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Zeolite Encapsulated Organometallic Complexes as Model Catalysts

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Abstract

Heterogeneities in the structure of active centers in metal-containing porous materials are unavoidable and complicate description of chemical events occurring along reaction coordinates at the atomic level. Metal containing zeolites include sites of varied local coordination and secondary confining environments, requiring careful titration protocols to quantify the predominant active sites. Hybrid organometallic-zeolite catalysts are useful well-defined platform materials for spectroscopic, kinetic, and computational studies of heterogeneous catalysis that avoid the complications of conventional metal-containing porous materials. Such materials have been synthesized and studied previously, but catalytic applications were mostly limited to liquid-phase oxidation and electrochemical reactions. The hydrothermal stability, time-on-stream stability, and utility of these materials in gas-phase oxidation reactions are under-studied. The potential applications for single-site heterogeneous catalysts in fundamental research are abundant and motivate future synthetic, spectroscopic, kinetic, and computational studies.

1. Introduction

Heterogeneous catalysis is an essential enabling technology for feeding the ever-increasing global population and ensuring a high quality of life in both the developed and developing world. In the coming century, the chemical industry will need to make further strides to reduce material extraction/mining requirements and their associated societal and environmental burdens, as well as reduce the energy required for chemical production over heterogeneous catalysts. Such progress will require a multi-faceted portfolio of technologies including alternative modes of molecular excitation beyond solely thermal catalysis (e.g., biocatalysis, electrocatalysis, plasma, microwave, inductive heating, etc.). At their core, rational design of improved catalysts in any of these systems requires reliable comparisons of relative metrics of catalyst performance. One essential metric is the per-active-site reaction rate, or turnover frequency (TOF).[1-3] While the TOF is relatively easily measured in homogeneous catalytic systems, measurement of TOFs over heterogeneous catalysts is typically challenging, and complicates comparison of materials with varied local and/or secondary active site structures.

The local coordination and geometry of transition metals that act as primary binding sites in transition-metal-containing porous materials have implications on catalysis, and heterogeneities in these structural features lead to distributions of reactivity and the necessity for active site quantification under the conditions of catalysis in order to quantify turnover rates and calculate intrinsic kinetic and thermodynamic parameters. These challenges are exemplified in many promising metal-containing porous materials, which are desirable in practice due to their high per-volume surface areas and hydrothermal stabilities.

Metal organic frameworks (MOFs) with catalytically active open metal sites situated in their nodes contain distributions of metal sites including framework M sites, defect M sites, and others that result in catalytic diversity.[45] Aluminosilicate zeolites can also contain multiple crystallographically unique tetrahedral sites (T-sites) and Al atoms of varied local proximity, with measurable impacts on catalysis.[6] The same heterogeneity is present after M ion-exchange of H-zeolites and mesoporous materials, with the additional complications that M atoms can bind to the support in multiple ways.[7, 8]

A promising way to reduce the structural complexity of metal containing porous materials is to encapsulate a well-defined molecular complex within the pores of an ordered, hydrothermally stable host material. Such materials allow for studies of metal-catalyzed reactions (e.g. oxidations,[9, 10] hydrogenations[11, 12]) in porous materials wherein beneficial effects of confinement on reactivity or selectivity might be observed without the inherent heterogeneity in active site structure encountered in conventional metal-containing porous materials. These materials provide the opportunity for shape selective chemistry over organometallic complexes, based on the surrounding void size (which can be tuned via the size of exchanged cations[13]). Encapsulation in zeolites can avoid agglomeration typically encountered in solution for some macrocycle complexes, allowing their reactivity to be maintained for extended periods. Thermally stable complexes, such as phthalocyanine, can be used for gas phase chemistries at elevated temperatures. The tunability of the local structure of the complexes and their surrounding void environment have vast possibilities to enable extremely high per site reactivities for a range of metal primary binding sites (e.g. from V to Zn) with identical local and secondary structures. This ability to select a local site and surrounding void size on demand could have benefits in a range of societally relevant chemistries.

