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# Nanoporous Polymers: Bridging the Gap between Molecular and Solid Catalysts?

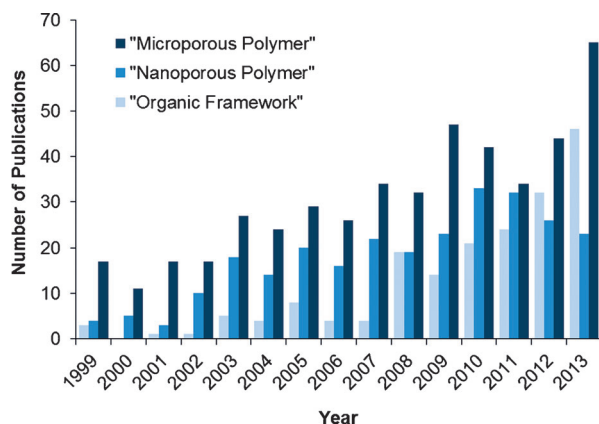
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The combination of the advantageous properties of molecular and solid catalysts is considered the "Holy Grail" in catalysis research. Great potential is provided by nanoporous polymers. Chemically well-defined moieties in combination with a high stability render these materials suitable as catalyst supports for liquid-phase and even aqueous-phase catalytic processes, especially regarding the transition from fossil resources to renew-

able resources. In this Minireview, recent developments are summarized, covering the three main approaches: solid metal-free organocatalysts, immobilized molecular catalyst species, and supported metal nanoparticles and clusters. Their potential is evaluated and the question as to whether nanoporous polymers can bridge the gap between homogeneous and heterogeneous catalysis is critically discussed.

## Introduction

Nanoporous polymers and metal-free organic frameworks have attracted increasing attention in the last decade mainly within the scientific community (Figure 1). They are investigated and



**Figure 1.** Total number of new publications per year according to a SciFinder search (on 15.11.2013) for "microporous polymer", "nanoporous polymer", and "organic framework" (refined: "not metal" to exclude MOFs).

evaluated for various applications such as gas and energy storage, separation, purification, sensor applications, as well as catalysis.<sup>[1]</sup> Especially for the latter application they offer enormous potential, which has by far not yet been explored comprehensively. This Minireview summarizes recent developments of nanoporous polymers in catalysis and critically discusses the opportunities and challenges these materials offer.

Recent developments were mainly initiated in 2005 when Omar Yaghi's group reported "covalent organic frameworks" (COFs) for the first time.<sup>[2]</sup> Since then, plenty of new materials have been developed, representing an independent class of porous solids.<sup>[3]</sup> Porous polymers in general, derived from classical polymeric chemistry, have been known for decades, for example, produced by phase separation, emulsion polymerization, or templating methods.<sup>[4]</sup> The renewed interest in nanoporous polymers within the last decade was initiated by the lack of chemical stability of a majority of metal-organic frameworks (MOFs), especially for catalytic applications. By using covalent bonds between organic building blocks (linkers) instead of coordinative bonds to metal ions and clusters, polymeric materials with high permanent porosity, high accessible specific surface areas, as well as significantly enhanced stability were achieved. These nanosponge-like materials combine the modular construction concept and tunable porosity of MOFs with the chemical stability of highly cross-linked polymers.<sup>[5]</sup> Thus, the network topology and pore properties can be tailored by varying the connectivity, size, and geometry of the organic building blocks to a certain extent, mainly limited by the amorphous structure.

Compared to established catalysts and support materials such as zeolites, metal oxides, ceramics, activated carbons (ACs), and macroreticulate and gel-type ion-exchange resins,<sup>[6]</sup> nanoporous polymers offer unique properties for the future development of catalytic processes. They are composed of highly cross-linked organic building blocks and, thus, provide a chemically well-defined inner surface with rather low polarity. By means of the versatility of organic chemistry, various functional moieties can be incorporated by pre-synthetic and post-synthetic modification in addition to intrinsic structural diversity. The modular framework construction provides pores that are well accessible, in some cases even combined with the opportunity to tailor hierarchical pore systems for enhanced transport kinetics. Another important aspect is formability.

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Many porous materials occur as fine powders and require special procedures and binders to produce molded bodies. A few of the nanoporous polymers form monoliths during synthesis. Thereby, simple shaping is enabled by cutting or grinding to particles of a uniform size and shape. The rather low thermal stability of nanoporous polymers compared to that of conventional inorganic catalysts is attributed to their organic composition. Decomposition in air occurs typically at temperatures between 200 and 400 °C for the majority of materials. This drawback prevents applications of nanoporous polymers in high-temperature catalytic processes, which are typically performed in the gas phase. However, owing to exclusively covalent bonds mainly between carbon atoms, they exhibit enhanced stability at moderate temperatures in liquid-phase reactions. Especially under hydrothermal conditions, which induce structural changes or even decomposition of certain oxidic materials, many nanoporous polymers might be the catalyst of choice.

These unique properties render nanoporous polymers suitable as catalysts or support materials for liquid-phase and even aqueous-phase catalytic processes. This is especially of interest regarding the transition from fossil resources to renewable resources. Whereas fossil feedstock is processed mainly in the gas phase, renewables such as biomass-derived feedstock often require liquid-phase processing owing to the high polarity of the compounds as well as their intrinsic water content.<sup>[7]</sup> Besides their suitability for novel catalytic processes, nanoporous polymers provide versatile opportunities for process intensification by catalyst engineering. This includes mainly their feature of incorporating various functional moieties for the immobilization of molecular catalyst species, which is shown below for selected examples. Thus, typical engineering improvements by using heterogeneous catalysis instead of homogeneous catalysis are enabled. Additionally, advantages in shaping as well as the opportunity to tailor pore systems for enhanced transport processes offer great advantages.

Overall, nanoporous polymers offer a number of advantages over conventional solid catalysts for selected challenges in catalytic process development and intensification. Nonetheless, drawbacks such as lower thermal stability and costly production ought not be neglected. Chemically well-defined nanoporous polymers can be used as support for catalytically active metal nanoparticles and clusters by providing enhanced stabilization effects compared to conventional inorganic supports. In contrast, defined functional moieties enable the immobilization of molecular metal species, which thereby bridges the gap between homogeneous and heterogeneous catalysis. Last but not least, the organic building units can be tailored pre- and post-synthetically to incorporate organocatalytic functional groups within a solid catalyst. In the following, first a brief

overview of the different types of materials and their classification is given; this is followed by selected and critically discussed examples of recent catalytic applications as well as challenges in the characterization of catalytically active species in nanoporous polymers.

## Materials Classification & Overview

Nanoporous polymers can be produced by a broad variety of cross-linking reactions to form covalent bonds between molecular building blocks.<sup>[3]</sup> Two basic approaches have been identified and can be used to further classify the different types of materials (Table 1).<sup>[19]</sup> On the basis of MOF methodology of

