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Perspective

Porous frustrated Lewis pair catalysts: Advances and perspective

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SUMMARY

Frustrated Lewis pairs (FLPs), well known for the ability to activate small molecules via the concerted action of Lewis acid and Lewis base, have inspired an ever-widening scope of chemistry. The rapid development of this class of catalysts has promoted research into a promising direction: porous heterogeneous FLP catalysts, which possess several advantages for industrial application, such as controllable synthesis, tunable structure and composition, high surface area with abundant and accessible active sites, efficient mass transfer, and easy separation and reuse. This perspective summarizes recent progresses and provides an outlook in designing porous FLP catalysts for applications in heterogeneous catalysis.

INTRODUCTION

The evolution of catalysts uncovers new reactions and advances the field of catalysis, wherein the research on low-cost and environmentally friendly catalysts toward practical applications represents a priority. Over the last two decades, rapid progress has been witnessed on this aspect,[1,2] with "frustrated Lewis pairs (FLPs)" being one of the most prominent areas.[3–7] The notion of "frustrated Lewis pairs" was first conceived by Stephan's group to depict the discovery that sterically encumbered phosphines and boranes could reversibly activate H_2.[8] Since then, FLP catalysts have been extensively investigated for the activation of small molecules and C–H bonds[9] in thermocatalysis,[10] photocatalysis,[11] and electrocatalysis.[12] Furthermore, the range of catalysts exhibiting FLP reactivity has been expanded from main-group elements to transition metals and rare earth metals.[9] The high activity and intriguing selectivity of FLP catalysts have stimulated an increasing interest for researchers in various areas.

Many FLP catalysts are based on main-group elements, with B/Al compounds acting as the Lewis acids and N/P compounds serving as the Lewis bases,[3–7] and so they have intrinsic advantages of low toxicity and low cost. Such advantageous characteristics have triggered an enduring and extensive investigation into molecular FLP catalysts in homogeneous systems. As for homogeneous catalysts, it is a long-sought-after goal to ease catalyst-product separation and improve the stability and recyclability toward practical applications. As such, the design and construction of heterogeneous FLP catalysts is an attractive direction. Computational work early in 2012 suggested that zigzag graphene and graphene nanoribbons might operate as a heterogeneous FLP catalyst with alternating Lewis acid and Lewis base edge substituents,[13] which was shortly thereafter confirmed by experimental results from Parvulescu and co-workers.[14,15] In 2014, Guo's group validated a surface FLP catalyst using both experiment and calculation, with the Lewis acid and Lewis base being Au(111) surface and linked imine/nitrile, respectively.[16] Singh and co-workers developed another surface FLP system based on

The bigger picture

Challenges and opportunities:

- Porous FLP catalysts combine the merits from both fields of molecular FLP and porous materials, while their development is still in the infancy stage.
- The synergistic/cooperative effect in porous FLP catalysts will be impactful but has yet to be exploited.
- Current progress in efficient transformations using porous FLP catalysts manifests their potential in advanced catalysis.

hydroxylated indium oxide nanocrystals $In_2O_{3-x}(OH)_y$,[17–19] where surface unsaturated indium coordination sites act as Lewis acids and surface hydroxide sites serve as Lewis bases. Chang and co-workers reported their findings on a Ceria-based surface FLP catalyst that uses lattice O^{2-} as the Lewis base and two adjacent Ce^{3+} ions as the Lewis acid.[20] Despite the fact that the development of heterogeneous FLP catalysts is still in its early stage, these pioneering efforts continue to inspire the exploration of new systems.[21,22]

Porous catalysts are largely demanded in industry because of their large surface areas, high density of active sites, well-defined structures, superb stability, and controllable compositions. That being said, developing porous FLP catalysts would be attractive for two reasons: (1) to expand the diversity of heterogeneous FLP catalysts, which are currently narrowed to surface FLP catalysts, and (2) to boost the activity of FLP catalysts by utilizing the merits of porous materials. For example, porous ceria nanorods have a higher concentration of defects than their non-porous counterparts, and these defects aid in the construction of more FLP sites.[20] Among the widely accessible porous supports, traditional inorganic molecular sieves with intrinsic porosities, such as zeolites, have been employed as excellent catalyst supports. However, the difficulty in modifying their pore shapes and compositions casts a shadow on their development as porous FLP catalysts.[23–26] Considering the large library of organic chemistry, polymer supports that are comprised of monomers with Lewis acid or/and base character can offer a greater compositional flexibility.[27–37] Unfortunately, the lack of crystallinity for the polymer will usually lead to poor and unpredictable porosity. In contrast, highly crystalline metal-organic frameworks (MOFs) are tunable in structure and function, as well as pore size and pore environment. As a result, MOFs are commonly employed as supports for catalytically active species of varied sizes, such as organometallic complexes, metal nanoparticles, and enzymes. Similarly, the highly crystalline covalent organic frameworks (COFs) with controllable structures and properties can be used as non-metal framework supports for FLPs. The feasibility of designing MOF-based FLP catalysts has been suggested through a series of computational studies since 2015.[38–43] The noteworthy experimental breakthrough was achieved by Ma's group in 2018,[44] in which FLP was introduced to MOF via a stepwise manner. Following that, four additional works were reported for MOF-supported FLP systems.[45–48] It was recently reported that FLP could also be introduced into porous COF.[49,50] With the fast growth of porous framework materials (e.g., MOF and COF) and the rapid advancement of FLP chemistry, the blueprint for porous FLP catalysts can be envisioned when these two topic research fields start to merge.

PREPARATION OF POROUS FLP CATALYSTS

The porosity of heterogeneous catalysts has attracted a lot of attention in order to improve its reaction efficiency and atomic economy. Possessing the advantages of both molecular FLP catalysts and porous materials, porous FLP catalysts are advancing rapidly, but they remain challenging to design in terms of heterogeneity and porosity. Although heterogeneity and porosity can be readily accessible for pure inorganic porous substrates, the lack of structural flexibility largely limits their broader development as porous FLP catalysts. Polymers have been investigated as good matrices because of their ease in design and pore introduction, but they have low porosity and limited pore tenability as well as lacking a clear structural definement.[51] Thus, it is highly desirable to design and prepare crystalline porous frameworks that can help to unveil the subsequent structure-property relationships for heterogeneous FLP catalysts. Based on the current work of Ma's group and other

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https://doi.org/10.1016/j.checat.2021.12.001