Faujasite (FAU) zeolites are a useful host in this regard, as they are readily synthesized and commercially available, and contain large internal voids known as "supercages," with diameters of ~1.2 nm, that are accessed via 0.7 nm pore openings. Organometallic complexes encapsulated in FAU are colloquially termed "ship-in-a-bottle" materials, as once the complexes are formed, they cannot escape from the micropores of the zeolite. A common complex for these approaches is metal phthalocyanine (MPC), both for its commercial availability, high thermal stability, and the ability to synthesize it by "ship-in-a-bottle" approaches. These materials have been synthesized via a conventional, hydrothermal "zeolite synthesis" approach in which the organometallic is added as an additional synthesis reagent in the zeolite synthesis gel,[14] or by incorporating metal atoms post-synthetically, followed by treatment protocols that form the desired complex around the metal precursor atoms within the already-crystallized zeolite ("post-synthetic synthesis," **Figure 1**).[15] After careful washing and pretreatment protocols, these procedures can produce materials with solely encapsulated complexes without any metal-free complexes or stray ion-exchanged metal cations. Perhalogenation of MPCs prior to encapsulation via the zeolite synthesis route is required in order to increase solubility during hydrothermal zeolite synthesis in aqueous solutions[16] and thermal stability under reaction conditions.[17, 18] Nevertheless, the total metal loadings for materials synthesized via "zeolite synthesis" approaches are consistently lower (by up to an order of magnitude) than those achieved through "post-synthetic synthesis."

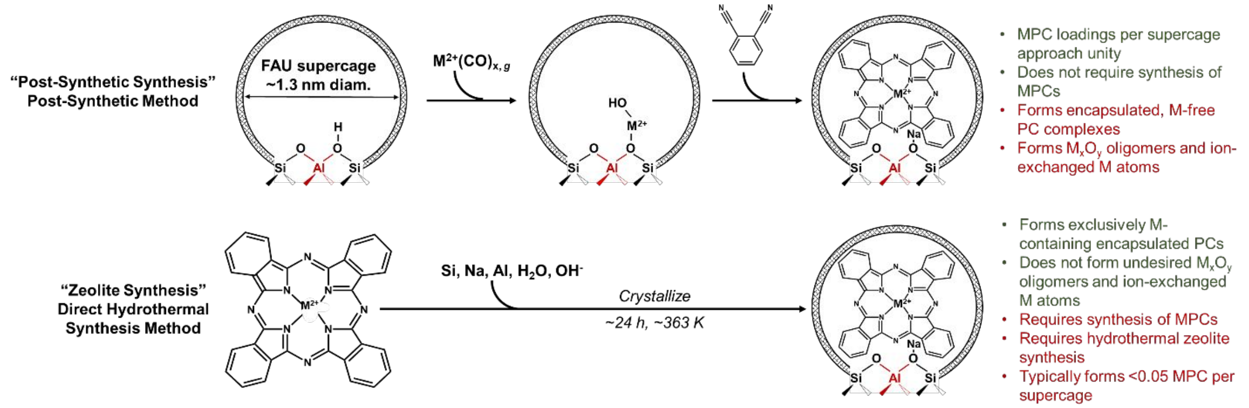

Figure 1. Post-synthetic synthesis (top) and zeolite synthesis (bottom) approaches to produce MPC@FAU materials.

Here, we summarize the state-of-the-art in use of organometallic complexes encapsulated within porous materials as model heterogeneous catalysts that avoid the site heterogeneity of other metal-containing heterogeneous catalysts. These materials have been extensively studied for liquid-phase chemistries (Table 1), however, their use in gas-phase oxidation reactions is much less studied (Table 2). We *speculate* that this area is potentially under-studied because organometallic synthesis, zeolite synthesis, and gas-phase chemistry are not typically skillsets contained within single research laboratories or even across single departments at universities, but rather require significant collaboration between research groups. Heterogeneous catalysts have generally received more attention, especially for industrially relevant applications than homogeneous catalysts owing to separation, stability, and reusability issues of homogeneous catalysts.[19, 20] The heterogenization of organometallic catalysts by developing hybrid materials using porous materials is an attractive new field, combining the properties of both compounds to generate new hybrid heterogeneous catalysts. In addition, ligands attached to the metal active site may also further blur the line between the catalyst's homogeneous and heterogeneous nature by acting as a source of electrons to the metal site, thus altering its electronic structure and activity.[21-24] The resultant materials are similar to supramolecular complexes, but are amenable to gas-phase chemistry.[25, 26]Some complexes, like MPC, have similar square planar binding sites to biological enzymes that catalyze alkane oxidation,[27, 28] distinguishing them as candidates for this and other gas phase oxidation chemistries. Although other materials, including MOFs, have also been used for heterogenization, the present Frontiers article places emphasis on the use of zeolites in the process of heterogenization.