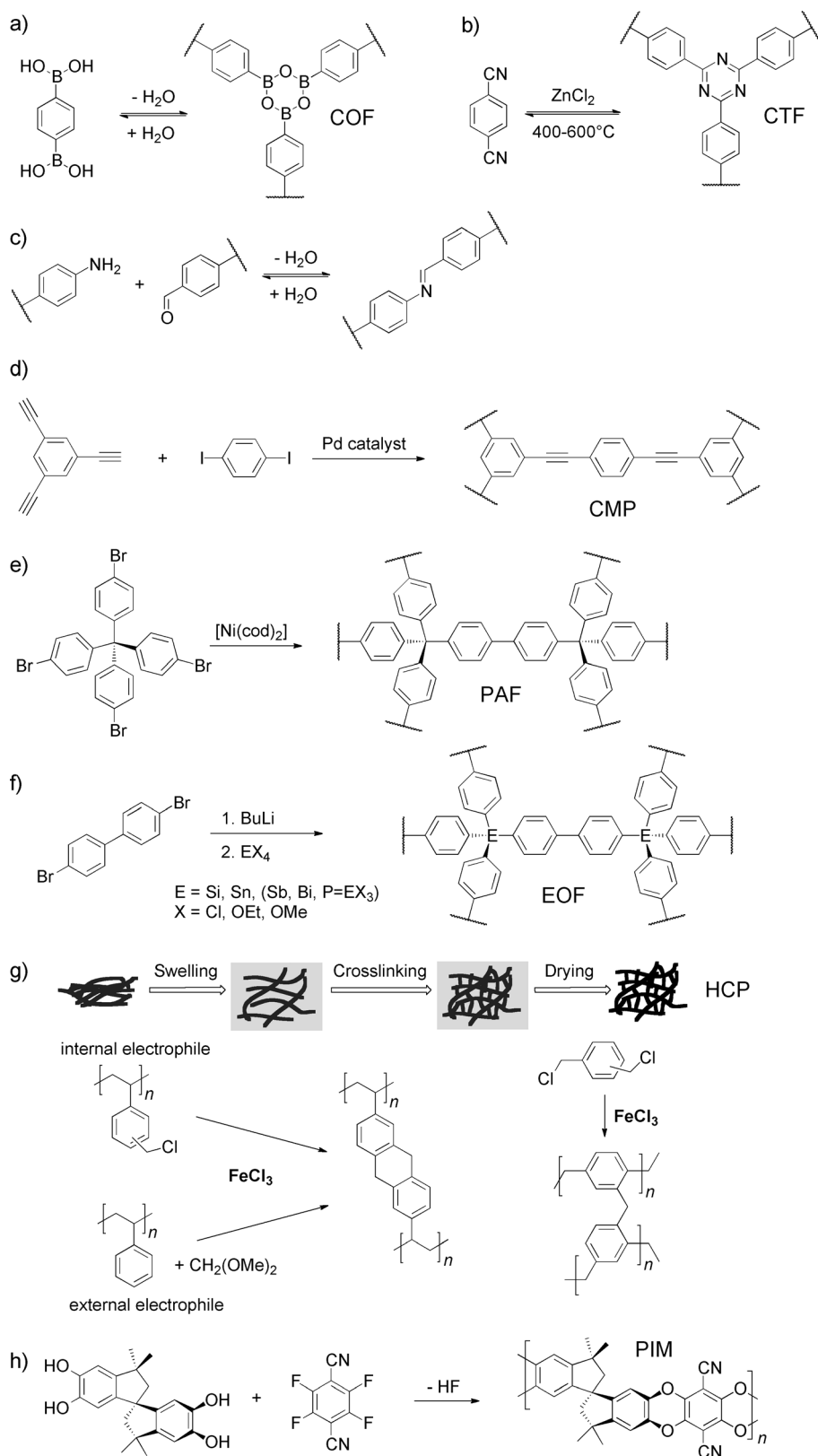
**Table 1.** Classification of nanoporous polymers.

	Organic framework		Polymeric network	
Concept	modular	modular	cross-linked polymers <sup>[a]</sup>	rigid, distorted monomers <sup>[b]</sup>
Cross-linking	reversible	irreversible	irreversible	irreversible
Structure	ordered	disordered	disordered	disordered
Porosity <sup>[c]</sup>	exactly defined	controlled	poorly controlled	poorly controlled
Examples	COF	CTF, PAF, CMP, EOF, etc.	HCP	PIM

[a] Cross-linked polymer chains as well as monomers. [b] Mainly linear and soluble polymer chains. [c] Tunability of pore size/distribution, specific surface area, and pore volume based on modular concept by building block variation.

modular construction, multifunctional building blocks are cross-linked by well-defined coupling reactions to form two- (2D) and three-dimensional (3D) organic framework structures. In contrast, methods derived from classical polymeric chemistry result in hyper-cross-linked polymers (HCPs) and polymers of intrinsic microporosity (PIMs). Their intrinsic porosity is derived from rigid and sterically hindered units. The structure and porosity of the materials are mainly controlled by the degree of cross-linking, which thus renders the cross-linking reaction itself an important parameter. It directly influences the structural properties, that is, the long-range order of the building blocks and the size of the crystalline domains. Despite hundreds of materials with their corresponding analytical data, details of the structure formation and its relation to the resulting porosity are still not yet well understood.

Organic framework-type materials can be further divided into ordered and disordered materials (Table 1), although in many cases, precise differentiation is difficult. To obtain a well-ordered structure within an organic framework, a thermodynamically controlled reaction is required. Ideally, the cross-linking reaction is reversible under the applied conditions. In that case, reorganization of the building blocks to a highly ordered structure can occur similar to the formation of MOFs by crystallization. The initially reported COFs are microcrystalline materials that are formed by a self-/co-condensation reaction of multifunctional aromatic linkers containing boronic acid groups (Scheme 1 a).<sup>[2,3c]</sup> Self-condensation results in the formation of boroxine rings (B<sub>3</sub>O<sub>3</sub>) as connecting species, whereas co-condensation with vicinal hydroxy-functionalized aromatic monomers yields five-membered C<sub>2</sub>O<sub>2</sub>B rings. In both cases, water is



**Scheme 1.** Reactions most often used for the synthesis of nanoporous polymers from multifunctional organic building blocks.

linking are achieved, which yields microcrystalline particles. Specific surface areas of up to 4000 m<sup>2</sup>g<sup>-1</sup> in the case of COF-103 have been reported.<sup>[8]</sup> Recently, tetrahedral building blocks were linked by the reversible formation of azodioxy bonds to form single crystals of an organic framework for the first time.<sup>[9]</sup> The disadvantage of such highly ordered materials is that the ideal structures tend to form multiple interpenetrated networks, which intrinsically block the available pores. Additionally, all cross-linking reactions forming weak covalent bonds or being easily reversible, for example, COF decomposition by the addition of water, are less suited for the formation of materials with high chemical stability. Thus, stronger covalent bonds are preferred, which are formed by irreversible and/or kinetically controlled reactions.

In 2008, the group of Arne Thomas reported a different synthetic approach—the formation of covalent triazine-based frameworks (CTFs, Scheme 1 b).<sup>[10]</sup> Multifunctional nitriles were used as building blocks, which underwent a cyclotrimerization reaction to yield aromatic triazine rings (C<sub>3</sub>N<sub>3</sub>) as connecting species. The reaction was performed in a molten salt at temperatures of 400–600 °C. Under these ionothermal conditions, the reaction was reversible and yielded poorly ordered materials, according to the broad diffraction peaks observed by powder X-ray diffraction analysis.<sup>[10,11]</sup> Due to the reversibility of the cyclotrimerization reaction only at high synthesis temperatures in combination with the aromatic nature of the linkers and the connecting triazine rings, the CTFs exhibited exceptionally high thermal and chemical stability. This feature was used successfully in

eliminated. Owing to the reversible reaction and rearrangement under solvothermal conditions, high degrees of cross-

catalytic applications, as shown below. Additionally, CTFs possess high specific surface areas of up to 2475 m<sup>2</sup>g<sup>-1</sup>.<sup>[12]</sup> There-

by, the pore properties can be tuned on the one hand by varying the size and geometry of the linkers according to the modular concept. On the other hand, the use of an excess amount of  $\text{ZnCl}_2$  as the molten solvent increases the specific surface area by a templating effect. Additionally, an increased synthesis temperature results in partial decomposition and release of gaseous species to yield foam-like monoliths with increased surface area and a lower than expected nitrogen content. Because of the many structural defects in the latter two cases, mainly amorphous materials are obtained.<sup>[10,12,13]</sup> In analogy to nitrogen-rich CTF materials with a high concentration of coordination sites, several approaches have been reported involving amines as functional groups. Thus, nitrogen-rich materials with different degrees of crystallinity are obtained by forming, for example, imine (Scheme 1c),<sup>[14]</sup> imide,<sup>[15]</sup> aminal,<sup>[16]</sup> hydrate,<sup>[17]</sup> and isocyanurate<sup>[18]</sup> linkages.

