Design of Organic/Inorganic Hybrid Catalysts for Energy and Environmental Applications

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ABSTRACT: Controlling selectivity between competing reaction pathways is crucial in catalysis. Several approaches have been proposed to achieve this goal in traditional heterogeneous catalysts including tuning nanoparticle size, varying alloy composition, and controlling supporting material. A less explored and promising research area to control reaction selectivity is via the use of hybrid organic/inorganic catalysts. These materials contain inorganic components which serve as sites for chemical reactions and organic components which either provide diffusional control or directly participate in the formation of active site motifs. Despite the appealing potential of these hybrid materials to increase reaction selectivity, there are significant challenges to the rational design of such hybrid nanostructures. Structural and mechanistic characterization of these materials play a key role in understanding and, therefore, designing these organic/inorganic hybrid catalysts. This Outlook highlights the design of hybrid organic/inorganic catalysts with a brief overview of four different classes of materials and discusses the practical catalytic properties and opportunities emerging from such designs in the area of energy and environmental transformations. Key structural and mechanistic characterization studies are identified to provide fundamental insight into the atomic structure and catalytic behavior of hybrid organic/inorganic catalysts. Exemplary works are used to show how specific active site motifs allow for remarkable changes in the reaction selectivity. Finally, to demonstrate the potential of hybrid catalyst materials, we suggest a characterization-based approach toward the design of biomimetic hybrid organic/inorganic materials for a specific application in the energy and environmental research space: the conversion of methane into methanol.

1. POTENTIAL OF HYBRID ORGANIC/INORGANIC CATALYSTS

Heterogeneous catalysts form a cornerstone of the chemical industry and are arguably one of the most crucial technologies for a sustainable future. Industrial processes necessary for the production of food, reduction of pollution, efficient use of energy and resources, and improvement of living standards have greatly benefited from the use and increased performance of heterogeneous catalysts. Despite the increased efficiency of current catalytic systems, there is continuous need for further improvements as the world demands less energy-intensive processes and curbed greenhouse emissions, yet increased access to energy and resources for a growing population. More efficient catalytic materials will be a key part of meeting current and future demands, but important advances in the design of heterogeneous catalysts still need to be made to achieve these goals.

Typical heterogeneous catalysts are composed of inorganic materials, mainly metals and metal oxides, due to their high thermal stability, which is necessitated by many industrial applications. The high temperatures currently used for many processes are not always a thermodynamic necessity; in systems without low-temperature thermodynamic constraints, high temperatures are often required due to sluggish low-temperature kinetics in order to achieve appreciable reaction rates. An illustrative example is that of the fixation of molecular nitrogen to obtain ammonia, one of the most important industrial reactions. This reaction is performed industrially at high temperatures (400–600 °C) and pressures (150–300 bar) due to kinetic limitations. If scientists could create catalysts that are more active at lower temperatures, such catalysts could be composed of a much broader range of materials, which would otherwise be unstable at higher operating temperatures. Therefore, high temperature stability for heterogeneous catalysts is not the only consideration in catalyst design; if more active catalysts could be found, they could be used under milder conditions. Additionally, if we were able to transition many current industrial processes to lower temperature and pressure conditions, huge energy and...
environmental savings and opportunities for process decentralization could be achieved.

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Relaxing the requirement of high thermal stability for certain applications allows researchers to expand the set of tools available for heterogeneous catalyst design. The use of organic components in addition to commonly used inorganic components presents a promising opportunity to augment the synthesis toolkit with chemical functionality that can be introduced by organic chemistry. Here, nature provides us with great inspiration in the field of catalyst development. Enzymes very often contain metal centers nested within organic components that serve to modulate their reactivity and control the diffusion of species in and out of the active sites. By taking advantage of these properties, biological catalysts such as the nitrogenase enzyme can perform difficult reactions, such as ammonia synthesis, at room temperature and pressure (Figure 1). Inspired by physical and chemical properties optimized over millions of years, scientists are continuously working to understand and improve upon the structure–property relationships found in enzymes. Enzymes are capable of achieving high rates and selectivity in converting and producing many complex substrates necessary for sustaining life. The main drawback in using enzymes in industrial processes is their strict requirements for specific reaction conditions and their relatively low volumetric throughput. For example, even if nitrogenase enzymes worked interminably to produce ammonia, it would require \( \sim 10^{30} \) enzymes operating throughout the year to produce the \( \sim 200 \) million metric tons consumed annually on our planet.14–16

Recent advances in microscopy characterization (such as cryogenic electron microscopy or cryo-EM)17 and computational tools (with increasing computational power for simulations and modeling) allow researchers to observe and predict the structure of organic and biological molecules with unprecedented precision. As the atomic and molecular structure of materials becomes increasingly clear, catalysis researchers are increasingly realizing an unlocked potential for developing bioinspired materials for energy and environmental applications.20 The closer the resemblance of artificial materials to biological counterparts, the more challenging is to synthesize and characterize these hybrid materials, which leads to widespread challenges in taking advantage of such biomimetic materials for many applications. Therefore, as many new materials such as supramolecular polymers, metal organic frameworks (MOFs), and nanocrystal-organic composites are being developed, it is imperative to study their structure and mechanism of action in detail.9,21–25 Such materials demonstrate increased tunability, selectivity, and reaction rates, while maintaining the potential for industrial scale, productivity, and separability of traditional heterogeneous catalysts.26 It is expected that in the near future, more approaches highlighting this potential will appear from the improved understanding and control of such organic/inorganic interfaces in heterogeneous catalysts.

Several reasons motivate research in the design of organic/inorganic hybrid catalysts. There is the possibility of widening the catalyst design space via the introduction of multiple organic chemistry functional groups which may lead to improved catalytic reactivities. Similar to alloying, organic coordination can modify the electronic state of metal surfaces through the direct interaction between the organic functional groups and metal surfaces and benefits from an expanded toolbox of organic compounds. Additionally, there is the opportunity to define novel, different scaling relations compared to traditional heterogeneous catalysts.25,28 Scaling relations predict that adsorbate energies and transition state energies scale with each other, therefore posing limitations to control the selectivity. Catalyst design that can “break” or modify these relations in adsorption and transition energies could provide much higher rates or different selectivities in many transformations.29,30 One way to achieve this aim is to use organic functional groups in the proximity of metal surfaces to influence the adsorbate and transition state energies by different amounts, consequently achieving different scaling relations, much like ligands affect the reactivity of homogeneous catalysts (Figure 2). In this respect, organic/inorganic hybrid materials represent a very exciting direction for the field with untapped potential.

The goal of this Outlook is to illustrate the opportunity to use hybrid organic/inorganic catalysts to improve the efficiency of reactions related to energy and environmental applications, and to discuss translatable tools related to their design. From a theoretical perspective, we discuss the potential mechanisms of catalytic enhancement that may be designed into organic/inorganic materials, and identify key demonstrations of such catalysts. One of the biggest challenges and a main focus on this perspective is that of hybrid material characterization, which requires the combination of multiple
spectroscopic and analytical tools for a complete understanding. While numerous techniques exist for characterizing purely organic or inorganic materials, many techniques used for studying interactions between organic and inorganic materials are less developed or utilized. However, these organic/inorganic interactions are crucial for the overall functioning of catalytic systems. Furthermore, techniques to probe the interface between these phases are needed for understanding the properties of these unique materials. A central topic in this Outlook therefore involves the use of characterization techniques to motivate the rational design of hybrid organic/inorganic biomimetic materials; to this end each study is discussed with an important focus on the key characterization techniques critical to the material’s design.