2. Examples of Encapsulated Organometallics in Zeolites Background/history

Many studies have hoped to leverage the metal centers of these encapsulated complexes to model the active sites of enzymes[29-31] Encapsulation in zeolites has been shown historically, there are several archival examples (Table 1). Typical complexes include phthalocyanine, porphyrin, salen, carbonyl complexes, and bipyridine complexes. For example, Balkus, Jacobs, and others have reported phthalocyanines in zeolites synthesized by both "bottom up" and "ship in a bottle" methods.[32-34] Gates and colleagues have generated metal carbonyl complexes in zeolites.[35] Ellis and Lyons encapsulated metalloporphyrins in the supercages of faujasite.[36, 37]

These zeolite-encapsulated catalysts have been studied in liquid–phase chemistries, including oxidations and hydrogenations (Table 1). Balkus and colleagues[38] showed that faujasite-encapsulated perfluorinated RuPC ($RuPCF_{16}$@FAU) had a ~10× higher turnover frequency than unencapsulated $RuPCF_{16}$ for cyclohexane oxidation with tert-butyl hydroperoxide (TBHP) at room temperature (2.4 mmol TBHP, 6 mmol cyclohexane, 0.002 mmol $RuPCF_{16}$, acetone solvent), with no deactivation observed over 20,000 turnovers. Balkus et al.[39] further demonstrated the encapsulation of $RuPCF_{16}$ in FAU by comparing the rates of cyclohexane and cyclododecane oxidation with TBHP, wherein, the rate of cyclohexane oxidation was ~10× greater than that of cyclododecane oxidation over $RuPCF_{16}$@FAU. However, the rates of these oxidations were identical over unencapsulated $RuPCF_{16}$, suggesting the difference in rates over $RuPCF_{16}$@FAU resulted from the slow diffusion of cyclododecane to the encapsulated complexes.[39] Further, hydrogenation reactions have been explored, wherein small olefins (e.g., butene, 1-octene, cyclohexene) were readily converted while larger olefins that cannot easily diffuse into the zeolite pores (e.g., cyclooctene) were not noticeably converted.[40]

However, the viability of these materials for gas solid reactions is less studied (Table 2). Additional classes of organometallic complexes could be amenable to occlusion within zeolites as model catalysts, provided they have the necessary characteristics for bottom-up synthesis (i.e., diameter <1.2 nm, stable and soluble in high pH aqueous synthesis gels), or possible to assemble post-synthetically within the pores by ship-in-a-bottle approaches, and have stability in a gas phase reaction. These synthetic approaches limit agglomeration of complexes in solution, and thus can promote use of complexes that are otherwise considered undesirable for homogeneous chemistry.

The known structure of the primary binding sites is attractive for computational-experimental collaborations. As computational methods and computing power have increased over the past 30 years, it is increasingly possible to model both the local structures of the organometallic complexes as well as their porous hosts (see Table 2). Such models provide geometrical parameters of encapsulated complexes,

Table 1. Examples of organometallic complexes encapsulated in zeolites used in liquid-phase reactions.