Modularly constructed organic frameworks that are derived by kinetically controlled and, thus, irreversible cross-linking reactions are usually amorphous. Nevertheless, high specific surface areas can be obtained, and the pore size can be tailored to a certain extent. Typically, metal-catalyzed cross-coupling reactions are used to connect different types of organic linkers. The reaction most often applied is the Pd-catalyzed Sonogashira–Hagihara cross-coupling of aromatic halides and ethynyl-functionalized building blocks (Scheme 1d). Materials derived by this reaction are known as conjugated microporous polymers (CMPs) and were reported for the first time by the group of Andrew Cooper in 2007.<sup>[19]</sup> A high structural diversity has been reported in recent years.<sup>[3b,20]</sup> Specific surface areas as high as  $1200 \text{ m}^2 \text{ g}^{-1}$  have been achieved by using sterically demanding linkers with a trigonal or tetragonal geometry.<sup>[21]</sup> As a result of their extended conjugated  $\pi$ -electron systems, various applications in light emitting, harvesting, sensing, and electrical energy storage have been reported.<sup>[3b]</sup> Similar network topologies with comparable pore properties and specific surface areas of up to  $1380 \text{ m}^2 \text{ g}^{-1}$  were synthesized by using Pd-catalyzed Suzuki–Miyaura coupling of aromatic halides with boronic acids.<sup>[22]</sup> In difference to the cross-coupling reactions, also homocoupling was used for the connection of multifunctional linkers. Alkyne linkers gave open porous frameworks with specific surface areas of up to  $842 \text{ m}^2 \text{ g}^{-1}$ ,<sup>[23]</sup> whereas the use of the Yamamoto reaction, a Ni-catalyzed variation of Ullmann homocoupling, resulted in porous polymers with outstanding properties (Scheme 1e).<sup>[24]</sup> Despite the kinetically controlled metal-catalyzed reaction, these porous aromatic frameworks (PAFs) derived from tetrahedral linkers exhibited a few very broad peaks in the X-ray powder diffraction pattern. This is indicative of partially long-range ordered structural elements. This feature within the 3D framework resulted in a specific surface area of  $5640 \text{ m}^2 \text{ g}^{-1}$ , which is amongst the highest values ever reported.

Besides coupling reactions to form the final linkers, non-catalyzed routes yielding framework materials with an open and permanent porosity have been reported as well. Multifunctional nucleophilic organolithium species, generated in situ, can be connected by single atoms of all elements, which form the respective stable element–carbon bonds. By the addition of elec-

trophilic precursors to the synthesis solutions, these element organic frameworks (EOFs) precipitate as amorphous materials with surface areas of up to  $1040 \text{ m}^2 \text{ g}^{-1}$  and high chemical and thermal stability (Scheme 1f).<sup>[25]</sup> Recently, this concept was extended from using silicon as the connector species to other elements such as tin, antimony, bismuth,<sup>[26]</sup> and phosphorus<sup>[27]</sup> with interesting catalytic properties.

Nanoporous polymers, which are not modularly constructed as organic frameworks, have been known for several decades.<sup>[28]</sup> Applying methods for the cross-linking of polymer chains to yield HCPs is used to produce commercial ion-exchange resins as well as adsorbents and absorbents. Such materials are known as Davankov resins and have attracted renewed attention in recent years.<sup>[29]</sup> Mainly microporous HCPs can be derived by chemical cross-linking of dissolved or swollen polystyrene or its derivatives (Scheme 1g). The cross-linking reaction usually applied is Friedel–Crafts alkylation by using external or internal (reactive groups on the monomers such as chloromethylene) electrophiles. After the cross-linking reaction, workup, and drying, the polymer chains are unable to pack efficiently in space as a result of the interconnected chains, and thus, an insoluble network with permanent open porosity is obtained. In recent years, this method has been widely used to cross-link multifunctional aromatic monomers by using internal<sup>[30]</sup> and external<sup>[31]</sup> cross-linking groups. Also, the incorporation of functionalized and heteroatom-containing monomers has been reported, which is of special interest for catalytic applications.<sup>[32]</sup> By this approach, predominantly microporous materials with high specific surface areas of up to  $2000 \text{ m}^2 \text{ g}^{-1}$  have been obtained, despite the non-ordered structure, but as a result of a very high degree of cross-linking.<sup>[30]</sup>

Compared to all aforementioned types of nanoporous polymer, the PIMs, initially reported in 2002 by the groups of Peter Budd and Neil McKeown, are based on a different concept (Scheme 1h).<sup>[33]</sup> Most of these materials consist of non-cross-linked, and thus soluble, polymer chains.<sup>[34]</sup> Their microporosity originates from the inefficiently packed chains resulting from the sterically demanding, contorted, and highly rigid monomers. For polymerization, multifunctional aromatic alcohols with vicinal hydroxy groups undergo a condensation reaction with fluoro- or chloro-containing monomers under formation of dioxane rings as connecting species between the aromatic building blocks. By this approach, specific surface areas of up to  $1760 \text{ m}^2 \text{ g}^{-1}$  have been obtained for a triptycene-based PIM.<sup>[35]</sup> Despite their amorphous structure, these materials provide large functional variability. Owing to the various feasible monomers, such as derivatives of spirobisindane,<sup>[36]</sup> binaphthyl,<sup>[34a]</sup> porphyrin,<sup>[33b,37]</sup> and phthalocyanine,<sup>[33a,37]</sup> the immobilization of molecular metal species enables advanced catalyst development. The unique feature of PIMs is that their porosity is maintained upon dissolving and subsequent drying/precipitating. Thus, advanced processing is feasible. The formation of flexible membranes with outstanding performance mainly in gas separation has been proven already.<sup>[36a,38]</sup> Incorporating catalytically active sites into these membranes could enable a new generation of high-performance catalytic membrane re-

actors by combining reaction and separation in terms of process intensification.