Characterization takes two roles: to understand the (1) structural nature and (2) mechanistic behavior of the synthesized material. Clarifying examples motivate the importance behind characterization in the rational design of hybrid organic/inorganic biomimetic materials; to this end each study is discussed with an important focus on the key characterization techniques critical to the material’s design. Characterization takes two roles: to understand the (1) structural nature and (2) mechanistic behavior of the synthesized material. Clarifying examples motivate the importance behind characterization in the rational design of hybrid organic/inorganic biomimetic materials; to this end each study is discussed with an important focus on the key characterization techniques critical to the material’s design.

2. CLASSES OF HYBRID ORGANIC/INORGANIC CATALYSTS

At the end of the 20th century, organic/inorganic hybrid materials were defined as “biphasic materials, where the organic and inorganic phases are mixed at the nanometer to sub-micrometer scales,” and structural properties are not just the sum of the individual components, but the interface plays a predominant role. In such materials, organic and inorganic phases are often bound together covalently through oxygen-containing functional groups or more weakly bonded/adsorbed via nitrogen- or sulfur-containing groups. Although there may be several ways to categorize these hybrid materials and interfaces, we here divide them into four different categories based on the atomic, molecular, and bulk natures of the organic and inorganic phases, as shown in Figure 3. Each of these classes of hybrid organic/inorganic materials possess specific properties desirable for certain applications. On the other hand, obvious trade-offs emerge when moving between the different material classes. In this Outlook, details about the key structural aspects of these four material classes are presented, and the properties that make each material class promising for catalytic applications are described.

2.1. Atomically Dispersed Catalysts with Molecular Ligands. Catalytic materials that contain molecular organic components, such as ligands or organic linkers surrounding atomic inorganic centers, make up a set of well-defined organic/inorganic hybrid catalytic materials. Although homogeneous metal complexes would be part of this class of materials, they are not considered in this Outlook. In this class of materials, we consider metalloporphyrins, metal organic frameworks (MOFs), organic modified atomic catalysts, as well as catalysts prepared through surface organometallic approaches. In many ways, these hybrid materials are structurally closest to enzymes in terms of having atomic metal species as active sites and a catalytically relevant ligand environment. The design of these materials is often inspired by biological and homogeneous catalysts, and these materials

Figure 2. Strategies to overcome scaling limitations in catalysis include ligand effects in homogeneous catalysts (top) and tethering approaches in heterogeneous catalysts (bottom). The latter approach can be realized by using organic moieties in close contact with metal surfaces, i.e., where E is an organic functional group in the hybrid catalyst. Reproduced with permission from ref 29. Copyright 2012 American Chemical Society.

Similar to alloying, organic coordination can modify the electronic state of metal surfaces through the direct interaction between the organic functional groups and metal surfaces and benefits from an expanded toolbox of organic compounds.

Figure 3. Different classes of organic/inorganic hybrid materials that are the focus of this Outlook based on the atomic, molecular, and bulk natures of the components: (a) atomically dispersed catalysts with molecular ligands, (b) atomically dispersed catalysts on bulk organic supports, (c) organic functionalized metal and oxide surfaces, and (d) inorganic nanoparticles and organic matrices.
also often allow for the finest control of catalyst structure compared to the other classes of hybrid materials. Consisting of one or few metal atoms/ions coordinated by ligands, specific coordination environments of homogeneous catalysts are often described with atomic detail. Ligand effects on activity are often invoked due to steric or electronic considerations. Some of the recyclability issues encountered with homogeneous catalysts can be potentially solved by these hybrid materials, although with the trade-off of a more rigid catalyst structure imposed by the ligand environment.

2.2. Atomically Dispersed Catalysts on Bulk Organic Supports. Supporting single metal atoms (or clusters with low nuclearity) on bulk organic materials is a synthetic approach to control the reaction environment of metal centers. Examples have emerged utilizing graphene, carbon nitride, carbon nanotubes, and various organic polymers across a variety of catalytic applications.53–49 Carbon-supported atomic catalysts take advantage of the conductivity properties of the support useful in the design of hybrid electro- or photocatalysts.50,51 In addition, single atom catalysts utilize the more rare metal component (i.e., Pt) in a very cost-effective manner due to the high metal dispersion, as long as single atoms maintain catalytic reactivity,42,52,53 a topic which is still under debate in the community and that deserves continued efforts. These catalysts promise better control over the atomic metal environment compared to inorganic supports such as oxides. In fact, they may contain a larger variety of organic groups (e.g., nitrogen-, sulfur-containing groups) that can be tailored for stronger or weaker binding more easily than the oxygen functional groups on oxides. The challenge in this class of materials is that atomically dispersed metal atoms have a tendency to agglomerate to reduce metal surface energy, which often leads to decreased activity or changed material properties.44

2.3. Organic Functionalized Metal and Oxide Surfaces. Metal and oxide surfaces functionalized with organic or organometallic compounds represent hybrid interfaces created by chemically grafting, condensing, or adsorbing organic moieties. These hybrids can be realized by binding organic molecules (often containing thiols, amines, or carboxylic and phosphonic acids binding groups) to metallic and metal oxide surfaces, such as nanoparticles, metal oxide supports, metal films, and electrode materials,45–38 or by covalently binding organic molecules (often silanes) to metal oxide surfaces.49–63 In some cases, such as in colloidal synthesis, organic ligands bind to the metal surface during the synthesis process, while in others, postprocessing via ligand addition or monomer condensation is used.64 An advantage of this method is that a variety of organic molecules and functional groups can be applied, provided that there is a binding group responsible for surface anchoring. For example, such functionalization approaches have been used to prepare heterogeneous chiral catalysts, where metal surfaces are chemically modified with chiral ligands such as cinchonidine.65,66 Often, these materials help control the transport properties of a typical metal or oxide material. While these approaches often promise ease of scalability and synthesis, they may lack the molecular specificity and reactivity of organometallic complexes.59

2.4. Inorganic Nanoparticles and Organic Matrixes. In this class, we include materials where both organic and inorganic phases are considered bulk, i.e., well beyond the atomic and molecular size. Polymer/inorganic composites are an example of this class of hybrid materials, where the organic phase is a macroscopic polymer, and the inorganic phase is a nanoparticle with large nuclearity. Many routes in the preparation of stable nanoparticles involve their coating with stabilizing polymers or dendrimers to ensure dispersibility in solvents;67 however, in this section we consider materials that are used for heterogeneous catalysis applications. These materials typically possess extensive organic/inorganic interfaces, flexible polymer matrices, and in the case of encapsulated nanoparticles, an ability to control diffusion into and out of the active site via tunable polymer chemistry.68,69 Here, the bulk inorganic phase may be supported on the organic phase or embedded entirely inside.70,71 Aside from polymer chemistry, these materials possess other customizable properties including polymer ordering, porosity (i.e., hierarchical vs microporous), conductivity, and tunable branching.72–74 While these materials possess the tunability and separability of heterogeneous catalysts, a noteworthy challenge of this material class lies in the difficulty of characterization. The large fraction of organic component in the polymer matrix makes it difficult to understand the relevant structure at the interface of the organic and inorganic phases, and often it can be difficult to study inorganic phases which are buried deep within polymer composites.75

3. STRUCTURAL CHARACTERIZATION OF HYBRID ORGANIC/INORGANIC CATALYSTS

It is critical to understand the structure of a material in order to correlate specific structural features with catalytic properties. For any catalyst, knowledge of the available interfaces and active sites is a prerequisite to understanding its reactivity. Especially in organic/inorganic hybrid materials, it is important to not only understand the structure of the “as-synthesized” catalysts but also their “dynamic structure” under operating conditions, given that structural changes can occur with soft materials under conditions of temperature and/or pressure. Especially for organic phases, conformational mobility, ligation/de-ligation, phase changes, and even partial degradation may occur under operating conditions. It is therefore crucial to characterize these potential changes with appropriate tools which are able to distinguish between interfacial sites and the bulk of the materials. Although there are a host of standard and familiar characterization techniques for purely inorganic or organic components, there are less widespread approaches for studying interfaces. Many of the techniques discussed below, especially infrared spectroscopies, X-ray photoelectron spectroscopy, and nuclear magnetic resonance, are inspired by their success in studying catalytic intermediates on metallic surfaces. Although not a comprehensive evaluation of all characterization techniques, this section aims to highlight a few key techniques that have proven especially useful in characterizing the structure of hybrid organic/inorganic materials. Discuss specific technique applications to the material classes discussed in the previous section, and explore future opportunities to better understand these organic/inorganic interfaces and their reactivity.