Complex	**Host**	**Chemistry(ies) Tested**	**Year(s)**
Metal Phthalocyanine (MPC, M= Co, Cu, Fe, Ni, Rh, Ru)	FAU EMT[41] VPI-5[10, 42, 43] MCM-22[43]	alkane oxidation with *tert*-butyl hydroperoxide (TBHP),[9, 10, 42, 44-47] Photocatalytic benzothiophene degradation[48] Ethylbenzene oxidation with O_2[41, 49] Ethanethiol oxidation with O_2[49] Alkane oxidation with iodosobenzene[50-52] Photocatalytic degradation of cyanide[53] Olefin epoxidation with iodosobenzene[54] Alkane oxidation with O_2[43, 55] Naphthalene & phenol oxidation with H_2O_2[43] Oxyhalogenation of aromatics with H_2O_2[56] Styrene epoxidation with TBHP[57] Toluene oxidation with H_2O_2[58] Alkene oxidation with O_2[59]	1985,[29] 1986,[51] 1988,[50] 1989,[49] 1990,[60, 61] 1991,[10, 31, 52, 62] 1992,[63-65] 1993,[59] 1994,[17, 18, 41, 45, 9, 42, 54] 1995,[46] 1996,[43, 47] 1997,[55, 56] 1999,[44, 58] 2000,[57] 2005,[48] 2008[53]
Metal Porphyrins (M=Co, Cu, Fe, Mn, Ni)	Zeolite-Y (FAU)	alkane oxidation with O_2,[36, 37, 66] H_2O_2[67] alkene oxidation with TBHP[68]	1989,[36] 1990,[30, 37, 67] 1996,[66] 1998,[68, 69]
M-Schiff Base (M=CO, Cu, Fe, Mn, Ni, Pd, Rh, V(O) Periphery ligands: Br, I, CH_3, OCH_3, OH, NO_2, t-butyl)	Zeolite-Y (FAU)	Sulfoxidation of methyl phenyl sulfide[70] Cyclohexane & cyclohexene oxidation with TBHP[39] Olefin oxidation with iodosylbenzene[71] Photoaquation[72] Alkene hydrogenation[11, 12] Biomimetic activation of O_2[73] Alcohol oxidation with TBHP,[74] O_2,[75] H_2O_2[76-78] Selective hydrogenation of hexene[79] Oxidation of cyclooctane with O_2[80] Styrene oxidation with TBHP,[81-83] O_2[84] Electrochemical oxygen reduction[85]	1983,[72] 1986,[86] 1990,[71, 87] 1991,[79, 88] 1993,[73] 1994,[11] 1996,[39, 75] 1998,[76, 84] 2001,[83] 2006,[77, 80-82] 2010,[74, 85] 2017,[70] 2018[78]
Metal Carbonyls (M=Fe, Os, Pt, Ir, Rh)	FAU	Selective alkene hydroformylation[89, 90]	1978,[90]
Metal bipyridine (M=Co, Mn, Ru)	FAU	Alkene oxidation with H_2O_2[91]	1994,[91] 1998,[92]
Metal allyl (M=Rh)	FAU	Olefin hydrogenation[40]	1982[40]
12-molybdophosphoric acid	FAU	Esterification of acetic acid[93]	2003[93]

computational spectra such as UV-VIS or vibrational spectra, and electronic descriptors which may explain experimental catalytic activities.

Table 2. Examples of organometallic complexes encapsulated in zeolites used in gas phase reactions.

Complex	Host	Chemistry(ies) Tested	Year(s)
Metal Phthalocyanine (MPC, M= Co, Fe, Ni)	FAU	Propene oxidation with O_2[94] Butadiene hydrogenation[61] CO oxidation with O_2[64] NO reduction with H_2[64, 65]	1984,[94] 1990,[60, 61] 1992,[63-65]
M-Schiff Base (M= Pd, Rh, Ru)	Zeolite-Y (FAU)	Alkene hydrogenation[11, 12]	1995,[12]
Metal Carbonyls (M=Fe, Os, Pt, Ir, Rh)	FAU	Selective alkene hydroformylation[89, 90] Alkane hydrogenolysis[95] Water-gas-shift[96-98] CO hydrogenation[99-102] NO reduction by CO[103] CO isotopic exchange[104]	1986,[96, 105] 1988,[100] 1989,[89, 95] 1990,[104, 106] 1991,[99, 101] 1992,[103] 1993,[102]

This approach has been employed by several researchers (see Table 3). Since the local structure can be relatively known (provided the complexes remain intact) compared to the ambiguity inherent in conventional zeolite catalysts, the task for the computational researcher is considerably simplified. It is not necessary to model all the possible tetrahedral sites in the zeolite or consider every possible linker, node, and plausible defect in a MOF, while risking missing the active sites because experiments cannot conclusively determine which defects or minority sites are catalytically relevant.

Table 3. Examples of combined computational/experimental studies of organometallic complexes encapsulated in zeolites.

Complex	Host	Chemistry(ies) Tested	Year(s)	Computational Methods
Metal carbonyls (M=Co, Ir, Rh, ligands = CO, acetylacetonate)[c]	Zeolite HY	Olefin hydrogenation	2015[107, 108]	Complex: B3LYP/aug-cc-pVDZ (Ir:aug-cc-pVDZ-pp)[109, 110] Host: B3LYP/CRENBL,[111, 112] B3LYP/cc-pVDZ//PM6[109, 113]
MPC (M=Cu, Periphery ligand = Cl)[a]	Zeolite-Y (FAU)	Allyl alcohol epoxidation	2018[114]	B3LYP/6-31G(d,p)[109, 115, 116]
Schiff Base (M=Pd, Periphery ligands: Br, CH_3, OH)	Zeolite-Y (FAU)	Bromobenzene coupling with styrene	2019[117]	B3PW91/6-31G(d,p) (Pd: LanL2DZ)[109, 115, 116, 118, 119]
M-imidazole-salen (M = Cu, Zn)	Zeolite-Y (FAU)	Benzyl alcohol oxidation	2018[78]	B3LYP/LanL2DZ[109, 118]
M-pyrrolyl-azine	Zeolite-Y	Phenol oxidation	2016[120]	M06-2X/6-311++G(d,p)[121-124]