## Nanoporous Polymers in Catalysis

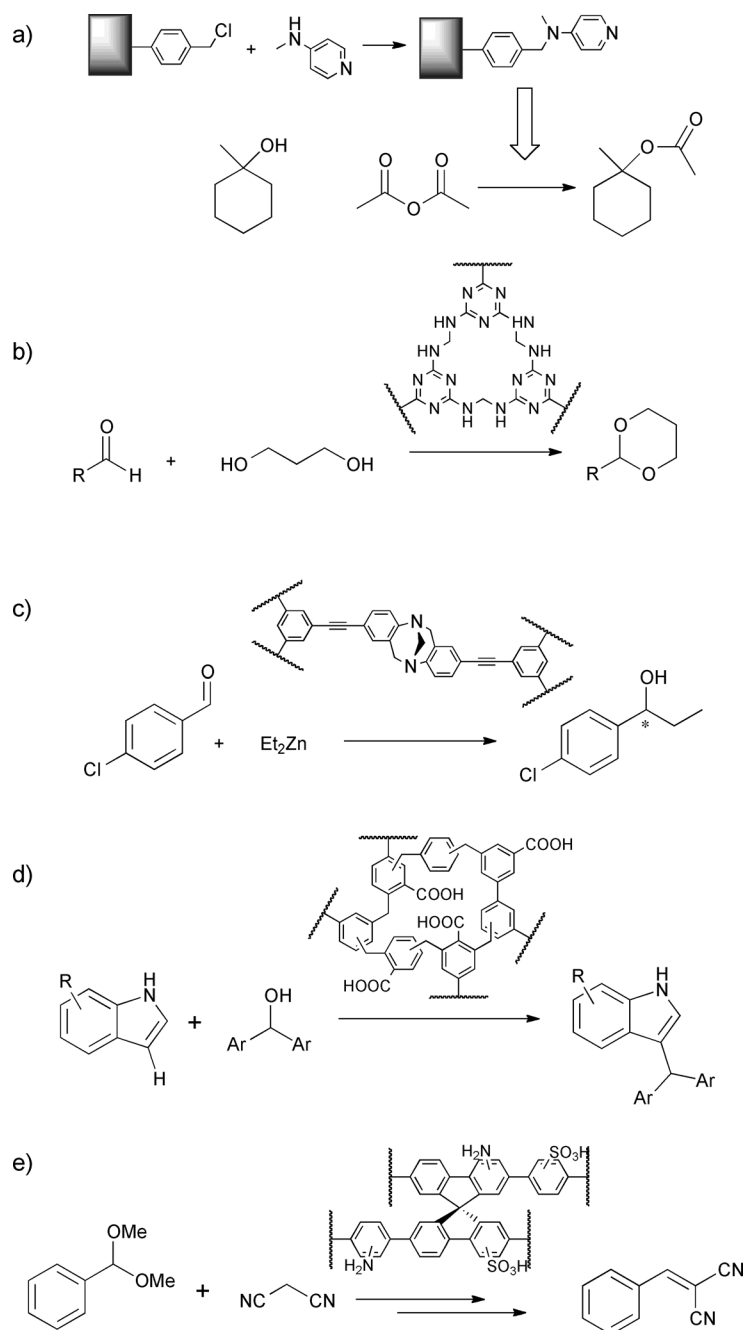
### Metal-free organocatalysts

The tunable organic nature of polymeric frameworks in combination with high specific surface areas and thus a high dispersion of catalytically active centers within a solid material provide versatile opportunities for catalytic applications. As known for industrially utilized ion-exchange resins,<sup>[39]</sup> mainly acid- and base-catalyzed reactions require metal-free organocatalysts. Although the potential of nanoporous polymers in this regard is enormous given the versatility of organic chemistry that can be used for the formation and functionalization of frameworks, only a few examples have been reported to date. Functional groups can be directly incorporated into the framework structure by using the respectively functionalized monomer. However, post-synthetic functionalization of nanoporous polymers allows a broad spectrum of functional groups. Both approaches have been applied thus far and selected examples are presented below.

Using nitrogen-rich moieties in nanoporous polymers enables various Lewis base catalytic applications. A HCP derived from a poly(styrene–divinylbenzene) high internal phase emulsion polymer monolith<sup>[40]</sup> by swelling and internal cross-linking was used for post-synthetic functionalization (Scheme 2a).<sup>[41]</sup> It exhibits a hierarchical pore system of macro- and micropores. Residual chloromethylene groups were used for covalent anchoring of 4-(*N*-methylamino)pyridine as a basic moiety.

The material was tested in the acylation of tertiary methylcyclohexanol with acetic anhydride. The high catalytic activity was shown to be comparable to that of molecularly applied (dimethylamino)pyridine. Additionally, an advantageous effect of the high surface area in comparison to the non-cross-linked material was observed. Applying the same reaction conditions, the cross-linked HCP achieved full conversion, whereas the non-cross-linked HCP gave only 65% conversion. The monolithic shape in combination with the macropore system for enhanced transport properties render this type of catalyst interesting for fixed-bed continuous plug-flow reactors.

A very convenient material in terms of synthesis as well as availability and cost of the monomers is a mesoporous melamine–formaldehyde resin (Scheme 2b).<sup>[42]</sup> It consists of triazine rings interconnected by aminal groups and, thus, provides a very high content of aromatic and aliphatic secondary amine groups. It was applied as a catalyst in the acetalization of various aldehydes and showed activity superior to that of molecular melamine; this increased activity was attributed to the



**Scheme 2.** Organocatalytic reactions catalyzed by N-containing Lewis bases within a) hyper-cross-linked high internal phase emulsion polymers,<sup>[41]</sup> b) melamine-formaldehyde resin,<sup>[42]</sup> c) Tröger's base CMP,<sup>[44]</sup> d) Brønsted acids such as a HCP with carboxylic acid groups,<sup>[32d]</sup> and e) an aromatic framework containing amine and sulfonic acid moieties.<sup>[45]</sup>

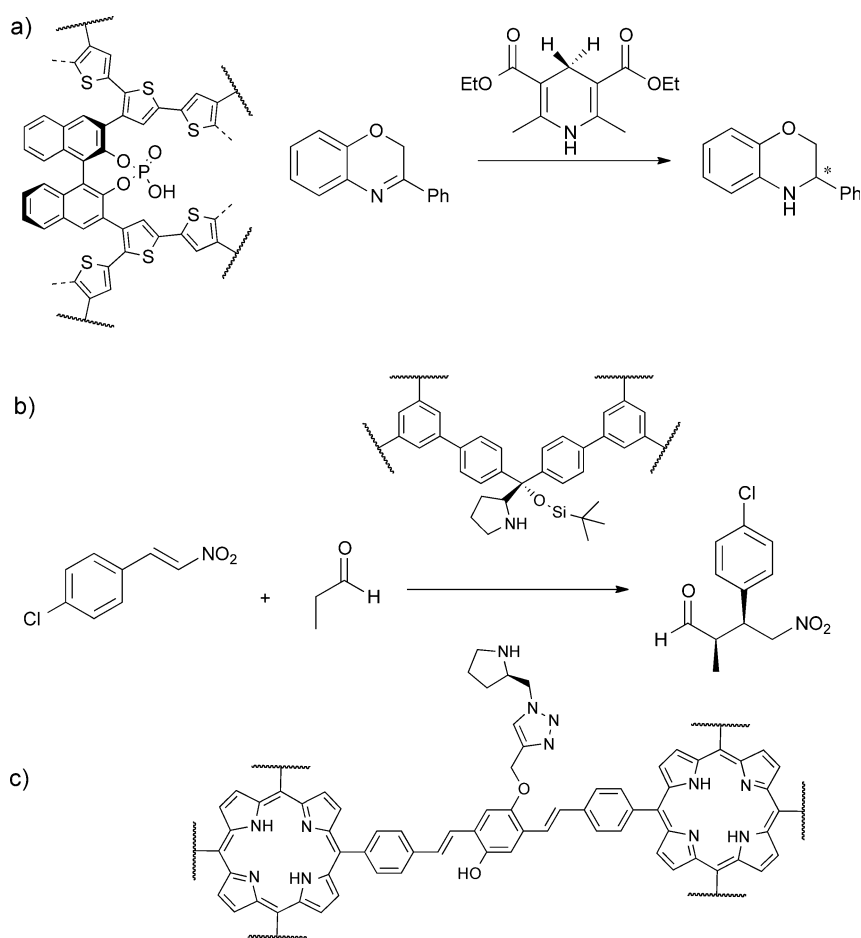
aminal groups. This catalyst was also shown to be recyclable over five runs without any loss in activity. A third approach in terms of nitrogen-containing solid bases is the incorporation of molecular, exactly defined catalysts as linkers within the structure of the framework. This was done by using Tröger's base derivatives as building blocks for the formation of porous PIMs<sup>[43]</sup> as well as CMPs (Scheme 2c).<sup>[44]</sup> The latter was applied in the catalytic addition of diethylzinc to 4-chlorobenzaldehyde. The CMP showed yields of 50–60%, which were slightly

lower than those shown by molecular species. Though, the heterogeneity was proven. The catalysts could be easily removed from the reaction and recycled three times without activity loss.