3.1. Electron Microscopy. Electron microscopy has been one of the most important techniques for revealing structural details of nanomaterials at atomic resolution. While aberration-corrected microscopes allow for direct observation of surfaces, spectrometers integrated within the microscope reveal key details of elemental distribution (i.e., element-specific chemical mapping using energy-dispersive X-ray spectroscopy, EDS) and oxidation state distribution (i.e., using electron energy loss

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spectroscopy, EELS). In recent years, cryo-electron microscopy has begun to take center stage for characterizing sensitive organic and biological materials in a nondestructive way.\textsuperscript{18} For such hybrid materials, microscopy provides opportunities for direct observation of the hybrid organic/inorganic interface, diffractive characterization of the level of order of organic phases, and even three-dimensional description of the organizational structure of these materials via tomography. The increasing availability of sensitive electron microscopes ensures that electron microscopy, once reserved for resilient single-crystal samples, will command an increasing presence in characterizing organic and organic/inorganic hybrid materials.

A key contribution of microscopy characterization of hybrid materials has been in the area of inorganic phases embedded within bulk organic phases. For many materials which possess transport control via pore structures, such as in inorganic nanoparticles within organic matrices, encapsulation is key to controlling diffusion of reactants and products to and from the active site. Microscopy allows for nanoscale proof of organic materials surrounding inorganic cores. Although planar micrographs add evidence of encapsulation, a definitive proof relies on electron tomography, where multiple images taken while tilting the sample at different angles provide a reconstruction, or a 3D representation, of the object. Here, it is possible to prove that each active site is surrounded by organic material within a 3D spatial barrier, suggesting how diffusional barriers can likely be tuned or modified (Figure 4).\textsuperscript{60,68} In niche applications 1 decade ago, electron tomography has proven useful to show encapsulation of Au NPs inside ethosome bilayers, suggesting that electron tomography techniques can be sensitive and highly useful for studying hybrid materials.\textsuperscript{76} However, these techniques suffer from sample degradation because the sample is subject to a high electron dose for often large amounts of time. Therefore, more sensitive detectors (for example, direct electron cameras) and cryogenic holders that have been developed in recent years lead to improved characterization of hybrid materials.

Electron microscopes paired with EDS detectors allow for spatial localization of atomically dispersed active sites within organic matrices, such as in MOFs. It is possible to observe the overlap between organic and inorganic phases, which allows for an understanding of the structure of the regions related to active catalytic sites and confirm that the inorganic component is atomically dispersed in the organic matrix.\textsuperscript{77} This finding is key to compare these composites with those formed by nanoparticles inside MOFs, which may behave in a very different catalytic manner. Recent examples showed how it is possible to create catalysts with both atomically dispersed and nanoparticulate active phases, and EDS mapping is particular useful to distinguish between the two (Figure 5).

Figure 4. Electron tomography of inorganic nanoparticles within organic matrices. (a) Surface generated after segmentation of the organic polymer and inorganic nanoparticle phase. No particles are visible on this surface. (b) The same surface as in part a but with 60% transparency of the polymer material. Here, the Pd particles (red) are clearly visible, indicating full encapsulation. Reproduced with permission from ref 68. Copyright 2019 Springer Nature.

Figure 5. Elemental mapping of FePt@MOF material, showing spatial distribution of atomically dispersed Fe, C, and nanoparticulate Pt. Reproduced with permission from ref 77. Copyright 2019 The Royal Society of Chemistry.

Using aberration-corrected microscopy, direct confirmation of the organic/inorganic interface can be observed.\textsuperscript{43,78} Here, clear proof of single atomic metal atoms on the organic supports is demonstrated, and their connectivity within the carbon environment can be investigated and understood. In an
exemplary case, FeN₄ centers in a graphene matrix could be directly visualized and modeled to confirm the atomic structure of the FeN₄ active site for the oxidation of benzene (Figure 6).⁷⁹

As one of the ultimate characterization techniques with respect to spatial resolution, electron microscopy will play a larger role in the future for characterization of organic/inorganic materials, especially with the widespread use of cryo-EM. We envision HR-EM techniques to be increasingly useful to characterize the highly sensitive organic/inorganic interface, especially via direct visualization, due to the increased availability of dedicated cryo-EMs across all four hybrid material classes. We also imagine the evolution of new localized diffraction experiments to understand the ordered/disorder structure of interface organic species in materials such as MOFs, functionalized metal/metal oxide surfaces, or metal–polymer composites materials.⁸⁰ Finally, we suggest that localized EELS experiments could be of interest to understand the oxidation state or electronic structure changes at the organic/inorganic interface.

3.2. Infrared Spectroscopies. Infrared (IR) spectroscopies are key techniques for understanding bond strength, intermolecular bonding interactions, and molecular distortions in catalysis.⁸¹ In organic/inorganic hybrid materials, absorption frequencies of organic bonds are altered due to local chemisorption or bonding to metal/metal oxide surfaces, and this shift can be characterized with IR spectroscopies. Specifically, in many cases the interaction of organic components, such as ligands or linkers, with metallic nanoparticles or atoms produces visible shifts in the signals related to organic species compared to the pure compound, thus indicating change in electronic structure of the composite catalyst. However, often the largest challenge in such spectroscopies stems from understanding which signals are from relevant bonded components and which may be from uninteresting bulk contributions. The choice of blank samples to deconvolute background signals becomes therefore important. Various IR spectroscopies including transmission IR, attenuated total reflectance IR, diffuse reflection IR, and polarization-modulated IR are among the most commonly used and each has unique sensitivity to surface and bulk vibrational contributions.⁸²

For many materials, but especially for atomically dispersed catalysts with molecular ligands, transmission IR or attenuated total reflectance (ATR)-IR techniques have been developed to understand bulk material vibrations. For these types of materials, transmission IR is appealing because of the material uniformity, i.e., in principle these materials may possess a molecularly precise structure. It is therefore possible to use so-called “breathing” modes, or nanoscopic channel vibrations, in MOF solids to observe conformational variations and movements in the materials (Figure 7).⁸³ The modes are IR-
here translational opportunities to use these techniques to study functionalized metal/metal oxide surfaces or polymer-bulk metal composite materials. In this vein, the width and position of various IR vibrations have been used in many works to investigate chain conformation and molecular ordering on functionalized metal surfaces. In work by Medlin and coworkers, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) has been shown to characterize the extent of ordering of various thiol ligands on Pd surfaces, demonstrating that longer thiol chain lengths led to observable shifts in the methylene $d^\pi$ strength mode of the coordinating ligands, suggesting higher degrees of molecular ordering at longer chain lengths. Here, DRIFT experiments provided surface sensitivity for a thoughtfully crafted system consisting of Pd/Al$_2$O$_3$ coated with thiol molecules using dilute ethanolic solutions of various thiols.

A promising yet under-utilized approach to study polymer–metal composites or functionalized metal/metal oxide surfaces targeting IR vibrations at interfaces is polarization modulation-infrared reflection-adsorption spectroscopy, which was developed in the mid 1990s. For typical in situ studies at metal surfaces, polarization-modulated IR experiments are needed to cancel out effects of gaseous species. This approach has provided notable successes for the in situ observation of surface bound CO to bare metal surfaces. However, this technique could be useful for organic/inorganic composite structures, where similar polarization modulation could be used to cancel out bulk organic contributions in favor of the organic contribution at the interface of a metal and organic phase. A great example of this technique is discussed below in section 4 for mechanistic understanding of selective hydrogenation reactions.