complex (M= Cu, Fe)	(FAU)			
Salen (M=Cu, Ni)	Zeolite-Y (FAU), MWW	Methylene blue degradation with H_2O_2, Biginelli reaction	2017,[125] 2022,[126] 2023[127]	B3LYP/6-31++G**,[109, 128] M06-HF[123]/(C, H, N, O: 6-31G(d),[129] Cu: LanL2DZ[118]), PBE/Plane wave of 680 eV cutoff[130]
M-pyrazolone (M= Co, V)	Zeolite-Y (FAU)	Limonene oxidation with H_2O_2	2018[131]	B3LYP/6-31G(d)[109, 129]
MPC (M = Pd)[a,b]	-	CO_2 reduction	2022[132]	PBE/Numerical basis set[130]
MPC (M =Fe, Mn, Periphery ligand: NO_2)[a,b]	-	Chromogenic reactions using chlorophenol	2017[133]	B3LYP/(C, H, O, N, Cl: 6-31G(d,p), Fe: LanL2DZ)[109, 115, 116, 118]
[a]computation only [b]homogeneous catalysis [c]gas-phase reaction				

3. Opportunities to Leverage Model Zeolite Catalysts in the Near-Future

Given the stability of the zeolite hosts under a wide range of operating conditions, and the stability of some organometallic complexes in the absence of solvent and presence of ambient air, it is intriguing to consider expanding the applications of these model catalysts to gas-phase chemistries. In particular, societally essential small-molecule transformations including precious-metal-free dehydrogenation of formic acid,[134, 135] small alkane dehydrogenation[136] and selective oxidation of small alkanes.[5] The scope of complexes is broad (See Tables 1-3), and many of these can be accommodated within the cages of cage-pore zeolites like LTA and FAU, and perhaps window-cage frameworks like CHA. It is plausible that many other frameworks could be explored, using approaches similar to those developed recently to identify promising organic structure directing agents for new and existing zeolites.[137] In this way, we expect it would be possible to expand the scope of both the encapsulated complex library and the zeolite hosts beyond those listed in Tables 1-3.

By leveraging these attributes of zeolite-encapsulated organometallic complexes, it will be possible to perform computationally friendly laboratory experiments to benchmark and/or tune computational methods (e.g., adsorption energies, vibrational frequencies, and other spectroscopic/experimental measurements), before using those functionals/approaches for more complex heterogeneous systems present in technical catalysts. This could include development scaling relations/prediction of desirable active site structures with experimental validation, which can then be used to design practical catalysts (e.g., M-N-Cs) with comparable active site identities.

To have a realistic model of encapsulated complexes, a large cluster of the given system may need to be modelled. However, considering all possible conformers, electronic states, intermediates, and transition states can make DFT studies consume considerable time and computational resources. Therefore, simple correlations between a catalyst and its properties can help to accelerate predictions by potentially reducing the size of the computational model in addition to the number of calculations required.[138] By calculating descriptors instead of full reaction mechanisms, qualitative trends in catalyst performance can be captured for a series of analogous catalysts from which useful predictions can be made.[114, 133, 139]

Descriptors have commonly been used in catalysis through the application of linear free energy relationships (LFERs) which derive chemically meaningful relationships between catalyst structure and reactivity by comparing reaction energetics or activation barriers for a series of homologous systems/reactions.[138] Scaling relationships are a type of LFER well-known in heterogeneous catalysis which correlate surface bond energies of different adsorbed intermediates and transition states and enable the calculation of many parameters that affect the rate onto only a few DFT-calculated descriptors.[140, 141] The resulting descriptor-activity relationship can then be visualized using the so-called Sabatier or "volcano plot" analysis.[140, 142-144] Due to its simplicity, volcano plot analysis has also recently been imported into homogeneous catalysis.[145-147] However, its applicability has been limited in homogeneous catalysis so far due to large variations in molecular catalyst structures, as various conformers and steric groups of the catalyst can influence activity in a non-linear manner.[138, 148] Nevertheless, we expect that volcano plot analysis will be successfully applicable to zeolite-encapsulated organometallic catalysts since the metal active site is well-defined and the catalyst geometry is confined by the zeolite cage making steric groups and conformational freedom less relevant in this case. A few computational approaches towards this are described next, including machine learning, quantum mechanics/molecular mechanics, quantum mechanics/quantum mechanics, and machine learning force fields.