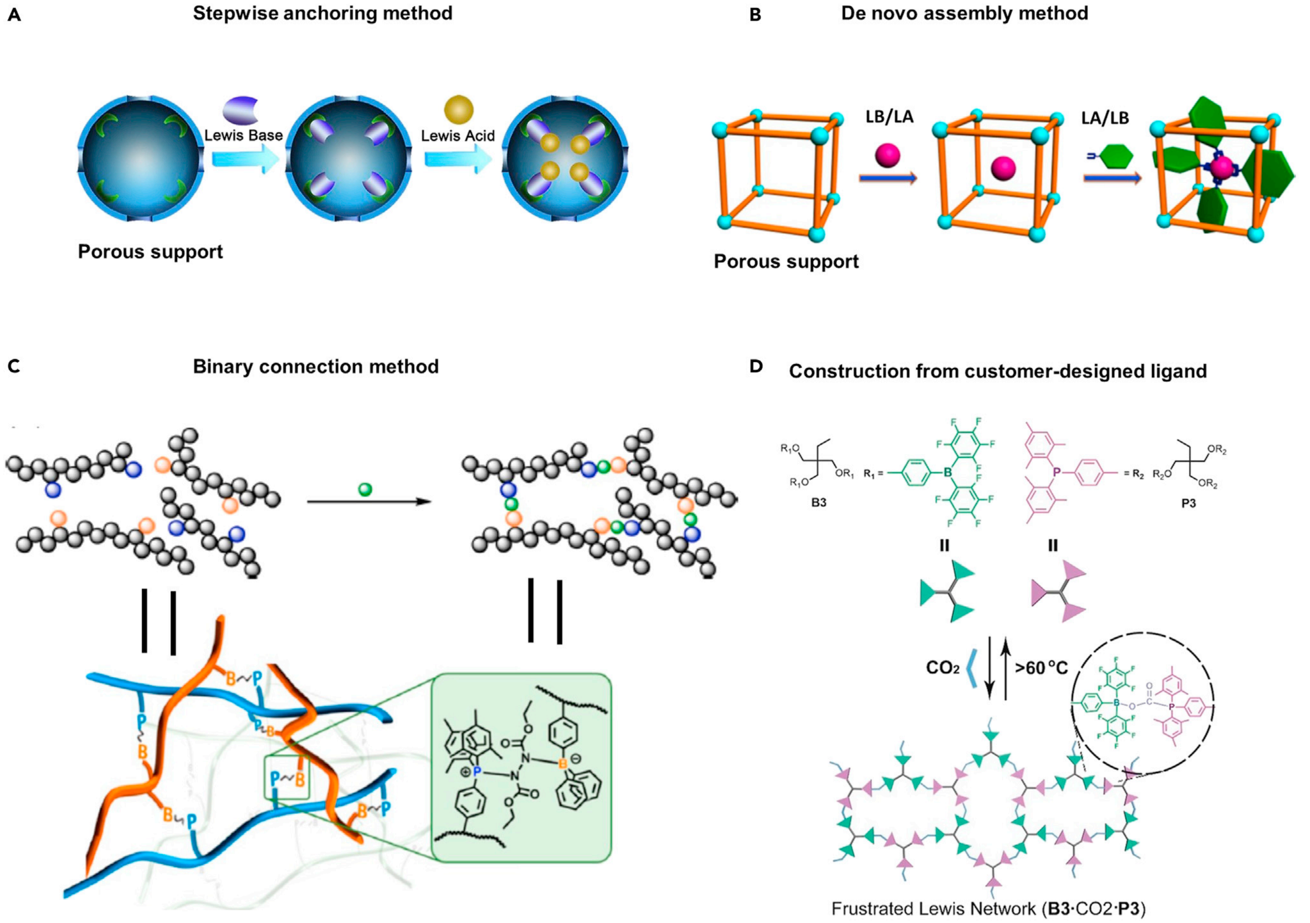

Figure 1. Four strategies to prepare porous FLP catalysts

(A) Scheme for preparing porous FLP catalysts following the stepwise anchoring method. Reproduced with permission from Ma and co-workers.[44] Copyright 2021 Elsevier.

(B) Scheme for preparing porous FLP catalysts following the *de novo* assembly method. Reproduced with permission from Ma and co-workers.[52] Copyright 2021 American Chemical Society.

(C) P polymer and B polymer connected by diethyl azodicarboxylate for preparing porous FLP catalysts. Reproduced with permission from Shaver and co-workers.[27] Copyright 2021 American Chemical Society.

(D) Customer-designed P and B bulky molecules for the construction of porous FLP catalysts. Reproduced with permission from Yan and co-workers.[29] Copyright 2021 John Wiley and Sons.

researchers on porous FLP catalysts, there are four strategies to construct porous FLP catalysts (Figure 1).

(1) Stepwise anchoring or grafting of FLP on porous matrices (Figure 1A): anchoring or grafting has generally been used to introduce guest molecules onto the host support. As for the construction of porous FLP, a typical example of introducing FLP into MOF was presented. Given that crystalline MOF is well defined yet tunable in pore structure and multifunction, it is quite promising for MOF to serve as the support for FLP. The first example was demonstrated by Ma's group via a stepwise anchoring strategy in 2018.[43] Specifically, the dehydrated MIL-101(Cr), $Cr_3(OH)O(BDC)_3$ (BDC [1,4-benzenedicarboxylate]) was chosen as a promising candidate to anchor FLP, due to its large pores or cages, abundant open metal (Cr) sites upon activation, and high stability. A classical FLP, consisting of tris(pentafluorophenyl)borane (BCF) as the Lewis acid and 1,4-diazabicyclo[2.2.2]octane (DABCO) as a strong Lewis base,

was chosen because the bifunctional N sites in DABCO can coordinate with the open metal site and pair with B of BCF simultaneously. A clever method like this could assure FLP's entrance and stability in MOF. The extension to other MOF systems may be foreseeable because of the large number of MOFs and their structural variety. In another study, conventional amines and phosphines, such as diethylenetriamine, diphenylpropylphosphine, triethylamine, and tetramethylpiperidine, were grafted or impregnated onto the surface of mesoporous Lewis acidic metalated SBA-15 to produce air-stable FLP.[26]

(2) *De novo* assembly of FLP within porous matrices (Figure 1B): bonding between host support and guest FLP is required for the anchoring or grafting method. It is expected that the *de novo* assembly will avoid such a need. Although no direct examples of this technique have been documented, a comparable assembly of cobalt(II) phthalocyanine in $Zn_8(ad)_4(BPDC)_6O \cdot 2Me_2NH_2$ (known as bio-MOF-1; ad [adeninate]; BPDC [biphenyldicarboxylate]), readers can be referred to Li et al.[52] Because the pore size of bio-MOF-1 prevents the direct integration of the large cobalt(II) phthalocyanine molecule, the *de novo* assembly was adopted to minimize guest/MOF structural disruption. In particular, the intrinsic counter-ions $Me_2NH_2^+$ in Bio-MOF-1 were easily exchanged to cobalt ions by immersing bio-MOF-1 crystals in a 0.1 M methanol solution of $Co(Ac)_2$ (denoted as Co@bio-MOF-1), and the corresponding cobalt(II) phthalocyanine assembled in bio-MOF-1 materials was successfully obtained after a 190°C heating of Co@bio-MOF-1 in a formamide solution of 1,2-dicyanobenzene for ~10 min. When the size of an individual component of FLP is less than the window or pore size of the porous support, the component can penetrate through a window and remain within the pore. The target catalysts might be prepared by immersing porous support in the solution of FLP individual components (Lewis acid and Lewis base) in a sequential manner.

(3) Binary connection of porous Lewis acid and porous Lewis base catalyst (Figure 1C): initially, FLP originated from the interaction of two parts (a Lewis acid and a Lewis base). Following this fundamental principle, the connection of the corresponding porous Lewis acid and porous Lewis base catalysts should be a reasonable approach for producing porous FLP catalysts. However, FLP cannot be generated by any Lewis acid and Lewis base interaction, and the difficulty of this route lies in: (1) the design and preparation of the corresponding Lewis acid and Lewis base in a porous manner and (2) searching for the right linker to bind them together at a proper distance. Recently, Shaver and co-workers presented a method for the design and synthesis of a macromolecular FLP that employs diethyl azodicarboxylate to link two linear copolymers.[27] One copolymer is made from styrene and 4-styryl-diphenylborane, while the other is made from styrene and 4-styryl-dimesitylphosphine.[31] Likewise, Yan and co-workers described CO_2 as the linker to connect two polymer chains made of styrene-based monomers with bulky 4-styryl-di(pentafluorophenyl)borane and 4-styryldimesitylphosphine as the FLP acceptor and donor, respectively.[30] One-pot synthesis could be used to upgrade the next-generation polymer-based FLP catalyst. Yan and co-workers,[29,32] demonstrated that *p*-phenyl-bis(pentafluorophenyl)borane and *p*-phenyl-dimesitylphosphine pendants as respective FLP acceptor and donor could be interconnected by CO_2 and result in the formation of an FLP network.