Finally, sum-frequency generation vibrational spectroscopy (SFGVS) can also be used for studying organic/inorganic interfaces. Due to the controlled geometries needed for SFGVS, the majority of studies are performed on single-crystal surfaces, which limits the applicability of this technique to model structures. Typical studies involve observing catalytic intermediates on the surface of single crystals or even polymer–air interfaces. In a 2009 work, Somorjai and coworkers showed how SFGVS is used to observe the presence of ligands on the surface of thin films of metal nanoparticles and studied the degradation of this ligand film after various ozone treatments. In model systems, SFGVS presents a promising opportunity for selectively observing IR vibrations at a metal–organic interface in more future works.

In most systems with organic bonds, IR can be a useful technique to study material structure. However, notable challenges exist: in inorganic nanoparticles/organic matrix composites, care needs to be taken to ensure the signal is coming from the interface and not the bulk organic structure. For single atoms on bulk supports, sufficient metal loadings need to be used to observe the effect of the metal phase on organic structure. However, given sufficient signal from the organic/inorganic interface, IR is a characterization technique broadly applicable to these hybrid materials. Additionally, systematic studies for bulk organometallic solids such as MOFs, with molecularly mixed organic and inorganic phases, highlight the successful broad use of this technique. Vibrational changes in organic linkers are characteristic due to connections to different metal ions. We therefore envision these techniques to continue to play a central role in the characterization of hybrid materials, and further improvements in sensitivity, both elemental and structural, will provide further incentive for their use in the community.

3.3. Localized Raman Techniques. Raman techniques can provide simultaneous information about catalyst structure and surface species within a single measurement. Raman processes help describe the change in polarizability of organic and inorganic phases in a hybrid catalyst compared to the pure organic component, which can play an important catalytic role. In many Raman techniques, we can obtain localized electronic information about catalysts, which is key to understanding the unique interfaces between organic and inorganic phases in hybrid catalysts. However, Raman processes are often challenged by low scattering efficiency or saturation due to intense material fluorescence responses. One of the earliest applications of Raman spectroscopy involved studying the structural interactions between organic and inorganic components in zeolites, which lead to adsorbate-induced structural changes of the zeolite. In this case, Huang et al. demonstrated that as a function of adsorbate loading (here p-xylene), one could observe both conformational changes of adsorbed organic species as well as phase transitions in the underlying ZSM-5 framework itself. Along these lines, many current uses of Raman spectroscopy involve using probe molecules to understand the structure of a catalyst. We suggest that these same techniques can be more broadly utilized in understanding the structure of hybrid materials, where instead of typical probe molecules like CO, the organic component of the hybrid organic/inorganic material structure is investigated.

There exists a great translational opportunity in utilizing surface-sensitive Raman techniques, which have been maturing rapidly, for studying organic/inorganic materials. These techniques include SERS (surface-enhanced Raman spectroscopy), TERS (tip-enhanced Raman spectroscopy), and SHINERS (shell-in-nanoparticle enhanced Raman spectroscopy). They can be useful for characterizing the interface between organic and inorganic phases and could be particularly crucial in polymer–nanocrystal composites and functionalized metal/metal oxide surfaces, where IR signals from bulk organic phases are more likely to drown out signals from the polymer–nanocrystal interface. In these techniques, plasmonic nanomaterials generate proximal Raman-active “hot-spots”, which amplify the signal around the plasmonic phase. This signal is useful for understanding the surface of nanoparticles at hybrid organic/inorganic interfaces. In many lucky cases, catalytic activity and SERS activity go together, but when trying to study the activity of nonplasmonic catalysts, novel nanostructures need to be developed. In SHINERS, noble metal nanoparticles are synthesized on top of <10 nm of dielectric oxide coatings, which are used to encapsulate the plasmonically active nanoparticles. In an interesting example by Weckhuysen and co-workers, researchers deposited various noble metal nanoparticles on SiO$_2$ supports and observed how CO binds via different orientations on different metal surfaces, explaining unique catalytic differences between noble metals for the CO reduction reaction. SHINERS has also helped explain activity differences in Pt-based catalysts for hydrogenation reactions. In recent work, Chen et al. created libraries of size- and composition-controlled nanocrystal catalysts for para-nitrothiophenol hydrogenation. Through the fabrication of pinhole-free shell-isolated nanoparticles, the researchers used in situ SHINERS spectroscopy to probe the Raman signatures of adsorbed species. Here, they observed alloyed PtNi and PtCu nanoparticles to be more reactive than...
monometallic Pt materials, which was explained by a unique electronic shift in the O–N–O stretch of para-nitrothiophenol on the various alloy surfaces (Figure 8).98

Figure 8. (a) Interaction of para-nitrothiophenol molecule with SHINERS nanocomposite during hydrogenation reaction. (b) Parannithrophenol conversion curves for Pt, PtCu, and PtNI SHINERS catalysts. (c) Operando Raman signature for the O–N–O vibration para-nitrothiophenol adsorbed on the same catalysts. Reproduced with permission from ref 98. Copyright 2019 John Wiley and Sons.

New opportunities could arise by using the same materials to study how organic components of hybrid materials interact with metal components through SHINERS. Rather than CO adsorbates, one could study interactions of other organic molecules, such as polymers or organic ligands, on various catalytic metals. These probes could become particularly useful when coupled to reactivity or under reaction conditions, thus taking advantage of the catalytic and optical properties of certain nanomaterials. SHINER techniques require bulk inorganic phases and are therefore not applicable to isolated metal atoms.

3.4. Nuclear Magnetic Resonance. Nuclear magnetic resonance has been an important technique in understanding the atomic connectivity of organic and inorganic compounds and therefore plays an important role in characterizing hybrid organic/inorganic catalysts. The chemical shifts associated with organic functional groups are perturbed by the presence of inorganic components that change the electronic state or structure of the organic moieties. Additionally, NMR of inorganic-active nuclei may also provide insights into the electronic structure of metal atoms in hybrid materials. NMR has been historically widely applied in the liquid phase and has been the principal technique to obtain chemical, structural, and electronic properties of organic molecules by analyzing chemical shifts of certain nuclei in the sample. Moreover, the development of advanced NMR techniques, such as multi-dimensional NMR and solid-state NMR, has enabled the characterization of complex molecules and even bulk inorganic materials. Almost routinely, researchers can probe structural shifts in inorganic catalytic components via NMR-active noble metals or via organic components from $^{13}$C or $^1$H NMR.99 It has been shown how this technique can provide valuable information on the adsorption strength of adsorbates on colloidal particles (Figure 9). By extension, organic/inorganic materials that are soluble in appropriate solvents can also be studied with this technique and adsorption strength of the organic components can be evaluated. NMR is irreplaceable in investigating the skeletal structures of organic ligand molecules surrounding nanoparticles especially in solution, as one can easily attribute the chemical shifts to protons and carbons connected to certain functional groups.100 NMR is therefore widely used to characterize structures of organic/inorganic bulk materials.101 $^{13}$C and $^{29}$Si NMR are used to confirm that organic components are indeed bound to inorganic bulk catalysts, a critical confirmation of structure which validates the mechanistic hypothesis as, for example, in organic ligands-coated zeolites.60

Besides directly probing the nuclei within the host material, guest molecules can be intentionally introduced to probe the structure of the host. This technique allows one to differentiate

Figure 9. Changes in chemical shift for formic acid adsorbed on various nanocrystals as a function of composition and size. (A) $^{13}$C NMR spectrum of formic acid and formate adsorbed on PVP-Pd nanoparticles (4.5 nm in diameter). (B) The relationship between the percent of formate species in each mode of adsorption and the size of the PVP-Pd nanoparticles. (C) The relationship between the percent of formate species in each mode of adsorption and the size of the PVP-Ru nanoparticles (pink, monodentate; blue, bridging; green, monodentate formates). Reproduced with permission from ref 99. Copyright 2011 AAAS.
different adsorption environments for organic molecules in a host. Luz et al. used ferrocene (FeCp₂) as the probe molecule and were able to characterize and differentiate FeCp₂ adsorbed inside either UiO-66 and UiO-67, two MOFs with only slightly different structural features. It has been previously reported that free FeCp₂ has a ¹H chemical shift at 4.4 ppm, which would not notably change upon adsorption onto MOF-5 (4.2 ppm) or MOF-177 (4.1 ppm). However, the authors clearly demonstrated that adsorption onto UiO-66 induced significant changes to the proton environments of FeCp₂, which was attributed to the strong interaction with UiO-66 organic nodes (Figure 10). Moreover, the researchers found that the relative ratio between the two types of protons at 5.58 and 2.30 ppm were always 1:2, which they assigned to octahedral and tetrahedral cavities, whose ratio is also 1:2.

