operation, as will now be described.

As depicted in the simple catalytic ratchet mechanism of **Figure 4A**, surface reactants and products cycle between states with stronger or weaker binding to surfaces with external perturbation, either absorbing or releasing energy, respectively. For this example, switching between two states (1 and 2) alters the heat of adsorption of A* and B*, with the net enthalpy changes defined as $\Delta\Delta H_A$ and $\Delta\Delta H_B$, respectively. The relative magnitude of these changes is determined by the mechanism of perturbation (e.g., strain or light) and the extent of perturbation (e.g., extent of strain, imposed light wavelength). The amount of energy input required to transition between states of differing enthalpy of surface adsorbates (e.g., input energy: 1 \rightarrow 2) for the catalytic system is then defined as,

$$\Delta H_{transition} = N_s \sum_i \theta_i \Delta\Delta H_i = (\theta_A \Delta\Delta H_A + \theta_B \Delta\Delta H_B) N_s \quad (1)$$

where the surface coverage of molecule i is θ_i , and the total number of surface sites is N_s . Unlike the ATP-to-ADP reaction which provides 0.29-0.36 eV per reacting ATP molecule, programmable catalytic systems can input a continuum range determined by the energy delivery mechanism. For example, larger changes in voltage applied to a catalytic condenser yields larger changes in surface binding energy.^[29] A significant advantage of inorganic programmable devices is the ability to precisely apply energy inputs or outputs with broader range and more temporal specificity.

The destination of energy put into a programmable catalyst is determined by both the mechanism of energy transfer and the energetics of

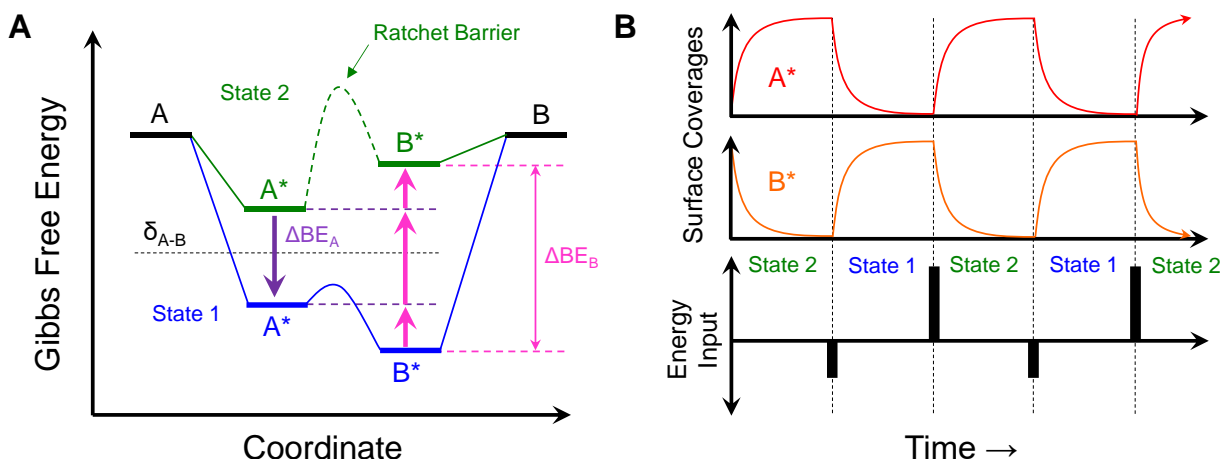


Figure 4. Energy Flows in Programmable Catalysis. (A) A programmable catalyst active site cycle energy diagram includes energy input to weaken the binding energy of B* in a state 1→2 catalyst change. A second step change strengthens the binding energy of A* between states 2→1. (B) A square waveform oscillation of the catalyst active site between state 1 and state 2, resulting in a turnover of the surface coverage between A* and B*. Energy input is required to weaken B* between states 1→2, while strengthening of A* binding energy between states 2→1 can either generate heat or output energy.

the entire programmable catalyst cycle (states 2 → 1 → 2). As depicted in one possible example of **Figure 4A**, molecule A adsorbs to the catalyst in state 2, ultimately covering the entire catalyst surface ($\theta_A \sim 1$, **Figure 4B**). In state 2, the transition state energy for the surface reaction of A* to B* is too high to proceed. The catalyst is then instantaneously shifted to state 1 with an energy difference, ΔBE_A , after which the surface reaction of A* to B* proceeds as dictated by the transition state energy of state 1, eventually fully populating the catalyst surface with B* ($\theta_B \sim 1$). The catalyst then instantaneously transitions back to state 2, with energy difference, ΔBE_B , after which B* desorbs and the programmable cycle begins again. A key observation is that B* will not react back to A* in state 2, since the transition state energy is too large, thereby forming the ratchet mechanism that preferentially converts A(g) to B(g).

The differences in energy inputs and outputs are determined by the linear scaling adsorption relationships of molecules A* and B*. The relative difference binding energy changes is defined by the $\gamma(B/A)$ parameter, defined as,

$$\gamma_{B/A} = \frac{\Delta BE_B}{\Delta BE_A} \quad (2)$$

For the example of **Figure 4A**, the heat of adsorption of B* changes twice as much as that for

A*, with $\gamma(B/A)$ of ~ 2 . For the forward reaction of A-to-B, twice as much energy is delivered to transition B* from state 1 to state 2 as is released to transition A* from state 2 to state 1. This difference becomes larger with even larger $\gamma(B/A)$.