(4) Construction of porous catalyst with customer-designed FLP ligand (Figure 1D): the advantages of composition diversity and structural flexibility in porous substrates allow for a delicate catalyst design from the start, while the bifunctional nature of FLP enables ligand design choices in both partial and full building methods.

In terms of the partial building strategy, Lewis acid or Lewis base is constructed into a porous support, and the target FLP catalyst is formed by post-interaction with the appropriate Lewis base or Lewis acid. Yamamoto polymerization, for example, was used to prepare porous polymers based on triphenylphosphine, and the porous FLPs catalysts were created by subsequent contact with $B(C_6F_5)_3$.[28] Rose and co-workers reported the preparation of a polyamine organic framework from N-alkylation of *p*-xylylenediamine and 1,4-bis(bromomethyl)benzene, and the porous FLP catalyst was generated via further interaction with $B(C_6F_5)_3$.[35] Similarly, MOF-545, which was constructed by connecting Zr_6O_8 clusters with tetrakis(4-carboxyphenyl) porphyrin ligands, also has intrinsically steric N Lewis base sites; therefore, FLPs were produced *in situ* by adding BCF molecules as guest molecules.[45] Furthermore, the FLP entity with BCF was generated by the exfoliated thin-layer porous aromatic framework (PAF-6) with two types of Lewis base sites ($N_{Piperazine}$ and $N_{Triazine}$).[47] Recently, ring-opening metathesis polymerization of tricoordinate organoborane monomer allowed for the incorporation of Lewis acid and the formation of FLPs by subsequent contact with imines.[36] Another study used a bulky Lewis acid-functionalized ligand tris(*p*-carboxylic acid)tridurylborane introduced into a water-tolerant SION-105 MOF that interacts with Lewis basic diamine substrates to afford FLP synthesis *in situ*.[46] Intriguingly, sputtering Pt into zeolite NaY resulted in the zeolite activating H_2 in an FLP mode, namely Na^+H^- and $O(H^+)$.[23] Another example described the grafting of Sn species to the inner surface of a dealuminated β-zeolite, in which Lewis acidic Sn sites collaborate with surrounding Lewis basic SiO^- as the FLP catalyst.[24] According to Li's group's research, the four-coordinated confinement of cationic nickel (II) by zeolite results in a heterogeneous catalyst with the property of activating H_2 molecules in a heterolytic dissociation.[25]

In terms of the full building method, this is demonstrated by using CO_2 directly to interact with an intramolecular FLP monomer, allowing the polymer to be formed.[33] Very recently, copolymerization of π-conjugated O-bridged triphenylborane and triphenylamines has also realized the production of B-N pairs in polymers.[36] In addition, Fontaine et al. proposed the preparation by polymerizing molecular ansa-*N*,*N*-dialkylammoniumtrifluoroborate based on a styrene motif.[31] Furthermore, Lewis basic P^{III} centers and Lewis acidic boron atoms were simultaneously introduced by a poly-condensation reaction in which the newly obtained tris(4-diisopropoxyborylphenyl)phosphine reacts with respective 2,3,6,7,10,11-hexahydroxytriphenylene and 2,3,6,7-tetrahydroxy-9,10-dimethylanthracene; therefore, the prepared COFs exhibit FLP characteristic.[49]

CHARACTERIZATION OF POROUS FLP CATALYSTS

Characterization is the next important step after acquiring the prepared catalysts. Prior to use in catalysis, the porous FLP catalyst should be examined with regard to three aspects: structure, porosity, and FLP formation confirmation.

Structure determination

In the amorphous polymer samples, the characteristic broad peak from powder X-ray diffraction (PXRD) will always be observed. However, in most cases, the increase in molecular weight detected by gel-permeation chromatography is used to confirm the success of polymerization.[27] PXRD can easily indicate the crystallinity of a porous support with known structure before and after the introduction of the FLP via the characteristic diffraction peaks. The unaltered PXRD peaks, for instance, revealed that the incorporation of FLP did not destroy the pristine structure of MOF (Figure 2A), and the successful introduction of FLP in MOFs has been validated by a suite

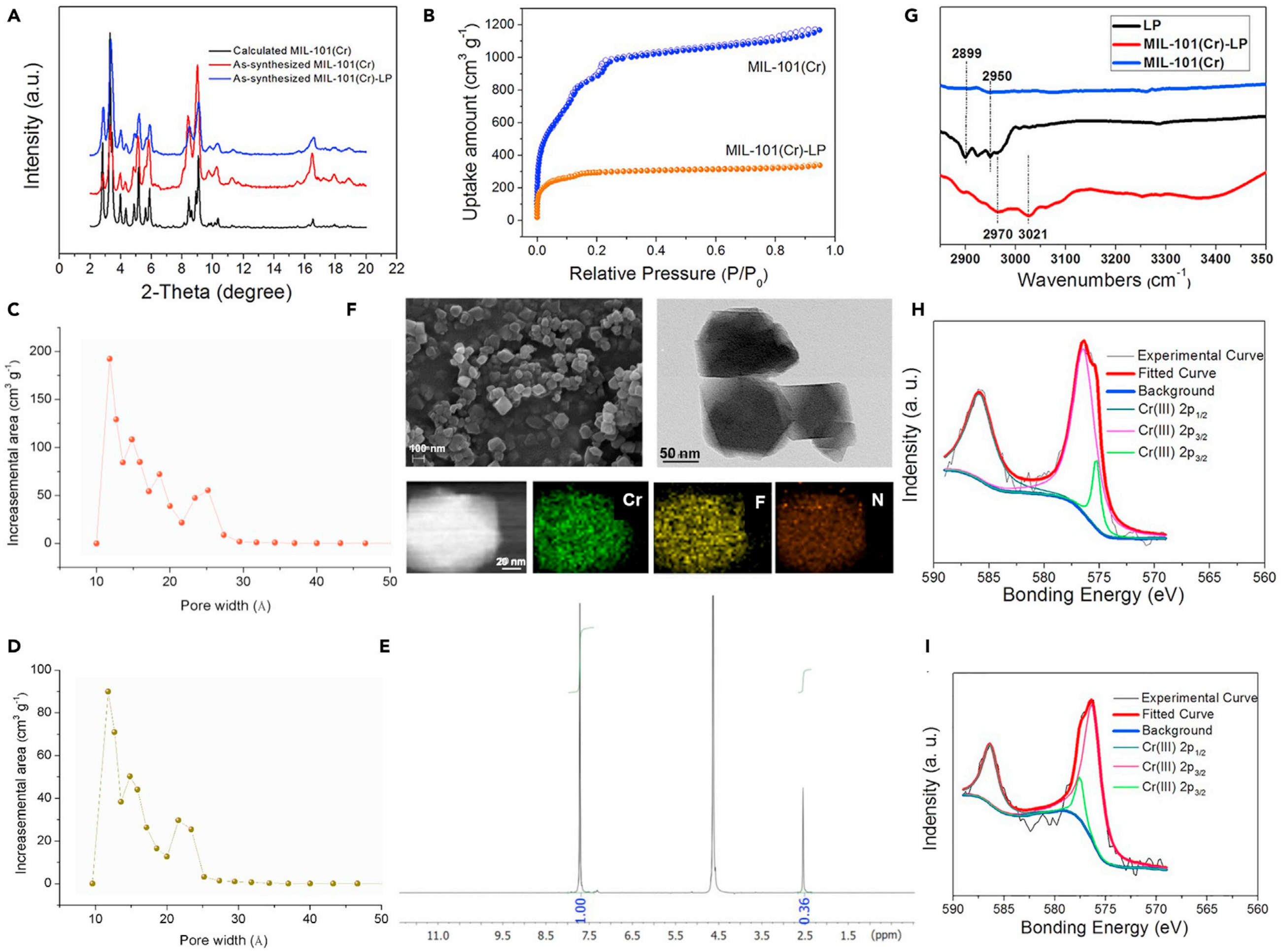

Figure 2. Representative characterizations for the porous FLP catalysts

(A) PXRD of MIL-101(Cr) and MIL-101(Cr)-LP.