Moreover, various catalytically relevant metals, such as Pt, are NMR active themselves and can be used as reporters from the inorganic phase to add to or complement the organic phase characterization. Rhodes et al. studied the spin−echo NMR of Pt/Al₂O₃ materials and found particle-size dependent NMR signals for Pt that were related to interactions of the surface Pt layers under certain conditions. Direct observation of a posited PtOₓ phase was concluded. This technique can prove particularly useful to characterize small changes in the environment around Pt sites brought by the adsorption of organic molecules/layers, especially given the high wide spectral window for Pt that leads to high sensitivity.

In addition to characterizing static skeletal and conformational structures depending on chemical shifts, it is important to emphasize that relaxation processes have also been investigated and can be closely correlated with dynamic processes occurring in organic components, adsorption affinities and reactivities. D’Agostino et al. employed ¹H NMR T₁/T₂ relaxation time measurements to assess the adsorption affinity of glycerol onto Au/TiO₂ catalysts and found that glycerol had a much stronger affinity with smaller Au nanoparticles. The authors concluded that the affinity was an important factor in promoting glycerol oxidation.

The examples above demonstrate that NMR is a broadly useful technique from which most hybrid catalysts with organic moieties can benefit. However, NMR is not specifically interface sensitive, such that conventional NMR may not be insightful for systems involving bulk organic phases with little contribution from hybrid interfaces such as for inorganic nanoparticles in organic matrices, and developing appropriate techniques or model systems for these applications would be extremely beneficial. Additionally, challenges still exist in experimental practices, as some nuclei have relatively low sensitivity and require complex pulsing techniques. Nevertheless, NMR has the potential to provide both static and dynamic description of the catalytic processes taking place in organic/inorganic materials.

3.5. X-ray Spectroscopies. In addition to structural modifications, electronic perturbations play crucial roles along with structural modifications in determining the catalytic behaviors of active sites, whose characterization is mainly facilitated by X-ray spectroscopies. X-ray spectroscopies give useful insight into both the structural and electronic properties of organic and inorganic components in hybrid materials. The oxidation state changes in metallic components due to the interaction with organic moieties can be readily measured and distinguished with appropriate materials. Similarly to previous techniques, distinguishing the signals related to the species of interest is crucial, and hybrid materials with uniform organic/inorganic interfaces are the preferred compounds to study. Again, MOF-based materials here can lead to particularly useful signals that can be traced with different X-ray spectroscopies. X-ray photoelectron spectroscopy (XPS) is specifically sensitive to surface oxidation states and reaction environments. In an exemplary case, Lee et al. were able to use XPS to study the oxidation state of Zn in a MOF structure that promoted remarkable activity for carboxylation of inert arenes on a silver surface. The researchers demonstrated a unique selectivity for this reaction accessible at room temperature and ambient pressure using the silver-MOF hybrid structure, rather than the commonly used higher temperature and pressure conditions. Impressively, they authors observed the formation of a new feature related to oxidized Zn species due to the coordination of the reactant with the Zn in the MOF when adsorbed on the underlying Ag surface (Figure 11). This...
molecular orientation promoted by the Zn-MOF layer led to increased pressures of CO₂ on the silver surface, as evidenced by in situ spectroscopic evidence. The impressive behavior allowed the carboxylation to occur at ambient pressure and temperature, a result that clearly could not be obtained if not for the presence of the organic/inorganic interface created in the hybrid materials. The X-ray spectroscopic investigation turned out crucial to explain the specific reactivity of the interface (Figure 11).

X-ray spectroscopies are also particularly useful in differentiating the electronic structures of inorganic components modified by different organic moieties. The electronic effects of organic adsorbates on inorganic components can be studied and clarified with hard X-rays that can penetrate through the organic moieties. In this sense, techniques such as X-ray absorption spectroscopy (XAS, both near-edge structure XANES and extended fine structure EXAFS) are particularly appealing for characterizing both atomically dispersed catalysts and bulk nanoparticles modified by organic ligands or bulk organic phases. The elucidation of organic promotion on inorganic components can be obtained through the preparation of libraries of composites where the organic compound is systematically varied. A variety of organic ligands (phosphines, thiols, weakly bound molecules, etc.) can be utilized to coordinate and modify metal nanoparticles and used to study the effect of the organic ligands on the nanoparticle reactivity.

Pd nanoparticles modified with several ligands and used for the selective hydrogen peroxide synthesis were subjected to Pd L₃-edge X-ray absorption near-edge structure. The authors found that the ligands that enhance catalytic performance also modulate the Pd electronic properties, significantly promoting the formation of surface hydrides and consequently hydrogen peroxide (Figure 12). In a similar spirit, Chen et al. demonstrated that by using ethylenediamine overlayers onto ultrathin Pt nanowire electrodes, the catalytic hydrogenation properties of metal nanocatalysts could be dramatically changed from full to partial hydrogenation. Using extended X-ray absorption fine structure (EXAFS) on the Pt catalysts, it was revealed that electron donation from ethylenediamine made the Pt surface highly electron-rich, which favored the adsorption of electron-deficient reactants leading to improved selectivity. In both cases, the correlation between electronic structure and catalytic properties was crucial to explain the mechanism of action of these hybrid catalysts, and a combination of X-ray spectroscopies clarified several aspects in these studies.

Successful as X-ray techniques are, challenges still exist when interpreting measurements. It is commonly found that XPS is very susceptible to interpretation bias in binding energy referencing and peak deconvolution, which makes definitive differentiation of multiple peaks difficult. This challenge is particularly true with organic/inorganic components, where...
multiple signals may overlap and lead to difficult deconvolution. Moreover, the interpretation of the structure of metal–organic complexes using X-ray absorption techniques requires the development of a plausible theoretical model, which may not be readily available for novel materials. The use of comparison samples and standards is crucial. We wish to highlight that computational methods may shed light on the modeling of such metal–organic interfaces, which will eventually boost the fundamental understanding of these hybrid catalysts.

4. MECHANISTIC CHARACTERIZATION OF HYBRID ORGANIC/INORGANIC CATALYSTS

In catalysis, advances in fundamental understanding are obtained through mechanistic proof. Either through direct kinetic studies, or in situ spectroscopic measurements, a greater understanding of how well-defined hybrid materials operate provides important guidelines for the rational design of next-generation hybrid catalysts. In general, hybrid catalysts demonstrate unique reactivity due to mechanisms involving (1) organic/inorganic charge transfer, (2) molecular orientation of reactants induced by the organic layer, (3) direct mechanistic participation of the organic moieties, or (4) transport control and shape selectivity induced by the organic layer (Figure 13). These mechanisms are not linked to an individual material class in section 2 but are general design motifs for targeting reactive mechanisms through hybrid materials. In this section, we highlight exemplary literature cases which use various techniques to demonstrate these mechanisms operating in hybrid catalysts.