Although Lewis base catalysts can be easily incorporated within the linker, only a few examples of acid-functionalized nanoporous polymers have been reported. In all cases, the Brønsted acid groups were formed by post-synthetic modification. For example, an HCP functionalized with methyl groups was treated under oxidative conditions ( $\text{KMnO}_4$ ) to yield the respective carboxylic acid groups with an acid site concentration of  $4.4 \text{ mmol g}^{-1}$  (Scheme 2d).<sup>[32d]</sup> This material was successfully used for the first time as a solid catalyst for the C–H activation of various indole derivatives under mild conditions at ambient temperature. Another example is a bifunctional catalyst that provides acid and base sites and that is based on a spirobisfluorene framework derived by Suzuki cross-coupling (Scheme 2e).<sup>[45]</sup> The unfunctionalized framework was first sulfonated by using chlorosulfonic acid. Subsequently, nitric acid was used for nitration, which was followed by reduction over  $\text{SnCl}_2$  to yield amine groups. The bifunctionality was used to prove the feasibility of a one-pot cascade reaction, which could not be performed with the respective molecular catalysts in solution as a result of adduct formation. Therefore, in the first step benzaldehyde dimethyl acetal was converted into benzaldehyde catalyzed by the acid, whereas in the second step, the reaction of the latter with malonitrile catalyzed by the basic sites occurred. The reaction was recycled over eight runs with varying product yields. However, a clear statement on deactivation is difficult, as the recycling experiments were performed at 100% conversion. A combined approach with the use of a cross-linked polymer of styrene and divinylbenzene with an additionally increased specific surface area and pore volume by nanocasting of inorganic templates such as silica was reported recently.<sup>[46]</sup> By post-synthetic sulfonation, acid catalysts were obtained. They showed high tunability of activity and selectivity in the dehydration of fructose to the biogenic platform compound 5-hydroxymethylfurfural (HMF). Thus, the feasibility of using convenient polymeric materials as versatile and valuable catalysts for future biorefinery processes was proven.

Despite structural and functional variety and the possibilities of organic synthesis, only very few examples of nanoporous polymers have been reported that deal with asymmetric organocatalysis. One example is a binaphthyl phosphoric acid (BNPPA) building block that forms a nanoporous polymer by oxidative cross-linking of thiophene functional groups (Scheme 3a).<sup>[47]</sup> It showed high activity and high enantioselectivity in the transfer hydrogenation of dihydro-2*H*-benzoxazine and 2-arylquinolines as well as in the asymmetric Friedel–Crafts alkylation of pyrrole and an aza-ene-type reaction. Especially, the first reaction is of commercial interest for the production of chiral amines. So far, only molecular derivatives of the catalyst have been applied, which has resulted in a broad range of enantiomeric excess (*ee*) values, depending on the substituents of BNPPA.<sup>[48]</sup> In up to 10 runs, constant conversions of 99% with 98% *ee* were reported for the porous polymer. This proved the high activity and separability of the heterogenized catalyst.

A second example is the immobilization of the Jørgensen–Hayashi catalyst. As an ethynyl-functionalized derivative, it was used as a co-linker in a nanoporous polymer derived by cyclo-trimerization of the ethynyl groups to 1,3,5-substituted phenylene rings (Scheme 3b).<sup>[49]</sup> Its catalytic activity was investigated for the asymmetric Michael addition of aldehydes to nitroal-



**Scheme 3.** Examples of asymmetric organocatalytic conversions based on a) a binaphthyl phosphoric acid,<sup>[47]</sup> b) an immobilized Jørgensen–Hayashi catalyst,<sup>[49]</sup> and c) a covalently bound pyrrolidine group.<sup>[50]</sup>

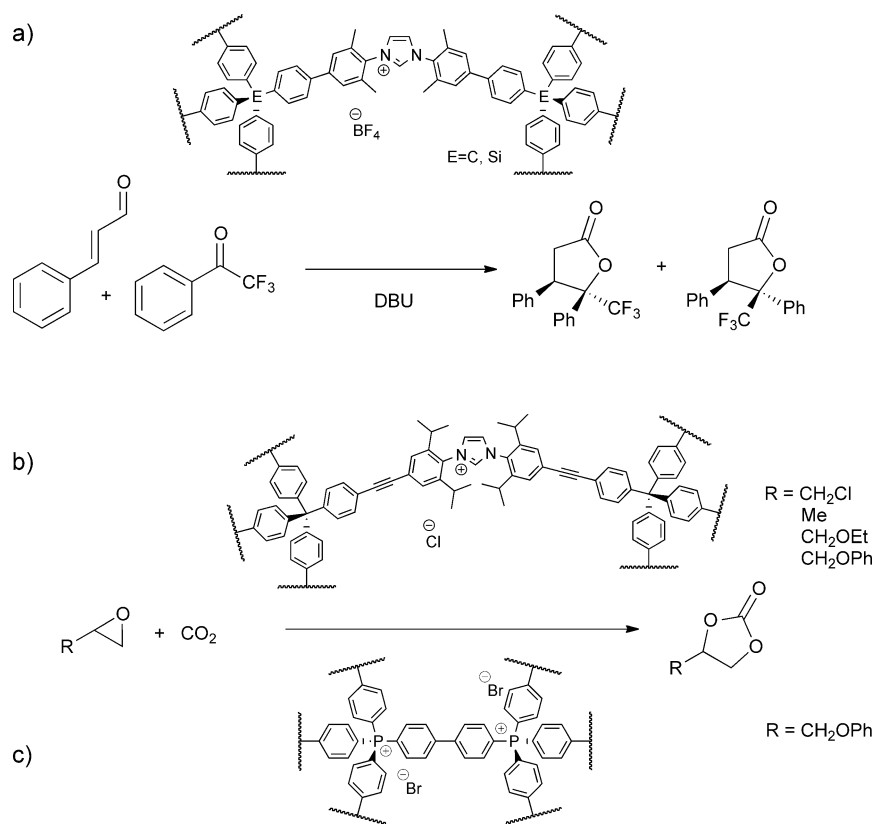
kenes. Depending on the solvents and reaction parameters, yields of 67–99% were obtained with high 93–99% *ee* and high diastereoselectivity (74:26 to 97:3 *dr*). Reuse experiments were performed over four cycles with constant enantioselectivity. However, after the second cycle the product yield decreased significantly, indicating catalyst deactivation by poisoning or leaching of the active species. Recently, the same reaction was catalyzed by a metal-free imine-linked polyporphyrin functionalized with pyrrolidine groups (Scheme 3 c).<sup>[50]</sup> This material was successfully used as a solid catalyst in a continuous fixed-bed reactor, and thus, the feasibility of advanced catalysis engineering was proven.

The building block approach was also used for the incorporation of molecular imidazolium species in nanoporous polymers. N-Heterocyclic carbenes (NHCs) are formed by in situ deprotonation, representing a class of very important organocatalysts.<sup>[51]</sup> In two different approaches, bifunctional imidazolium salts and tetrafunctional aromatic linkers were cross-linked to 3D porous framework structures by using Suzuki–Miyaura coupling (NHC-EOF)<sup>[52]</sup> as well as Sonogashira–Hagihara coupling (NHC-CMP).<sup>[53]</sup> The catalytic activity of the first compound was tested in the reaction of  $\alpha,\beta$ -unsaturated cinnamaldehyde with trifluoroacetophenone by conjugated umpolung (Scheme 4 a).<sup>[52]</sup> The catalytic performance was comparable to that of the molecular analogues with regard to product yield and stereoselectivity. The heterogeneity of the catalyst was proven by filtration experiments, which resulted in no further