(B) N_2 sorption isotherms of MIL-101 and MIL-101(Cr)-LP at 77 K.

(C) Pore size distribution curve of MIL-101(Cr).

(D) Pore size distribution curve of MIL-101(Cr)-LP.

(E) ^{1}H NMR spectra of digested MIL-101(Cr)-LP.

(F) Morphology characterization and element distribution of MIL-101(Cr)-LP.

(G) Infrared spectra of MIL-101(Cr), LP, and MIL-101(Cr)-LP. (H) Cr(III)2p XPS spectra of MIL-101.

(I) Cr(III)2p XPS spectra of MIL-101(Cr)-LP.

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of additional measurements (discussed in the FLP confirmation section). Regarding the single-crystal X-ray diffraction results of a catalyst with a new structure, this will be helpful for analyzing the structure, especially for samples obtained from the construction of a porous catalyst with a customer-designed FLP ligand.

The porosity measurement

In contrast to surface FLP catalysts, porosity is a significant parameter when assessing porous FLP catalysts. This is because efficient mass transfer throughout the pores plays a crucial role in the reaction process. In general, the N_2 sorption test is the standard measurement for determining the porosity of solid materials. The random and broad distribution of pore size in the polymeric system may result in poor utilization efficiency of the pore system. After introducing FLP, a uniform pore size distribution and a decrease in surface area can be anticipated in the sample prepared from porous crystalline support, especially for the catalyst obtained via stepwise or *de novo* assembly strategy (Figures 2B, 2C, and 2D), which is an indirect proof for the successful incorporation.

FLP confirmation

FLP confirmation is a crucial part of catalyst characterization. Because of the intrinsic multifunctional features of the catalyst, the reliable characterization always needs the combination of multiple measurements (Figure 2), as demonstrated in the study on the MIL-101(Cr)-FLP catalyst.[44,45] The resulting MIL-101(Cr)-FLP catalyst was digested using NaOD solution: then analysis was conducted using ^{1}H nuclear magnetic resonance (NMR) where the corresponding Lewis base—DABCO and skeleton of MIL-101—terephthalic acid was observed (Figure 2E). The presence of both FLP and MOF was demonstrated, and the FLP loading amount could be calculated using a quantitative assessment of the DABCO amount. Solid ^{11}B and ^{19}F NMR studies of MIL-101(Cr)-FLP were carried out to prove the successful introduction of Lewis acid—BCF. The existence of BCF is confirmed by the presence of B and F signals in the spectra. Also, the element (Cr, N, F) distribution of the obtained catalyst was studied using the elemental mapping in scanning transmission electron microscopy mode so that the individual support and FLP can be seen in the image (Figure 2F).

Fourier transform infrared spectroscopy analysis is helpful for indicating the presence of functional groups and is sensitive to chemical environmental changes, such as coordination. In comparison with the original spectrum of MIL-101(Cr), MIL-101(Cr)-FLP exhibited new peaks at high wavenumbers (2,800–3,200 cm^{-1}) due to the aliphatic C-H stretching vibrations of the FLP. Furthermore, noticeable peak shifts were found in FLP@MIL-101(Cr) compared with FLP peaks, indicating that the FLP N atoms were successfully coordinated with the open Cr sites of MIL-101(Cr) (Figure 2G). The presence of Cr, C, N, O, B, and F elements in MIL-101(Cr)-FLP was revealed by X-ray photoelectron spectroscopy results, and the higher binding energy in Cr(2p) compared with MIL-101(Cr) suggests an increase in the electron density of Cr(III), which can be attributed to the interaction between Cr and DABCO (Figures 2H and 2I). The frustration between Lewis acid and Lewis base is seen in the solid ^{11}B spectrum of FLP and MIL-101(Cr)-FLP-H_2 as a clear shift from 66 to -22 ppm (Figure 3A). Thus, the FLP component, structure, and function in MIL-101(Cr)-FLP have been comprehensively characterized using a variety of measurements.

Similarly, the ^{11}B spectra of the BCF, DABCO + BCF, and polyamine organic framework + BCF were collected, as shown in Figure 3B.[35] When compared with the peak of BCF, a shift from 60 to -5 ppm after the addition of DABCO indicates the strong interaction between them. A new peak that occurred at around -25 ppm after H_2 introduction suggests that H_2 activation was effective. According to the peak ratios of -5 and -25 ppm, heating and H_2 pressure are necessary for both homogeneous (DABCO + BCF) and heterogeneous manner FLP (polyamine organic framework + BCF) to efficiently activate H_2. Although most studies use the same method to characterize FLP in porous support-FLP, one study used vibrational spectroscopy to demonstrate the formation of interfacial FLP.[53] The self-assembled 4-mercaptobenzonitrile monolayers on the gold surface serve as sensitive vibration probes and lone pair Lewis bases (nitrile groups) pairing with BCFs. The vibrational sum-frequency generation data show a 90 cm^{-1} difference before and after the interaction with BCF (Figure 3C), which is attributed to surface frustration.

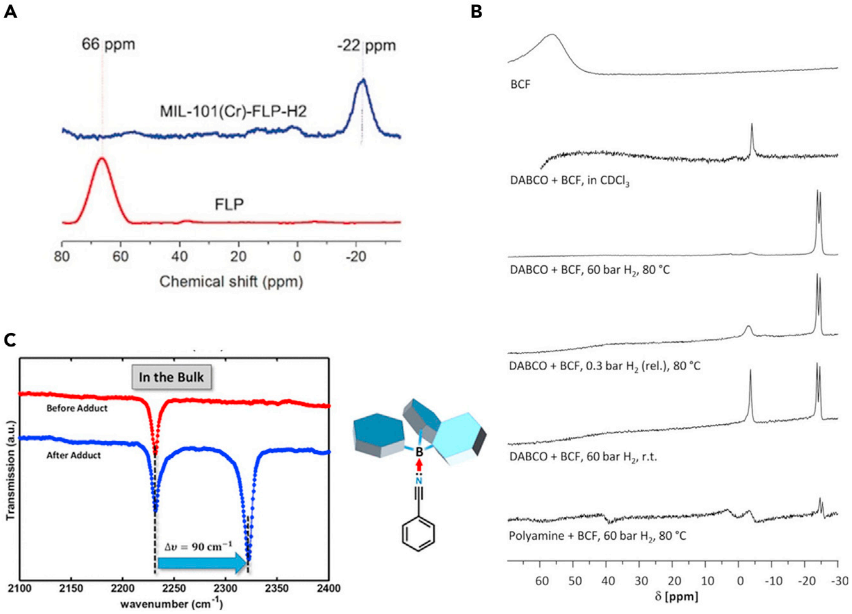


Figure 3. FLP confirmation measurements

(A) ^{11}B NMR spectrum of MIL-101(Cr)-FLP-H_2 and FLP. Reproduced with permission from Ma and co-workers.[45] Copyright 2021 John Wiley and Sons.

(B) ^{11}B NMR of samples prepared from different conditions. Reproduced with permission from Shaver and co-workers.[35] Copyright 2021 John Wiley and Sons.