The fate of energy released in state-to-state programmed transitions depends on the nature of the catalytic system. For the case of programmable photocatalysis, light imposed on a catalytic surface can excite a molecule to a higher energy level, but relaxation occurs via heat generation (light is not re-released). It is possible that other perturbation methods can be designed reversibly, such that energy put into the catalyst is partially or wholly recovered for state changes that result in a net increase in surface binding energies of all adsorbates. Energy recovery would result in a significantly reduced net energy input; as depicted in **Figure 4A**, the difference in magnitude of ΔBE_A and ΔBE_B is substantial. Energy output from the catalyst could offset about half of the energy input in this example (**Figure 4B**). This difference in change in binding energy remains until $\gamma(B/A)$ approaches ~ 1 , a unique condition at which there no longer exists a kinetic benefit to programmable catalysts, since the activation energy does not change between possible catalyst states by the rules of linear scaling of the surface heat of reaction.^[37]

The dissipation of energy as heat as part of a full cycle in the programmable catalytic mechanism

highlights the need to relate the rate of reaction to the amount of energy consumed per programmable cycle. Catalysts oscillating between two or more states can be operated in a variety of conditions with key design parameters of frequency and amplitude, in addition to more complex oscillation waveform shapes (e.g., sinusoid). Model kinetic systems have already demonstrated that there exist unique ranges of dynamic parameters with dramatically different catalytic rates. For one simulated example, extremely low (hertz) or high (megahertz) applied frequencies yielded negligible benefit for acceleration of catalytic rates; in these ranges of applied frequencies, increasing the oscillation of the catalyst between state 1 and state 2 consumed energy but did not further increase the rate of reaction.^[38] Alternatively, there existed a range of frequencies (~100 Hz) with a linear relationship between applied catalyst oscillation and catalytic turnover; the reaction accelerated as the catalyst oscillation increased. This desirable operation of a programmable catalyst also yields the best energetic efficiency, with additional energy input leading to additional enhancement of catalytic rate.

One key aspect of the programmable catalyst performance is the relationship between the speed of catalyst oscillation and the speed of surface reaction. The catalytic efficiency of programmable catalysts can be determined by the metric of *turnover efficiency*, η_{TOF} , defined as,^[24]

$$\eta_{TOF} = \frac{TOF_{dynamic} - TOF_{static}}{f_{app}} \quad (3)$$

where f_{app} is the applied frequency, $TOF_{dynamic}$ is the time-averaged turnover frequency of the oscillating programmable catalyst, and TOF_{static} is the averaged turnover frequency of the catalyst at static conditions of its different states. By this metric, turnover efficiency of 100% indicates that every oscillation of a catalyst active site between two or more states yields one catalytic turnover. Alternatively, low turnover efficiency indicates that the catalyst is using energy to oscillate between states without accelerating the catalytic rate. Conditions leading to high turnover efficiency have already been identified as applied programmable frequencies leading up to catalytic resonance.^[37]

The other design issue for programmable catalysts is the efficiency with which energy is

delivered to the catalyst active site. In photochemistry, not all light applied to the surface leads to catalytic reaction, and many photons are absorbed but only generate heat, rather than photochemically inducing reactions. The quantum efficiency (or quantum yield) is defined as the fraction of photons resulting in a catalytic turnover.^[39] Similarly, not all electrons delivered to a catalytic condenser surface occupy states that affect the catalyst active site. In the demonstrated Pt/graphene/HfO₂/Si catalytic condensers, about 10% of applied electrons or holes occupy states in graphene, and calculation of Bader charges in Pt films and nanoparticles indicate that much of the charge exists within the Pt overlayer away from the exposed catalytic surface where chemistry occurs. Design of photocatalysts and catalytic condensers to optimally use light and charge for maximum catalytic benefit remains an engineering design challenge.

The fates of unused photon absorption in photocatalysis and unused electrons in catalytic condensers are different; electron hole pairs generated by light will ultimately generate heat, which can be useful in maintaining the catalyst surface temperature (this energy would otherwise be put into the system through external heating). Alternatively, the catalytic condenser acts like a capacitor when exposed to an oscillating applied voltage; opposing charges remain separated on either side of an insulating layer like SiO₂ or HfO₂. While an ideal capacitor does not consume energy, real capacitors exhibit electronic inefficiencies associated with the flow of electrons. Contact resistance and electrical resistance across the catalytic condenser device consume electrical power and generate heat. In addition, leakage current through the device also acts as resistance that generates heat. While these can contribute negligibly to a well-designed device catalytic condenser operating dynamically, loss of power by these mechanisms must be quantified and minimized.

The principles of programmable catalysts provide the potential to design new catalyst devices that uniquely use energy to drive chemistry, possibly through more efficient means. But the mechanism by which energy is applied to catalytic reactors has more impact than overall efficiency; by delivering energy to catalytic reactions through a surface rather than a separate unit operation (e.g., a

compressor), we are changing the design requirements of entire chemical processes. Reactors with programmable catalysts that operate at milder conditions could be implemented in smaller applications in distributed form. Temporal utilization of energy only for specific elementary reactions with substantial kinetic barriers can operate more efficiently with less overall energy input. These new approaches will require a rethinking of the design, operation, and implementation of programmable catalysts, but the benefits for chemical reaction control can potentially break the traditional approaches of chemical manufacturing.

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