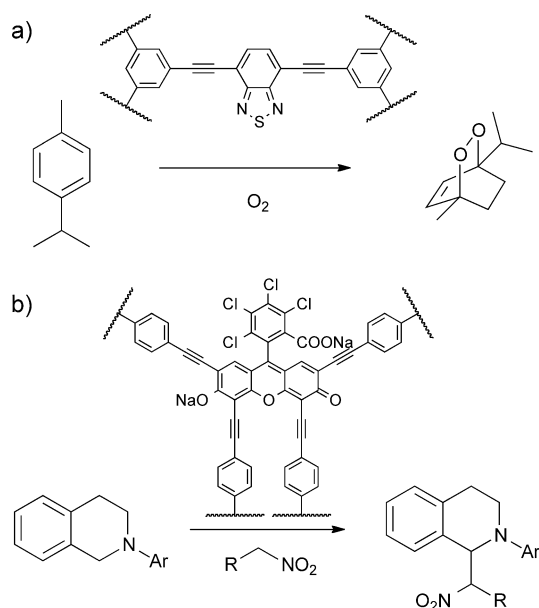
conversion upon catalyst removal. Recycling up to four times was possible with a negligible loss in activity and constant stereoselectivity. Given that NHCs are known to activate epoxides for the reaction with CO<sub>2</sub> to cyclic carbonates, the NHC-CMP was investigated in this model reaction (Scheme 4 b).<sup>[53]</sup> It showed high activity with turnover frequencies (TOFs) of 92–142 h<sup>-1</sup> and its recyclability was stated. This material is one of the few examples with a proven size selectivity effect due to confined reaction spaces within the pore structure. The activity of NHC-CMP decreased for the conversion of different substrates with increasing size from epichlorohydrin to glycidyl phenyl ether. In comparison, the activity remained constant for all substrates upon using a non-porous solid catalyst. The same reaction starting from glycidyl phenyl ether was catalyzed by a phosphonium-based polymer (Scheme 4 c).<sup>[54]</sup> It was synthesized by Yamamoto homocoupling of an ionic phosphonium species. Owing to partial decomposition of the phosphonium monomer, phosphine groups were also incorporated into the structure, which could have also contributed to the catalytic activity. A direct comparison of the results is not possible given the different reaction parameters that were applied. However, lower temperatures and only 1 atm of CO<sub>2</sub> instead of 10 atm resulted in up to 98% yield of the cyclic carbonate (1 atm = 101.3 kPa). Additionally, the catalyst showed only a minor loss in activity over five cycles, demonstrating its stability and recyclability.

CMPs provide extended conjugated  $\pi$ -electron systems.

Thus, photocatalytic applications seem feasible and have been proven recently. In one approach, a poly(benzothiadiazole) network was used for the production of singlet oxygen to form the peroxide of  $\alpha$ -terpinene, that is, to yield ascaridole (Scheme 5 a).<sup>[55]</sup> The photocatalytic properties could be related to the surface area, which was tuned by SiO<sub>2</sub> as an internal template. Although conversions above 90% were achieved, the reaction rates were approximately one order of magnitude lower than that of the best molecular catalyst. In a second approach, a derivative of Rose Bengal dye was incorporated as a co-monomer in a nanoporous CMP (Scheme 5 b).<sup>[56]</sup> Its photocatalytic activity was proven for various substrates in the aza-Henry reaction at ambient temperature. However, starting with 100% conversion after the third run, a steady decrease in the conversion down to 90% was observed in the 10th run, which raised



**Scheme 4.** NHC polymers derived through a) Suzuki<sup>[52]</sup> and b) Sonogashira<sup>[53]</sup> coupling and c) a phosphonium-based framework<sup>[54]</sup> that are used as organocatalysts. DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene.



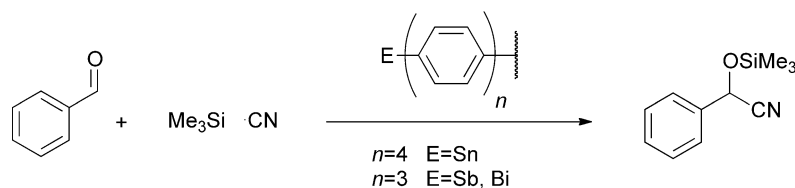
**Scheme 5.** Photocatalytically active CMPs based on a) a benzothiadiazole moiety<sup>[55]</sup> and b) immobilized Rose Bengal dye.<sup>[56]</sup>

a question regarding the stability of the polymeric materials during photocatalytic applications.

### Immobilized molecular metal species

The major advantage of nanoporous polymers is the combination of a chemically well-defined inner surface derived by the modular building block approach and a high surface area. Thus, molecular catalytically active metal species can be immobilized or even incorporated within the framework structure with exceptionally high dispersion and good accessibility due to the open-pore structure. Thereby, the properties of the molecular catalysts are combined with the good separability and recyclability of the solid catalysts.

Similar to certain MOFs with open metal sites at the connectors for catalytic applications,<sup>[57]</sup> nanoporous polymers with similar behavior have also been reported. Especially, EOFs that contain elements such as tin, antimony, and bismuth as species connected through covalent bonds to the carbon atoms of the aromatic linker were shown to be catalytically active (Scheme 6).<sup>[26]</sup> These materials are stable enough to be handled in air. Because of metal incorporation during the synthesis, no post-synthetic metalation step is necessary. By using a highly reactive organolithium species as the intermediate for



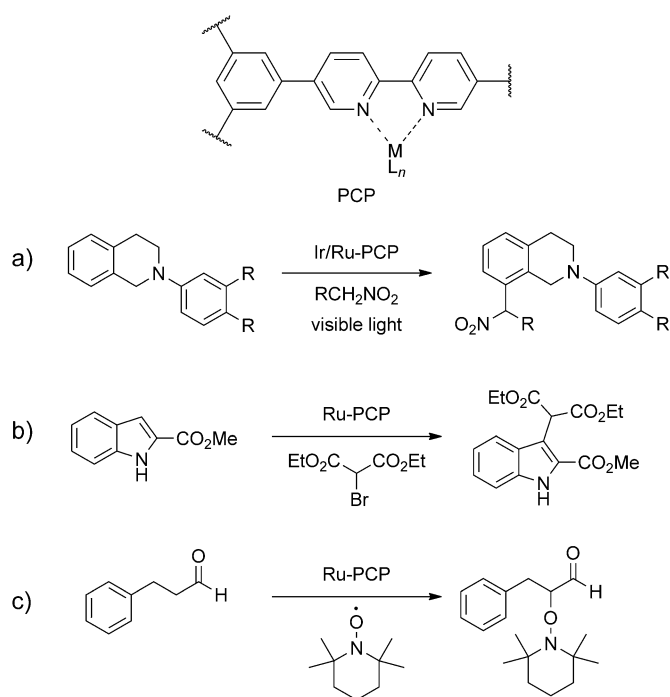
**Scheme 6.** Cyanosilylation of benzaldehyde as a test reaction for elemental organic frameworks containing Sn, Sb, and Bi as connectors.<sup>[26]</sup>

the formation of the materials, structural and functional “defects” are to be expected. Thus, open metal centers provide Lewis acidity, whereas, for example, hydroxy groups at the metal centers could function as weak Brønsted acid sites. To prove the catalytic activity of these materials, the cyanosilylation of benzaldehyde was used as a test reaction. Full conversion was observed after 15–25 h, for which Bi-EOF was the most active material. Leaching tests to prove the heterogeneity were performed by the “hot filtration” method. No further conversion after catalyst removal was observed. Additionally, catalyst recycling was also shown to be successful over at least a few cycles. The opportunity to immobilize molecular and thus highly disperse Sn species within porous solid materials might be of interest for industrial applications, such as the conversion of oleochemicals. Therein, molecular tin catalysts are often used, but these materials can be highly toxic depending on the substituents. Great efforts are often necessary to separate these compounds after the reaction. Thus, solid tin-containing catalysts might be a useful alternative in terms of process optimization and intensification.