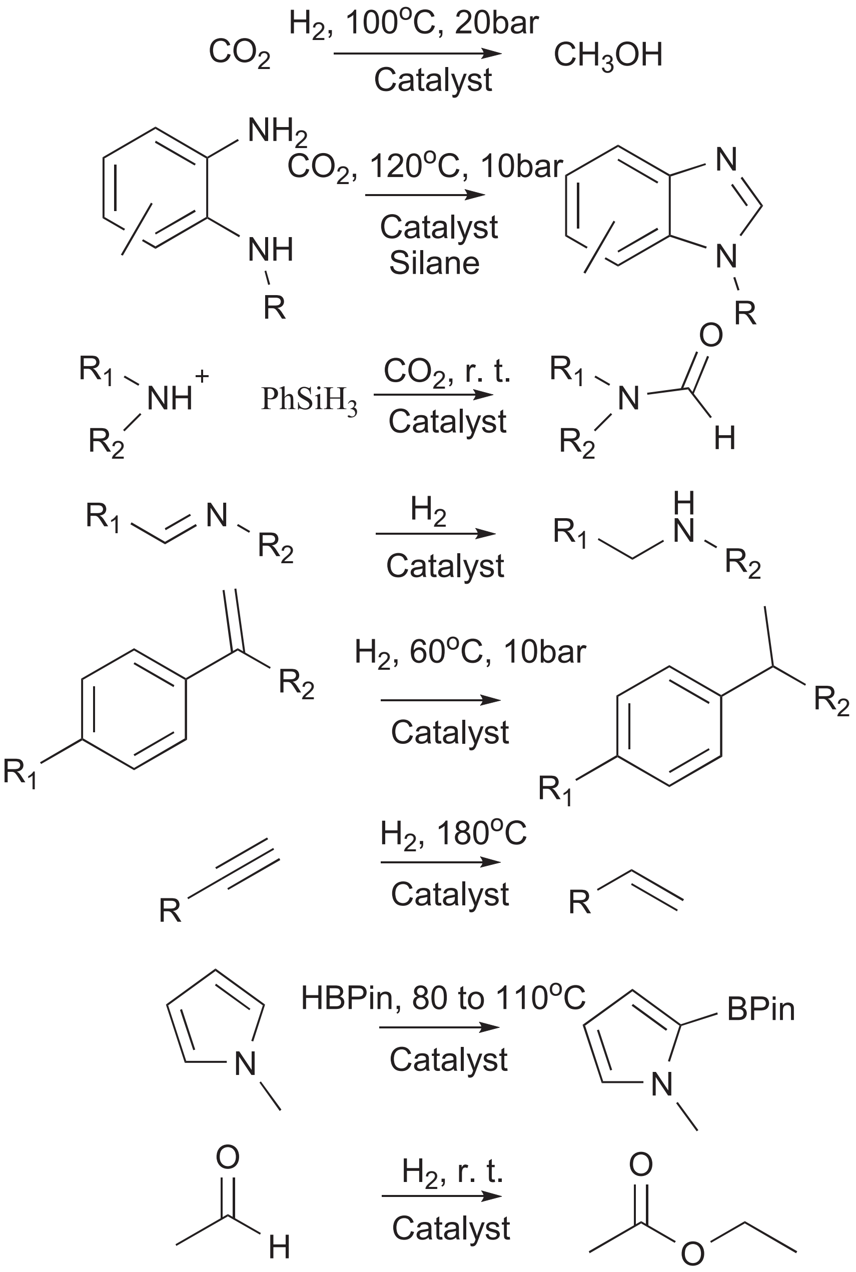
(C) Fourier transform infrared spectroscopy spectra of benzonitrile before and after adduct formation with BCF. Cartoons are representations of the LP interaction in the bulk. Reproduced with permission from Dawlaty and co-workers.[53] Copyright 2021 American Chemical Society.

POROUS FLP CATALYSTS FOR CATALYSIS

Catalysis plays a crucial role in the chemical industry and is also the driving force behind the design and preparation of FLP catalysts. Despite its infancy stage, porous FLP catalysts have been investigated in a variety of chemical transformations (Scheme 1).

CO_2 hydrogenation

The catalytic process enables the conversion of naturally abundant CO_2 feedstocks into value-added and reusable products, which represents a promising route to alleviate the greenhouse effect. However, efforts are still needed to boost these transformations, particularly the existing catalytic systems for the hydrogenation of thermodynamically stable CO_2 to alcohols, olefins, aromatics, and other chemicals. Commercially used $Cu/ZnO/Al_2O_3$ catalysts are effective in catalyzing CO_2 hydrogenation, but require high pressure and high temperature (50–100 bar and 200°C–300°C). It has been reported that noble metal catalysts, such as Pd- and Ru-based systems improve the activity and selectivity to some extent, but their high cost and unsustainability limit their widespread use in industry. Given that molecular FLP catalysts are known to activate CO_2 and H_2 under mild conditions, porous FLP catalysts with improved stability and recyclability are anticipated to be excellent options for heterogeneous CO_2 hydrogenation. Dyson and co-workers reported the *in situ* formation of FLP within MOF-545,[46] and the resulting catalyst exhibited high efficiency for hydrogenation of CO_2 in dry toluene to produce methoxylborane, which was subsequently hydrolyzed to yield methanol. Detected species $[(MeO)B(C_6F_5)_3]^-$ and $[(HO)B(C_6F_5)_3]^-$ showed that the catalytic process was similar to the homogeneous 2,2,6,6-tetramethylpiperidine-BCF FLP catalyzed hydrogenation of CO_2.[54] The corresponding conversion ratio based on BCF reached



Scheme 1. Representative reactions investigated in porous FLP systems

100% after 20 h at 100°C under 20 bar pressure, which is comparable with the industrially used catalyst, and the catalyst is recyclable.

Amine to benzimidazole transformation with CO_2

The versatility of porous FLP catalyst designs could lead to outstanding catalytic performance in various reactions. The assembled SION-105 MOF possesses intrinsic Lewis acid property due to the coordination of Eu^{3+} with the tris(*p*-carboxylic acid) tridurylborane ligand (Figure 4A), and the addition of *o*-diamines as the Lewis base may produce FLP within MOF.[47] To examine the possible FLP property, the obtained catalyst was employed in cyclization with CO_2. Similar to the BCF catalyzed

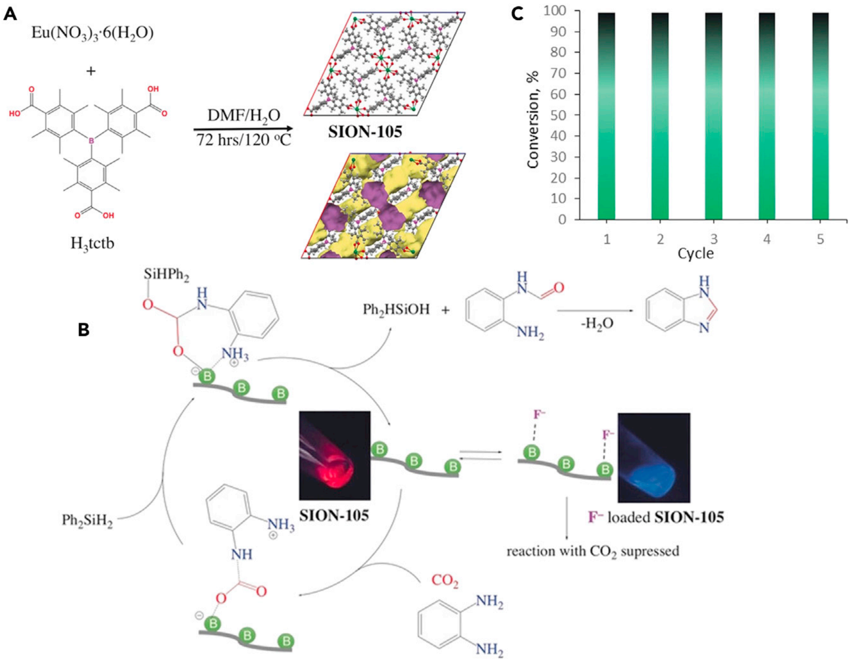


Figure 4. SION-105 preparation and application in catalysis

(A) Scheme for SION-105 preparation.