In traditional machine learning (ML) approaches, models are built based on a set of inputs/features/descriptors and correlated to some desired output (for example, catalyst performance).[149-151] In the context of catalysis, model inputs or descriptors could be obtained from experiments or computations and are typically features of the catalyst or substrates such as binding energies, 1D, 2D, or 3D structural representations, or electronic descriptors such as HOMO-LUMO gap.[152] Several studies have shown the applicability of ML approaches such as linear regression,[153-156] random forest regression,[157] support vector machines,[158, 159] and neural networks[160-162] in predicting reaction outcomes (yields, and selectivities) as well catalyst performance. Thus, by calculating descriptors and correlations to catalyst performance, insights into the interplay of multiple features of the catalyst system may be uncovered.

Hybrid quantum mechanics/molecular mechanics (QM/MM) approaches, popularly used to model large biological systems such as proteins where the region of interest in the protein is treated accurately with DFT while the rest of the protein is modeled using a force field,[163-165] has also been recently used to model zeolite-catalyzed[166-170] reactions. Here, a small cluster of the zeolite framework around the active site (for example, Brønsted acid sites) is modeled with DFT and the rest of the zeolite cluster is fixed and treated using a force field. This approach offers a balance between the computational cost of a more realistic model and required accuracy. QM/MM can also be applied to zeolite-encapsulated organometallic complexes whereby we consider the organometallic complex and adsorbates at DFT level while the zeolite is treated at force field level.

Similar to QM/MM methods, QM/QM methods have also been developed recently. In this regime, the system is partitioned into high-level and a low-level DFT regions, respectively, such as the ONIOM method implemented in quantum chemistry code GAUSSIAN 16[171] or the QM/XTB that utilizes Grimme's tight-binding methods as implemented in the ORCA code (version 5.0.2).[172] These methods avoid the need of using less accurate force fields and are particularly useful in cases where no reliable force fields are available.

Despite the opportunity to minimize cost of accurate DFT calculations by using hybrid QM/MM or QM/QM schemes, other challenges such as modelling local environment effects (for example, defects, Al distribution), or multiple unique T-sites that may have specific confinement effects may limit the applicability of hybrid schemes if only relatively small clusters are affordable computationally.[173-176] Machine learning based potentials (MLPs) have recently emerged as a promising method of accurately modelling the properties and dynamics of several systems and reactions.[177-185] As a result, MLPs are iteratively trained to 'learn' the potential energy surface of the system (based on limited DFT data) and can serve as a viable substitute for QM/MM and QM/QM schemes and apply to systems of arbitrary size at almost DFT level of accuracy. Consequently, MLPs can help to perform high-throughput screening of several catalyst configurations in multiple zeolites[179] if desired, in addition to being able to model system dynamics.[178]

4. Outlook/Conclusions

The design of efficient heterogeneous catalysts has historically occurred via trial-and-error by systematically varying the primary binding site identity, promoters, supports, and reaction conditions to ideally locate an optimal combination. The opportunity to leverage zeolite-encapsulated organometallic complexes as model catalysts for gas-solid reactions will only be realized via collaboration between chemists and chemical engineers with combined skillets in organometallic synthesis, zeolite synthesis, performance of gas-solid reactions, and computational chemistry. While synthetic approaches to generate model heterogeneous catalysts have been available for decades, the ability of computations to accurately model such systems is just coming on-line, providing opportunities for computationally driven rational catalyst design. Researchers can potentially model host-complex systems and compute chemical reactions with sufficient accuracy and provide relevant insights into the factors affecting reactivity in organometallic systems. Consequently, computations are increasingly interfacing with experiments and now routinely provides computational predictions which can be experimentally verified. Synthetic understanding in zeolite synthesis has also continuously improved, allowing for an expanded range of compositions, morphologies, and prediction of host-complex relationships that allow for crystallization of desired phases. The efficacy of these model materials to benchmark reactivity/predictions before application to practical heterogeneous catalysts may be significant to ensuring accurate calculations in the future, and prediction of unexpected catalyst formulations for existing and desired processes over both homogeneous and heterogeneous catalysts.

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Author Contributions

Ethan P. Iaia – literature review and manuscript composition
Ademola Soyemi – literature review and manuscript composition
Tibor Szilvási – manuscript composition and acquisition of funding
James W. Harris – manuscript composition and acquisition of funding

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