Instead of using the connecting species as a catalyst, the organic linker also provides various opportunities for pre-synthetic or post-synthetic functionalization with a molecular metal species. Very convenient is the synthesis of nanoporous polymers by using preformed metal-containing linkers. If these linkers are inert against the reaction conditions used in the formation of the framework, determination of the catalytically active species is much easier than for a post-synthetic metalation. In one such example, diethynyl linkers with bipyridyl moieties and coordinated molecular Ir and Ru species were used as co-monomers to form a porous framework through the Co-catalyzed cyclotrimerization of terminal ethynyl groups to yield stable 1,3,5-substituted phenylene rings as connecting species.<sup>[58]</sup> The obtained materials combine high porosity and thermal and chemical stability and have been investigated in photocatalysis as a result of their large conjugated  $\pi$ -electron systems. In comparison to their molecular analogues, the polymers showed even higher catalytic activity in different test reactions such as the photocatalytic aza-Henry reaction, the  $\alpha$ -arylation of bromomalonate, and the oxyamination of aldehydes (Scheme 7 a–c). The catalysts were successfully recycled over several runs without any observable metal leaching. The same cross-linking reaction was used for the in situ metalation of the bipyridyl co-monomer with  $\text{Co}_2(\text{CO})_8$  as the catalyst upon the formation of the framework.<sup>[59]</sup> Although no catalysis experiments were reported in the latter case, the authors showed that by a thermal activation process the ligated carbonyl was removed and the open metal sites of the molecular species were then exposed within the porous structure. A similar approach was used to incorporate Ir-, Rh-, and Re-bipyridyl complexes as well as cyclometalated Ir complexes in porous CMPs.<sup>[60]</sup> They were investigated in the reductive ami-

nylation of benzaldehyde as a test reaction for elemental organic frameworks containing Sn, Sb, and Bi as connectors.<sup>[26]</sup>





**Scheme 7.** Porous cross-linked polymers (PCPs) containing bipyridyl moieties have been used for coordination of various metal species and investigated in several catalytic model reactions.<sup>[58]</sup>

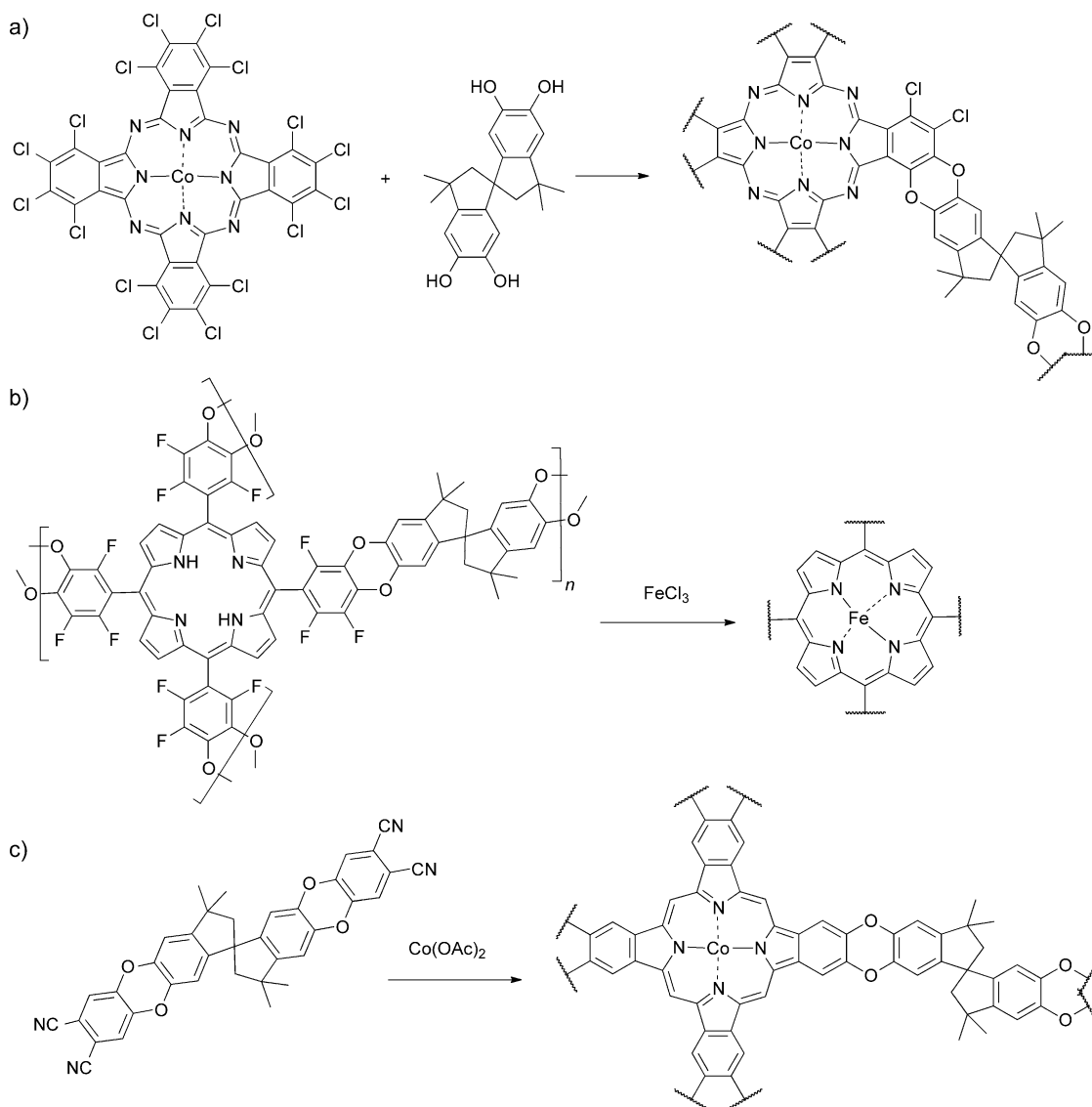
nation of ketones, for which, specifically, an Ir-containing CMP with the lowest specific surface area showed unusually high activity. This effect could not be explained, but certainly dynamic behavior of the flexible framework is involved. Another example in which porosity seems to be less important is the formation of a CMP by homocoupling of an ethynyl-functionalized Ru-containing trisbipyridyl complex.<sup>[61]</sup> The complex is formed prior to the cross-linking reaction. Presumably owing to the sterically demanding monomer, the specific surface area is below 200 m<sup>2</sup> g<sup>-1</sup>. Nevertheless, as a result of the preformed chromophoric linker, the material showed high photocatalytic activity in the aza-Henry reaction, aerobic oxidative amine coupling, and reductive dehalogenation.

Molecular metal species in exactly defined ligand spheres are provided within porphyrin and phthalocyanine compounds and have been used in catalysis for a long time.<sup>[62]</sup> Also, various approaches for their heterogenization are known. During the rising interest in nanoporous polymers, several examples have been reported for the incorporation of porphyrin and phthalocyanine moieties as catalytic active sites mainly within CMPs and PIMs.<sup>[37b,63]</sup> The advantage of these chemically exactly defined moieties within an open porous framework include high dispersion and good accessibility in comparison to the often densely packed molecular derivatives because of strong  $\pi$ - $\pi$ -stacking. For the synthesis of the respective nanoporous polymers, three strategies have been applied: coupling of preformed metal complexes,<sup>[37b,63b,64]</sup> post-synthetic metalation of the open coordination sites within the frameworks,<sup>[63d]</sup> and formation of metal-containing macrocycles as the cross-linking reaction for the formation of the framework (Scheme 8).<sup>[37b,65]</sup>

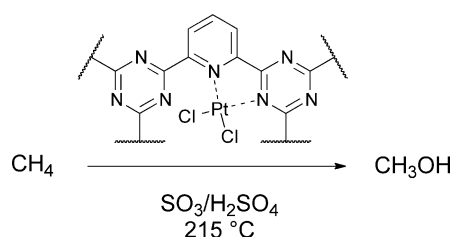
Several of these materials have been investigated in numerous relevant catalytic reactions. The advantageous effects of a Co-phthalocyanine-PIM compared to the molecular derivative was proven in the decomposition of hydrogen peroxide.<sup>[37b]</sup> Because of the high dispersion and the good accessibility of the metal centers, the porous polymer showed initial activity that was 20 times higher than that of the molecular derivative. These catalysts also showed good performance in the oxidation of cyclohexene, cyclohexane, and hydroquinone.<sup>[37b,63d]</sup> For purification of sulfide-containing water, the oxidation to elemental sulfur is of interest. A Co-phthalocyanine-PIM proved to be an efficient catalyst of sufficient stability for this reaction in the aqueous environment.<sup>[63a]</sup> A similar catalytic performance with high activity and good selectivity was shown for a Fe-porphyrin-CMP in the oxidation of organic sulfides to sulfones.<sup>[63b]</sup> An additional advantageous effect results from the local separation of the catalytically active sites within the framework structure. It prohibits self-decomposition under the oxidative reaction conditions. A similar Fe-porphyrin-framework was used for the efficient oxidation of HMF to 2,5-furandicarboxylic acid, a biogenic monomer with great potential for the production of novel biopolymers.<sup>[65]</sup> Another industrially important reaction is the epoxidation of alkenes. A Fe-porphyrin-CMP proved to be highly active and selective towards the epoxidation of diphenylethene by using molecular oxygen.<sup>[63c]</sup> For the epoxidation of styrene, the superior performance of a Mn-porphyrin-framework compared with its molecular analogue was shown.<sup>[63d]</sup> The polymer-based catalysts gave a turnover number (TON) > 2000, whereas the molecular species only achieved TON = 780. Recently, a high-surface area Fe-porphyrin-polymer was proven to be highly active in oxygen reduction for application as an electrode material in proton-exchange membrane fuel cells.<sup>[64]</sup>