(B) Proposed mechanism for SION-105-catalyzed CO_2 conversion.

(C) SION-105 recyclability tests in catalysis.

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cyclization of *o*-phenylene-diamines, which results in the formation of benzimidazoles in the presence of hydrosilane.[55] CO_2 as the C1 source could readily be activated by the resulting SION-105 MOF-based FLP catalyst to form an N-bound CO_2 adduct. Meanwhile, the boron sites in SION-105 activate silane, which then coordinates with the adduct. Next, formamide is formed: after a release of silane complex and catalyst, the desired product is obtained via a cyclization to dehydrate (Figure 4B). In contrast to water intolerance of BCF in homogeneous catalysis, SION-105 is water tolerant owing to numerous methyl groups surrounding the boron center and can be reused for five times without significant loss of activity (Figure 4C). Acetonitrile outperforms the other solvents tested (tetrahydrofuran, ether, dioxane, and toluene) in terms of reaction efficiency. Conversion and yield were determined by gas chromatography-mass spectroscopy (GC-MS) with ^{1}H-benzo[*d*]imidazole as an internal reference. It is worth noting that the introduction of F^- can have a significant influence on catalytic performance, owing to the deactivation of the B centers. Furthermore, the SION-105 MOF-based FLP catalyst is active in catalyzing different substrates.

Amine to formamide transformation

Another sustainable strategy is to utilize CO_2 as a C1 source for amine to formamide production. CO_2 might act as a linker connecting the respective P and B polymers, and is also activated by the freshly prepared FLP catalyst.[30] The formamides might be obtained by adding $PhSiH_3$ and secondary amines to the reaction system at room temperature and normal pressure. Aliphatic secondary amines, such as diethylamine, morpholine, and piperidine, were catalyzed to formamide products. The catalysis efficiency reached over 12,000 turnover number within 3 h, and the catalytic performance was evaluated by ^{1}H NMR and mass spectrum analysis.

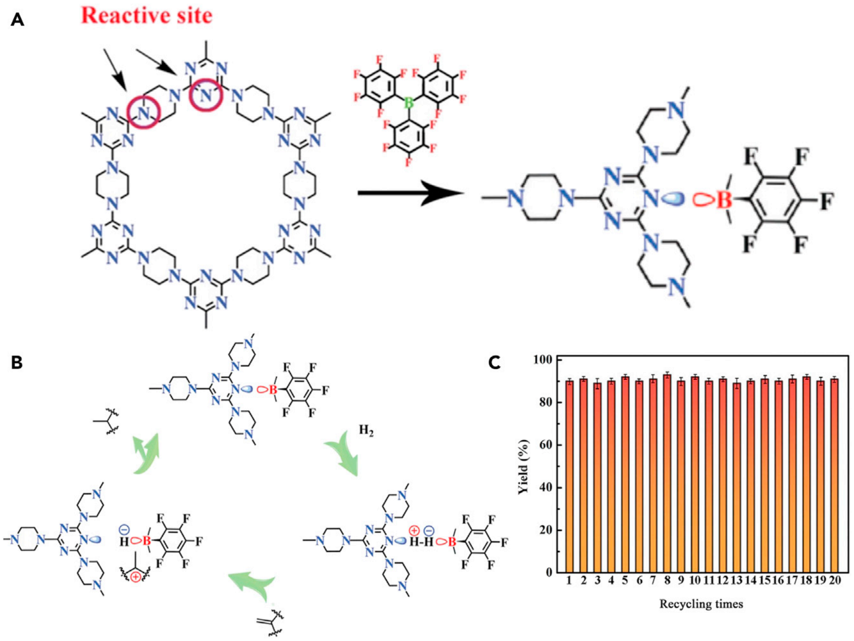

Figure 5. FLP construction in PAF-6 and application in catalysis

(A) PAF-6 nanosheets react with BCF molecules into NanoPAF-6@BCF.

(B) Possible mechanism for NanoPAF-6@BCF to realize the olefin hydrogenation via H_2 activation.

(C) Recycling performance of NanoPAF-6@BCF.

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Notably, as the steric hindrance increased at N atoms, the reactivity decreased; the same trend was observed when the N atom was connected with an electron-withdrawing substituent group. The electron-donating group had a positive effect on N atoms. In addition, when N-heterocycles were used as reagents, good performances were achieved.

Imine, olefin, and alkyne hydrogenation

Unsaturated groups, such as C=C, C≡C, and C=N, are ubiquitous in naturally available sources, but transformation to value-added products via hydrogenation requires improvement in both efficiency and selectivity. Advances in FLP chemistry have made hydrogenation possible with high selectivity under mild conditions.[10] MIL-101(Cr)-FLP has been adopted for the hydrogenation of alkylidene malonate compounds at 80°C and 60 bar H_2 for 24 h, and good to excellent yields (83%–95%) were obtained,[44] which is comparable with the performance of the homogeneous catalyst counterpart. Similarly, another example used the polyamine organic framework in combination with BCF as the porous FLP catalyst to investigate the hydrogenation efficiency of diethyl benzylidenemalonate at 80°C and 20 bar H_2.[35] Nearly 100% yield could be obtained based on GC results which adopted ethyl heptanoate as an internal standard. It was found that the pressure dependence of the reaction disappears when the hydrogen pressure exceeds 20 bar. Notably, the reactions in both cases were conducted in an anhydrous medium because even a trace amount of water would lead to the deactivation of the Lewis acid. Besides the use of anhydrous solvents, the reactor vessel and magnetic stirrer should be evacuated above 120°C to avoid the introduction of air and moisture. Although C=C and C=O coexist in alkylidene malonate, only C=C hydrogenation products were detected in both cases. Addition of BCF to the suspension of exfoliated PAF-6 reacts with the N sites, resulting in NanoPAF-6@BCF (Figure 5A),[49]

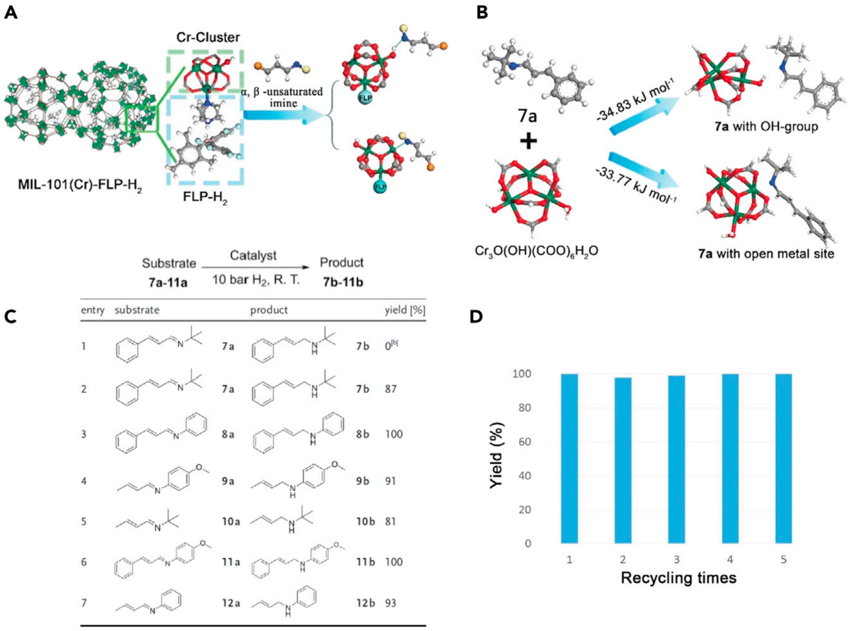

Figure 6. Selective hydrogenation of C=N bond with MIL-101(Cr)-FLP

(A) The role of $Cr_3(\mu_3\text{-}O)$ $(COO)_6(OH)$ $(H_2O)_2$ cluster in MIL-101(Cr)-FLP played in activation.