4.1. Charge Transfer. Similarly to how alloying two metals can affect the electronic structure of a metallic phase, studies demonstrate that proximal organic groups can change the electronic structure of a metal atom or nanoparticle to benefit catalytic activity. To control this effect, MOF-nanoparticle composites are rapidly emerging as a platform for tuning the electronic properties of nanoparticle surfaces. By embedding nanoparticles within frameworks of tunable chemistry, researchers have begun tuning the charge transfer between the MOF framework and the nanoparticle surface. Dongxiao et al. showed that for the hydrogenation of benzoic acid to cyclohexanecarboxylic acid, this charge interaction has a significant effect: different MOF chemistries, including UiO-66-Ome, UiO-66-NH2, UiO-66-3OH(Hf), and UiO-66-2OH show dramatically different activity (Figure 14a).110 To understand these catalytic differences, ab initio calculations were performed to show that an increased activity for this reaction is correlated to lower charge transfer interactions from the Pd nanoparticles to the MOF structure. In addition to calculations, the changed surface state was demonstrated by DRIFTS, where a monotonic shift in CO binding energy with MOF chemistry paralleled the increase in catalytic reactivity, suggesting that a shift in electronic structure at the Pd nanoparticle surface was responsible for the catalytic activity being tunable by MOF chemistry (Figure 14b). Given the variety of chemical functional groups that can be installed in MOF structures, this example shows how powerful this approach could be in manipulating the fine electronic structure of metal surfaces using systematic variations in the MOF ligands.

In supported single atoms on carbon, hybrid electrocatalysts are designed to take advantage of electronic metal–organic interactions. Charge transfer between organic supports and metal phases can be especially important in electrocatalyst design, where the electronic properties of the support play a direct role. Often, these organic phases are conductive organic substrates. Key electronic interactions between the metal phase and the organic phase can produce significant differences in activity for various reactions. Niancai et al. demonstrated that by tuning the size of the metal phase supported on nitrogen-doped graphene nanosheets, significant improvements in the hydrogen evolution reaction (HER) onset potential could be observed.111 To explain this result, the researchers performed XAS analysis, which indicated that when nitrogen-doped graphene nanosheets support small Pt nanoclusters or single Pt atoms, the support modulates the electronic structure of the metallic phase. Bader charge analysis revealed that Pt single atoms on the organic support can contribute four times as much electron density to hydrogen atoms compared to larger Pt nanoclusters. In this way, Pt single atoms are “less-metallic” than Pt NPs, which leads to the unique electronic structure and increased reactivity of Pt single atoms on nitrogen-doped graphene nanosheets.

MOF materials, and polymers in general, benefit from their flexibility introduced by the dynamic organic component complementing the inorganic nodes or by varying the degree of cross-linking, respectively. This property is very unique to organic materials and adds a new mechanistic dimension compared to fully inorganic catalysts. In the case of MOFs, this flexibility can be taken to an extreme by further taking advantage of dynamic chemistry at the node-ligand sites. Recent work demonstrated that MOF structure dynamically
ligates and deligates as a function of electropotential, as demonstrated by in situ UV−vis, resonance Raman, and IR spectroscopies, during electrochemical CO₂ reduction on MOF|TiO₂|FTO composites (FTO, fluorine-doped tin oxide) (Figure 15). These dynamic movements led to changes in the Mn oxidation state throughout the catalytic cycle. Specifically, the dynamic nature of the MOF coating was shown through potential-dependent Raman spectra, which exhibited potential-dependent changes that could be correlated to the transition from a five-coordinated Mn(III) to a four-coordinated Mn(II). Although this system was designed as a proof-of-concept demonstration, the authors acknowledged that it was challenging to understand the direct role of this dynamic behavior on the catalytic cycle, suggesting that it related to changes in the electronic state of Mn nodes in turn leading to changes in the ability of the system to shuttle protons or conduct charge.

These examples highlight how charge transfer effects can be used in directing catalytic performance in a unique way using organic moieties to tune inorganic components. The finely tunable electronic properties of hybrid materials are expected to play an important role in manipulating catalytic activity, and studies directed at controlling and understanding these phenomena are going to become very impactful in this nascent research area.

4.2. Reactant Orientation. Researchers have identified the opportunity to use organic catalyst components to modify the orientation of reactants as they approach a metal surface; this ability can lead to increased selectivity of certain reactions that depend on a functional group being directly adsorbed to the catalytic surface. This powerful strategy is reminiscent of the directionality by which enzymes control the reactivity of certain functional groups on substrates via the influence of amino acid groups proximal to the active site. In a demonstration of this idea, Kahsar et al. functionalized the surface of a Pt/Al₂O₃ catalyst with various thiol molecules, aimed at changing the reactive orientation of cinnamaldehyde for selective reduction of the formyl group rather than the carbon double bond (Figure 16a). Remarkably, the researchers found that tethering longer chain length aromatic thiols to a Pt surface led to increased selectivity for the aldehyde reduction to the respective alcohol, and shorter and alkyl chains led to increased selectivity for the olefin reduction.

To prove this effect was due to preferred molecular orientation of the reactant, the researchers performed in situ PM-RAIRS, a surface sensitive spectroscopy, on a model single crystal surface and calculated the intensity ratio of different vibrational modes at the interface of the catalyst and ligand (Figure 16b). In this measurement, they found that when the metal surface was functionalized with longer-chain thiols, there was increased absorption for the alcohol near the surface, compared to the olefin near the surface. This in situ molecular probe/spectroscopic approach conclusively demonstrated that this change in selectivity was due to molecular orientation caused by organic ligands. Other examples of reactant orientation, or molecular recognition, from the same group have demon-
strated the utility of self-assembled monolayers on metallic surfaces for controlling steric interactions and selecting active sites. Similar surface functionalization strategies using thiols on Pt/TiO₂ materials further strengthened the strategy of using molecular ligands to direct the orientation of reactants, with remarkable selectivity in the reduction of nitrostyrene. In this case, surface functionalization led to reduction of the nitro group over the olefin functionality.

MOF materials have also been used to control molecular orientation and drive selectivity. Embedding small metal particles inside MOFs is a strategy that could take advantage of both ordered pore structures and chemical functionalization of pore walls. Recent demonstration of this strategy showed how monodisperse Pt nanoclusters confined within cavities of functionalized metal–organic frameworks (UiO-66-NH₂) selectively hydrogenate cinnamaldehyde into cinnamyl alcohol with 91.7% selectivity. The authors proposed that the access of Pt active sites was hindered by the accessible channel sizes connecting tetrahedral and octahedral cages inside UiO-66-NH₂ (Figure 17). However, rather than completely excluding the reactant molecule, the size of interchannels (6 Å) forces the orientation of cinnamaldehyde molecules specifically favoring the linear conformation while making the flat C=CH bond adsorption sterically very hindered.

The few examples above highlight the reactivity of model materials and demonstrate the promise of this approach to use organic moieties to direct molecular orientation on reactive surfaces. These approaches are known to be crucial in zeolite catalysis as well as in enzymatic catalysis. The expansion of the approach to more complex substrates and the installation of precise groups to predictably tune molecular orientation, potentially suggested from computational studies, will be important in the future to continue to explore this method for selective transformations.