(B) Theoretical models to illustrate the interaction of substrate 7 a with $Cr_3O(OH)$ $(COO)_6H_2O$ trimer. Gray C; green Cr; white H; red O; blue N.

(C) Hydrogenation of α,β-unsaturated imine compounds with MIL-101(Cr)-FLP.

(D) The recycling tests of MIL-101(Cr)-FLP.

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and subsequent tests in which hydrogenation of olefin molecules, such as cumene, *p*-cumene, *p*-chlorocumene, and 1,1-diphenylethylene could afford excellent (up to >91%) yields. The corresponding mechanism scheme is shown in Figure 5B, in which H_2 undergoes a heterolytic cleavage process similar to the molecular FLP system. The reactivity of NanoPAF-6@BCF remained unchanged after 20 cycles (Figure 5C). Interestingly, the reaction pathway can be tuned by tailoring the pore environment in the porous FLP catalyst. For instance, interactions between the open Cr metal site of MIL-101(Cr)-FLP and the C=N bond of the substrate, and/or hydrogen bonding between the N atoms and the -OH groups from the framework, thermodynamically support the activation of the C=N bond (Figures 6A and 6B).[45] Selective hydrogenation between C=C and C=N bonds was observed utilizing such a recyclable catalyst, and only C=N hydrogenation products were obtained (Figures 6C and 6D).

In some cases of porous FLP catalysis, the hydrogenation of the C=N bonds proceeds in a multistep way. For example, to afford the target reduction products, the C=N bond undergoes the addition of HBpin first, followed by a hydrolysis step in an acidic solution.[44] Given the water generated during the condensation process, the porous FLP catalyst must be water tolerant for hydrogenation of the *in situ* formed C=N bond produced from the condensation of secondary amine and ketone.[37] With respect to C≡C reduction, cationic nickel ions confined in zeolites that have coordinatively unsaturated nickel centers were applied as the catalyst to replace palladium catalysts in acetylene semi-hydrogenation to ethylene.[25] Currently, good conversion of acetylene and high selectivity to ethylene can be simultaneously obtained. Temperature-programmed desorption studies showed that the adsorption of H_2 and acetylene on the catalyst surface was strong. However, the adsorption of ethylene was relatively weak. Heterolytic cleavage of H_2 was deduced from the Fourier transform infrared spectroscopy and the deuterium-labeling experiments. Specifically, after the introduction of H_2, the stretching mode of hydroxyl ions and the asymmetric stretching of perturbed T–O–T bonds (Si–O–Si and Si–O–Al) were presented.

Borylation of heteroarene

Activation of the C–H bond in heteroarenes, which can lead to the formation of useful products, has been mainly driven by transition metal complexes. However, the high cost of the catalyst itself and the difficulty in the subsequent separation of the catalyst from the final products have drawn the attention of many researchers to the development of metal-free and easy-separation catalysts. Fontaine et al. demonstrated that a non-metal molecular catalyst (1-TMP-2-BH_2-C_6H_4)$_2$ (TMP [2, 2, 6, 6-tetramethylpiperidine]) can activate the C–H bonds and realize borylation of heteroarenes.[56] Recently, they reported the molecules 1-RH^+-2-BF_3^--4-styrene (R = NMe_2, NEt_2, and piperidinyl), which incorporates C=C into the pre-catalyst,[31] succeeded in conducting polymerization, and gave rise to poly(1-RH^+-2-BF_3^--4-styrene) which could serve as a recyclable catalyst. With 1-methylpyrrole as the benchmark substrate, the conversion was measured based on the CH_3 moiety. Poly(1- piperidinyl-H^+-2-BF_3^--4-styrene) could afford a conversion of around 98% under neat conditions (16 h, 90°C), while poly(1-NMe_2H^+-2-BF_3^--4-styrene) and poly(1-NEt_2H^+-2-BF_3^--4-styrene) exhibited a conversion of 18% and 87%, respectively. Contrast tests with the corresponding monomers showed very low activities because the C=C group quenches the catalysis by hydroboration. Polymer catalysts with well-dispersed active FLP sites are expected to perform much better than the homogeneous (1-TMP-2-BH_2-C_6H_4)$_2$ catalyst, because (1-TMP-2-BH_2-C_6H_4)$_2$ needs to undergo cleavage to afford the active catalyst 1-TMP-2-BH_2-C_6H_4 FLP. However, for most catalysts the results obtained are not as good as that of the (1-TMP-2-BH_2-C_6H_4)$_{2,}$ which should be attributed to the inaccessible active sites and the irregular pore structure of polymers.

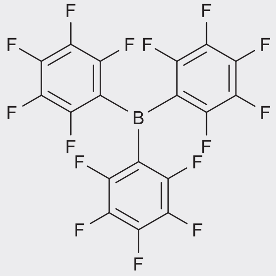
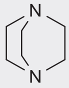
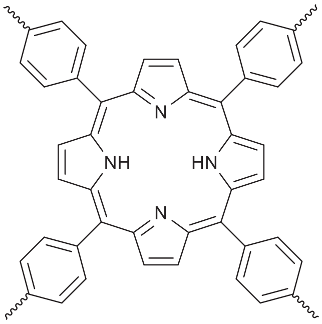
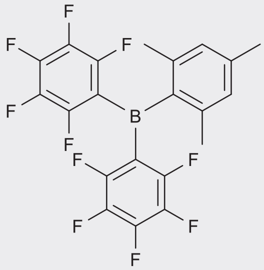
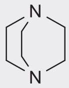
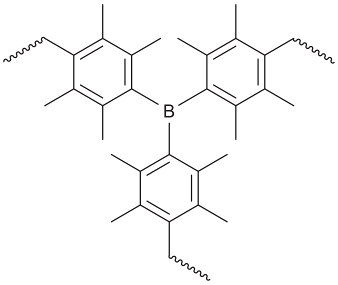
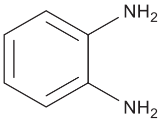
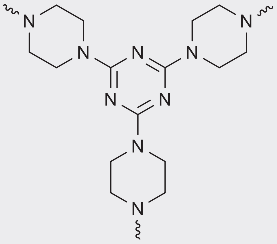
Esterification of acetaldehyde

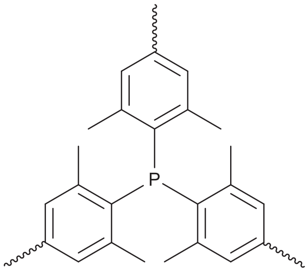
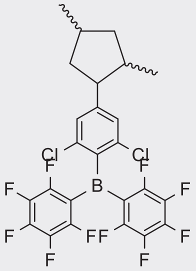
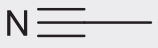
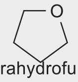
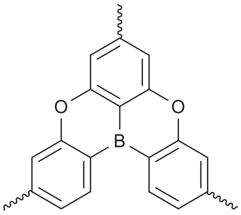
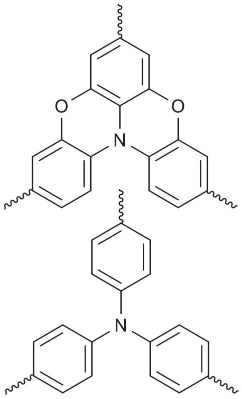
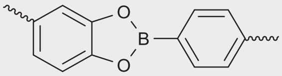
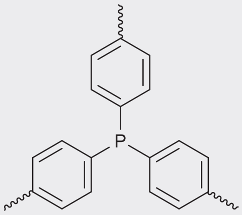
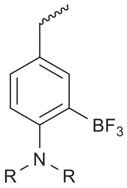
H_2 undergoes a heterolytic cleavage in the frustrated Lewis pair consisting of Na^+H^- and $O(H^+)$ in the H_2-Pt_x/NaY system.[23] NaH is a typical catalyst to couple two aldehyde molecules to form the corresponding ester molecule (Tishchenko reaction). Addition of H_2-Pt_x/NaY into a toluene solution of acetaldehyde for 12 h at room temperature results in the production of ethyl acetate, as revealed by GC analysis. Surprisingly, even after a longer reaction time (24 h), the introduction of larger benzaldehyde cannot lead to the formation of the corresponding ester product due to the pore size restriction in NaY zeolite.