4.3. Direct Mechanistic Participation. So far, the discussion revolved around passive ways for organic moieties to influence reaction dynamics, either by charge transfer or by directing molecular orientation. However, an exciting opportunity exists in the possibility of using organic moieties to directly affect reaction mechanisms and pathways, by directly interacting with the reactants, intermediates, or transition states to change reaction energetics. One way this effect could be realized is via partial coordination of the organic phase to the reactant molecule, thereby changing the energetics of various reactive intermediates. In recent work from our group, we demonstrated how this approach is possible using uniform nanocrystals embedded within porous polymers with a strong aromatic backbone, where polymer layers encapsulate nanocrystal active sites (Figure 18). In materials composed of Pd nanocrystals covered by polymers with different densities of amino groups prepared through imine bond-forming reactions, we observed that various polymer chemistries produce remarkable differences in rates and kinetic parameters for the CO oxidation reaction. To explain this phenomenon, a detailed kinetic analysis was performed, and it was discovered that the nature of the polymer layers affected the enthalpy and entropy.
of the reaction transition state (Figure 18). Because of the varied density of amino groups, polymer layers would adsorb CO₂ more or less strongly, leading to their influence on determining an early (weak binding) or late (strong binding) transition state structure. In this case, the polymer layers directly participated in affecting the reaction dynamics. Although selectivity is not a challenge for CO oxidation, the extension of this approach to other reactions involving CO₂ can further demonstrate the advantageous use of polymer modifiers to drive selectivity.

MOFs have also been shown to participate in changing reaction dynamics. In a noteworthy example, researchers showed how encapsulating nanoparticles in MOFs can be used to direct selectivity in the hydrogenation of enones. Typically, supported Pt nanoparticles show high selectivity for the hydrogenation of the C==C double bond in molecules containing both C==C and C==O bonds. Calculations demonstrated that when the enone substrate coordinates via the carbonyl moiety to the metallic node in the MOF structure (MIL-101, containing Fe³⁺ or Cr³⁺ metal nodes), the energetics of the reaction change such that the platinum nanoparticle catalyst produces the alcohol rather than the aldehyde. However, the authors showed that a different MOF overlayer flips this selectivity due to different thermodynamic pathways caused by the carbonyl coordination to the MOF. This example particularly demonstrates how transition state energies are modified by introduction of a new reaction pathway using MOF layers in the proximity to a nanoparticle surface.

There is ample room for exploring organic layers to directly affect reaction pathways. Given the large number of chemical functional groups that can be installed in the proximity of reactive metal sites, researchers are only just beginning to explore an area that can bear important fruit in catalysis for energy and environmental challenges. Systematic changes in functional group identity, distance, proximity, and active site composition can lead to intriguing changes in catalytic performance and to the establishment of rules that can be used to design these interactions a priori.

4.4. Transport Control. Enzymes are able to select substrates by controlling the transport of chemicals through the protein backbone and into the active site. Their mechanisms of action are as amazing as they are complex to reproduce. Nevertheless, these mechanisms provide inspiration to engineering transport control of species to improve catalytic performance and selectivity. Despite artificial catalysts only crudely controlling transport, the effects can have impressive effects. In many examples, control in the transport of reactants to the active sites has been shown as the main tool to engineer reactivity. Zeolites functionalized with organic moieties emerged early on as candidates to demonstrate shape-selective transport and reactivity. For example, the inner functionalization of zeolite pores with organic sulfonic acid sites allowed for selective ketalization of smaller cyclohexanone over the much larger 2,2-pentamethylene-1,3-dioxolane, which could not fit into the zeolite pores. More recently, this concept has been extended to polymeric materials with embedded nanocrystals by our group (Figure 19). Porous organic frameworks can indeed allow for selective access of reactants to an active site, driving selectivity for the hydrogenation of mixtures of olefins. By choosing organic overlayers with specific pore sizes (less than 6 Å), it was demonstrated that the materials selectively sieved away larger cyclic olefins, preventing their hydrogenation, while still allowing for the hydrogenation of smaller olefins like propene (Figure 19). By using physiosorption to characterize the pore structure and by selecting a probe reaction with species larger or smaller than the pore structure, it is possible to further explore how this controlled pore geometry, size, and chemistry can be tailored to perform size-selective catalysis.

Organic moieties can also be utilized to trap products, rather than exclude reactants. This ingenious effect has been recently employed by Jin et al., who studied AuPd nanocrystals encapsulated in the zeolite ZSM-5 for the liquid-phase conversion of methane into methanol. The researchers modified the surface of the zeolite with a hydrophobic coating using organosilanes in an attempt to tune the permeability of various hydrophobic and hydrophilic reaction intermediates, including hydrogen peroxide as a key oxidant for methane. It was found that modification of the surface of the zeolite with a hydrophobic silane dramatically increased the methanol yield produced by the catalyst system. The authors hypothesized that the hybrid organic/inorganic zeolite facilitated increased methane to methanol conversion due to containment of a critical peroxide intermediate, formed in situ from hydrogen and oxygen, within a hydrophobic shell. To prove this
hypothesis, the authors performed molecular probe experiments to observe how peroxide partitioned between the solid phase (pores) and the liquid phase (liquor) as a function of solid surface functionalization (Figure 20). Remarkably, it was found that H2O2 enrichment was present when the solids were protected with hydrophobic groups instead of hydrophilic groups or with no organic moieties. This effort helps substantiate the increased methanol yield due to increasing peroxide concentration within the reactive material.

Postsynthetic treatments are used to create and shape polymer−nanocrystal interfaces for selective transformations. In this case, the “soft” nature of polymer and organic compounds is a real asset. The design of these materials could then start from appropriate precursors, and the embedding of the active phase can be realized through postdeposition treatments. This type of approach has been recently demonstrated to provide very intriguing results for almost kinetic separation of intermediates leading to selective chemical transformations. Lee et al. showed that impregnating Pd nanoparticles on polyphenylene sulfide followed by acid and thermal treatments led to the nanoparticles being embedded in a thin polymer layer due to polymer chain mobility at higher temperatures. Interestingly, the researchers found these hybrid materials to be highly selective for acetylene hydrogenation to ethylene without further hydrogenating ethylene to unwanted ethane, when compared to either Pd/SiO2 or the hybrids that were treated at a higher temperature responsible for rigidifying the polymer rather than mobilizing it. In detailed isotope-exchange experiments, the researchers found that on these unique hybrid materials, H2/D2 exchange happened only in the presence of acetylene, but not in the presence of ethylene, while the latter was still possible on the control materials (Figure 21a,b). Overall, these mechanistic experiments support the hypothesis that in the case of the hybrids with Pd embedded within the polymer layers, there is selective coadsorption and activation of H2 only in the presence of acetylene but not in the presence of ethylene. This effect was attributed to the mobility of the polymer chains of the support. The high-temperature treated polymer support, which was found to be less mobile, did not have the unique selectivity. This property could only be engineered in the hybrid materials with the appropriate
structure and demonstrates how the fine-tuning of the structure could lead to tremendous positive implications for selective catalysis.

In summary, the control of the diffusion of reactants and products in and out of active sites is an appealing element that could be engineered with organic components much more finely than with inorganic ones. The tunability in the size and chemistry of organic building blocks allows researchers to build libraries of hybrid catalysts where spatial dimensions and chemical interactions can be tuned to a fine extent. This type of approach could be extended to multiple classes of hybrid materials but is especially exciting for those where active metals phases are encapsulated within the organic sieving layers. It is expected that this approach will provide novel ideas in several areas where the bridging of separation and catalysis could lead to innovative materials and concepts for efficient, selective catalysis.