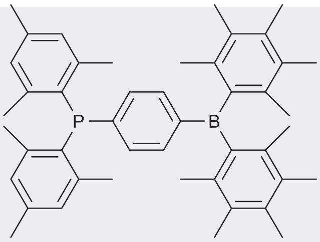
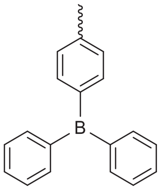
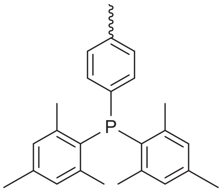
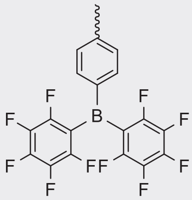
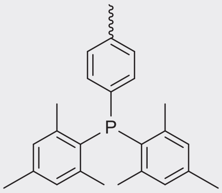
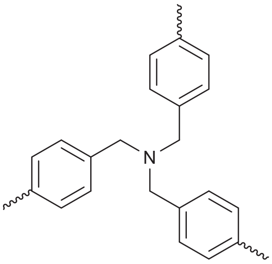
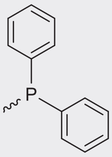
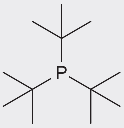
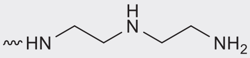
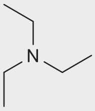
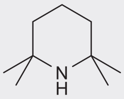
SUMMARY AND OUTLOOK

FLP chemistry has flourished in various directions and is now driving multiple transformations for the synthesis of value-added products under mild conditions.[57] In this perspective, the design, preparation, characterization, and application of porous FLP catalysts in various reactions have been summarized and discussed. Using the knowledge gained from homogeneous catalysts, the design of heterogeneous catalysts based on the established FLP systems is adaptable (Table 1). A potential challenge lies in the selection of suitable FLPs and supports when anchoring/assembling molecular FLP into porous supports. When constructing an anchoring site inside the porous support, the interactions between a chosen FLP and support must be considered. Catalysts produced by introducing metal or metal precursors into porous

Table 1. Summary of the reported FLPs in the porous materials

Lewis acid	Lewis base	References
FLP between organic parts		
 Tris(pentafluorophenyl)boron (BCF)	 1,4-Diazabicyclo[2.2.2]octane	Niu et al.[44]
BCF		Shyshkanov et al.[46]
 mesitylbis(perfluorophenyl)borane	 1,4-Diazabicyclo[2.2.2]octane	Niu and co-workers[44,45]
	 benzene-1,2-diamine	Shyshkanov et al.[47]
BCF		Meng et al.[49]

BCF	 tris(2,6-dimethylphenyl)-phosphine	Trunk et al.[28]
	 acetonitrile  Tetrahydrofuran	Vidal et al.[37]
		Adelizzi et al.[36]
		Pacholak et al.[50]
 R =$-CH_3$ $-CH_2CH_3$ $-CH_2CH_3CH_3$		Bouchar and Fontaine[31]

		Liu et al.[34]
		Wang and co-workers[27,32]
		Chen and co-workers[29,30,33]
BCF		Willms et al.[35]
FLPs between organic and inorganic parts		
Ti-, Al-, and Zr-SBA-15	    	Zakharova et al.[26]

FLPs in inorganic parts	
Ptx-loaded zeolite NaY	Lee et al.[23]
Sn active site in β-zeolite	Dijkmans et al.[24]
Cationic nickel confined in zeolite	Chai et al.[25]

supports are straightforward to make and are often stable during catalysis. However, both the preparation strategy and the activity are unpredictable. Thus, a systematic study on the combination of porous supports and metals/metal precursors is required to make them as FLP catalysts. A versatile and well-established preparation method for preparing porous polymer-based systems can expedite their preparation, and catalytic performance is comparable with their homogeneous FLP counterpart, and is more compatible in many solvents. However, active sites that are inaccessible due to their low surface area and non-uniform pore structure prevent further productivity gains. MOFs have been extensively studied as next-generation porous frameworks that simultaneously increase the surface area and introduce uniform pores.[58] Progress in the development of MOF-based porous FLP catalysts is foreseeable as the design and preparation of MOF-based catalysts are still in their infancy. MOF catalysts inevitably contain metal components, but the majority of them are derived from cheap metal salts. They also have greater potential to exploit synergy between FLP and metal centers for novel catalysis. COF-based porous FLP catalyst can avoid the involvement of metal and provide a metal-free version of porous FLP catalysts. To step into COF-based systems, one is anticipated to accumulate some experience in both organic synthesis and the preparation of crystalline COF, because the design and synthesis of multifunctional organic monomers typically require multistep synthetic procedure and multiple attempts are needed to develop optimal protocols for the growth of a new crystalline COF. From the aspect of characterization, assorted measurements may simply confirm the successful preparation and the activity of the catalyst. In addition to obtaining reliable results and conclusions in the field of catalysis, insightful studies through *in situ* and *ex situ* measurements to identify real active sites and explore catalytic mechanisms should be important future directions.

In terms of catalytic properties, porous FLP catalysts, as shown in most cases studied, are comparable with their homogeneous counterparts. Research should continue to focus on exploiting the advantages of catalyst heterogeneity, synergistic effects, and multifunction for advanced catalysis. In particular, the heterogeneity of the catalyst renders ease in separation from the reaction system and reusability for multiple cycles. Most of the reactions currently studied have been well investigated in homogeneous FLP systems. Notwithstanding, the untapped selectivity between two unsaturated groups has recently been achieved in porous FLP systems by the cooperation of porous support and the FLP active site.[45] Thus, cooperative and/or synergistic effects of porous FLP catalysts can make a difference. It can be envisaged that modifying the pore environment to preferentially interact with the reaction substrate will alter the activation energy, leading to different reaction pathways. The confinement and concentration effects due to the uniform pore size and tailorable nanospace will not only increase the efficiency of catalysis, but also size- and/or stereo-selectivity will be achieved, which are difficult to achieve in homogeneous FLP systems. There is a growing interest in exploring new reaction systems that combine the properties of the active FLP sites with the photochemical or electrochemical properties of the porous supports for sustainable photocatalysis or electrocatalysis. Besides, it is expected that increasing attention will be drawn to the development of chiral porous FLP catalysts for heterogeneous asymmetric catalysis, which so far has not been reported.

Marrying the current study field of porous material chemistry with the emerging research field of FLP chemistry, the porous FLP catalyst not only integrates the merits of both fields but also possesses certain unique properties of each individual field. The pioneering work summarized herein is merely the tip of the iceberg as there are enormous opportunities for porous FLP catalysts to evolve as a new platform for heterogeneous catalysis in industrial chemical transformations.

ACKNOWLEDGMENTS

This work was supported by the Robert A. Welch Foundation (B-0027).

AUTHOR CONTRIBUTIONS

S.M. and Y.Z. conceived the topic and wrote the manuscript. P.C.L. and K.M. helped with English editing.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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