5. ON THE DESIGN OF HYBRID CATALYSTS FOR METHANE-TO-METHANOL TRANSFORMATION

The previous sections highlighted different classes of organic/inorganic hybrid catalysts as well as their use in many catalytic applications related to energy and the environment. In this section, we concentrate on one particular application and provide a perspective on how these materials can help promote a challenging catalytic transformation. The transformation is that of methane into methanol, a reaction often labeled as a “holy grail” in catalysis. This reaction is particularly sought after because of the large amount of natural gas that is available since improved fracking practices started to be introduced, especially in the United States. Converting natural gas into a liquid commodity chemical, methanol, would provide a crucial improvement in industrial practice and an opportunity to use stranded natural gas resources that are otherwise flared. We believe this reaction to be a particularly interesting choice for hybrid organic/inorganic catalysts, as researchers working on this transformation have been often inspired by methane monooxygenase enzymes (MMO), hybrid biological catalysts which can turn methane into methanol at room temperature and ambient pressure in the presence of molecular oxygen. The enzyme contains metal ions in its active site (low-nuclearity Cu and Fe sites) to perform O₂ activation and C–H bond scission. Local ligand environments dictated by amino acid residues form reactive electrophilic metal–oxygen species. Hydrophobic binding pockets control the access of methanol to the active site through molecular pores and gating mechanisms, determining controlled transport in and out of the active site. Despite the fact that the complicated machinery behind the impressive reactivity of this enzyme is hard to replicate in all aspects, many studies have been trying to take a reductionist approach and simulate some of the steps that are considered crucial to obtain selectivity. There are certainly other important reactions in catalysis that can benefit from the use of organic/inorganic hybrid materials inspired by natural enzymes: examples are hydrogen peroxide synthesis from hydrogen and oxygen, carbon dioxide fixation, selective hydrocarbon oxidation, and C–C coupling reactions in complex substrates. Here, we decided to focus on methane oxidation, but the observations that we highlight can be extended to other reactions.

One of the most popular class of MMO-inspired catalysts is that of copper-exchanged zeolites. In these catalysts, isolated or low-nuclearity species have been identified to convert, in a stepwise or continuous manner, methane into methanol. Although the success of Cu-exchanged zeolites for this reaction bares some semblance to the low-nuclearity Cu sites in MMO enzymes, zeolites are inorganic materials, and caution must be exercised in describing their behavior as biomimetic. In this section, we propose approaches to utilize tunable hybrid organic/inorganic materials for the development of methane-to-methanol catalysts that use oxygen as the oxidant in a continuous process. This particular application exemplifies how this class of catalysts can contribute to tackle challenging transformations of benefit for energy and environmental applications.

Figure 22. Mechanisms theorized to increase yields of selective oxidation of methane to methanol. Adapted with permission from ref 136. Copyright 2018 American Chemical Society.
heterogeneous and homogeneous systems for methanol production in the literature. To simulate this solvating environment within a catalyst, organic moieties could be chosen to solvate the reactive methanol product. These local environments could be designed with appropriate ligand or polymer chemistries and tuned with organometallic and polymer chemistry toolboxes. Organic phases could be utilized in close proximity to the active site to increase the energy barrier needed to reactivate methanol for further oxidation, while still allowing methane to react. Such proximate organic ligands could lower activation energy barriers for the methane-to-methanol reaction for example by hydrogen bonding, allowing the reaction to occur at lower temperature where methanol would be less reactive. The same hydrogen bonding network could then be responsible for driving methanol out of the active sites, without overstabilizing it. Even organic phases at a distance could be useful in their solvation effect. Here, organic phases could extract methanol from the gas phase, thereby lowering the partial pressure of this product. However, discussion of this gaseous partial pressure effect needs to include a distinction between transient behavior in non-equilibrated systems compared to equilibrated systems: in the latter, after methanol sorbents are at capacity, the gas-phase methanol pressure will be the same with or without the local solvating environment.

Although it may be reasonable to intuitively predict a desirable solvation environment (i.e., hydrogen-bonding moieties), it is important to approach this challenge with quantitative characterization. Here, we suggest performing solvation and adsorption experiments of the desired methanol product with various organic chemistries to identify favorable adsorption environments. Such experiments could be performed in chemisorption and physisorption systems as well as in the form of breakthrough curves on model substrates. Similarly, one could perform adsorption equilibria experiments in the liquid phase, measuring the free quantity of methanol in the liquor as a function of various polymer or organic chemistries. Such experiments provide a measurement of the solvation effects of different ligands and monomers and would hint at key chemistries to include in organic components of hybrid organic/inorganic materials.

In addition to modifying reactant and product energetics, porous hybrid materials have the potential to be successful for the methane-to-methanol transformation thanks to the controlled diffusion of species to the active sites. Diffusional control can be used to either (1) selectively allow diffusion of specific species into and out of active sites or (2) reduce diffusivity of all molecules to make reactant diffusion step rate limiting. Clearly, a trade-off with productivity (i.e., reaction rate) will be realized, as already predicted in previous work. Both these strategies are targeted at increasing the relative reaction rate of methane activation and decreasing that of methanol activation. Despite the decrease in overall yield of the reaction, these diffusional barriers would increase the selectivity toward methanol by further increasing the activation energy. In typical metal oxide catalysts, diffusional properties are engineered via controlling pore size distribution (i.e., in zeolites) and pore length. Hybrid materials possess the same advantage, with the additional possibility of changing pore chemistry by using organic functional groups to decorate pore walls. For diffusional control, bulk organic phases allow maximum tunability, and polymers have been extensively studied for gas diffusion and separations. Metal organic frameworks however have also been touted for their diffusion control, mostly for their size-exclusion properties due to a well-defined pore structure. Both these solid materials provide opportunities to engineer transport phenomena that could maximize selectivity for the methane-to-methanol reaction. In addition to transport phenomena, MOF materials have also displayed cooperativity in binding substrates and tune molecular transport. This property is very promising for tuning molecular transport to and from catalytic sites encapsulated within organic layers. An example of molecular tuning of transport is related to separating propene and propane, which have a size difference of just 0.1 Å, due to fine control of the MOF pore structure. The higher diffusivity of propane is related to its lower activation energy of diffusion, leading to the potential for kinetic separation (Figure 23).

Translating this behavior for catalytic applications and reactive separations could turn out to be very fruitful in controlling selectivity of chemical transformations. For various organic/inorganic hybrid nanomaterials, similar uptake experiments comparing methane and methanol would lend great insight into kinetic and thermodynamic properties and advantages for engineering nanomaterial structure toward promoting methane reactivity and methanol rejection.

Restricting diffusion rates for all species can be another approach to maximizing methanol yield. With sufficient diffusional barriers, the difference in activation energies between methane and methanol approaches zero, as overall reactivity would be determined by the activation energy of diffusion rather than by the C–H bond breaking reaction. Increasing diffusional barriers can be achieved using certain organic/inorganic hybrid materials. For example, using nanocrystal–polymer composites with active metal nanocrystals embedded within polymer layers, the thickness of the polymer can be increased and the chemistry tuned to manipulate diffusion rates to the active sites. Pore characterization techniques, including physisorption or even more advanced spectroscopic techniques, may allow researchers to directly understand the diffusive pathway of species and the design of materials with the minimum diffusion length such that diffusion controls reactivity but is not more severe than it needs to be. Overall, hybrid organic/inorganic catalysts are particularly promising for driving reaction selectivity in...
challenging transformations. The conversion of methane into methanol is only one such potential application, and the broad applicability of these materials guarantees that successful examples will be reported for all the four categories of hybrids that we reported in this Outlook.

CONCLUSIONS

Organic/inorganic hybrid catalysts present an opportunity for tackling challenges in transformations related to energy and the environment. Much of this potential stems from the unique control of organic environments around inorganic sites within a single material, which allows for new properties inaccessible using purely organic or inorganic materials. A renewed interest in these materials has taken form in the past few years. This new interest has been promoted by novel characterization techniques, including cryo microscopy, surface-sensitive spectroscopies, and computational techniques, which now allow researchers to understand soft materials, organic structures, and biological materials which often serve as a motivation for synthesizing these hybrid materials. In this Outlook, we presented a path toward the directed design of hybrid organic/inorganic structures for various energy and environmental applications. Most importantly, we emphasized the key role of spectroscopies and characterization in understanding the structure of complex hybrid organic/inorganic materials and (2) mechanistically proving the behavior of these materials. The promising opportunity to catalyze the methane-to-methanol reaction is presented as just one of many important challenges in energy and environmental catalysis that can be approached using hybrid materials.

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