In terms of defined coordination sites, nitrogen-containing moieties are the most often investigated ones within nanoporous polymers. An imine-linked nanoporous polymer was used to coordinate Pd(OAc)<sub>2</sub> in between two imine nitrogen atoms of opponent layers within the semi-crystalline structure.<sup>[14b]</sup> The catalytic activity as well as its recyclability with negligible metal leaching was demonstrated in the Suzuki-Miyaura coupling of various substrates in a base-containing solution at 150 °C.

Outstanding stability was demonstrated by CTF materials loaded with a molecular metal species, which were used in oleum as a reaction medium at 215 °C (Scheme 9).<sup>[66]</sup> Owing to the high content of aromatic amine moieties, the coordination of molecular PtCl<sub>2</sub> by wet impregnation was possible. With various advanced characterization techniques, the molecular coordination of the catalytically active species within the amorphous framework structure was proven. This material was used in the catalytic oxidation of methane to methanol, a “dream reaction” for the conversion of methane from natural or biogas into a transportable liquid in terms of chemical energy storage. For the one-pot reaction, concentrated sulfuric acid (oleum) is required as the oxidant for the formation of methyl bisulfate as an intermediate species. The catalytically active site in the solid catalysts mimics the molecular analogue, a platinum bi-



**Scheme 8.** Highly dispersed porphyrin and phthalocyanine moieties within framework structures can be obtained by three different approaches: a) cross-linking of complexes, b) post-synthetic metalation, and c) in situ framework formation and metalation.<sup>[37b]</sup>

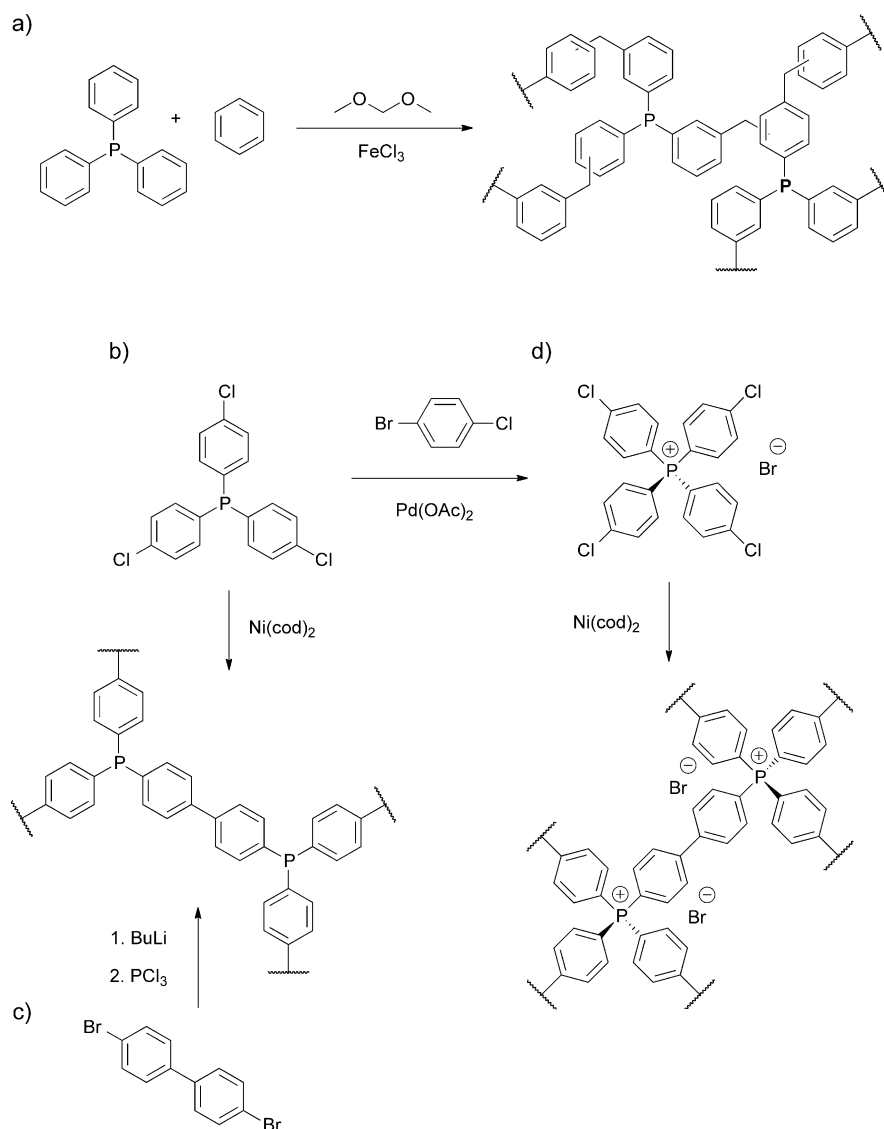


**Scheme 9.** Molecular Pt species coordinated in CTF have been successfully used for catalytic direct methane oxidation and showed outstanding stability under harsh reaction conditions.<sup>[66]</sup>

pyrimidine complex, known as a Periana catalyst. So far, no immobilization technique other than the Pt-CTF approach resulted in a catalyst with sufficient stability. Overall, similar activity of the molecular and solid catalyst was observed with TON = 200–300 and selectivity to methanol of 75%. The recyclability was proven for six cycles. However, for a large-scale process

the reaction conditions appear to be way too demanding for technological realization. Recently, bipyridine-containing linkers were used for the formation of a novel CTF material.<sup>[67]</sup> The coordination of various metal species was comprehensively investigated but without further catalytic studies.

Recently, phosphorous-containing porous polymers have attracted increasing attention. One approach is the synthesis of a HCP from benzene and triphenylphosphine as building blocks cross-linked by methylene groups (Scheme 10a).<sup>[32b]</sup> The mainly microporous materials exhibit specific surface areas of approximately  $1000 \text{ m}^2 \text{ g}^{-1}$  and, thus, a high dispersion of incorporated triphenylphosphine moieties. The measured amount of phosphorous in the material was, however, only 1.9%, which corresponds to approximately 25% of the amount theoretically possible according to the synthesis procedure. Thus, triphenylphosphine seems not to be the ideal molecule for incorporation into a porous framework by this route. In an alternative approach, the  $\text{Ni}(\text{cod})_2$ -catalyzed ( $\text{cod} = 1,5\text{-cyclooc}$ -



**Scheme 10.** Nanoporous polymers based on phosphorous as connecting elements to stabilize metal nanoparticles were synthesized by a) the hyper-cross-linking approach,<sup>[32b]</sup> b, c) Yamamoto coupling,<sup>[54,68]</sup> and d) the organolithium route.<sup>[27]</sup>

tadiene) Yamamoto coupling of tris(4-chlorophenyl)phosphine) was used to achieve porous polymers with  $1300 \text{ m}^2 \text{ g}^{-1}$  containing either phosphine or phosphine oxide moieties (Scheme 10b).<sup>[68]</sup> Materials derived from both routes have been used as supports for catalytically active Pd species by coordinating either  $\text{PdCl}_2$  or  $\text{Pd}(\text{PPh}_3)_4$  from solution, at least in the latter case also leading to the formation of metal nanoparticles. The resulting noble-metal-loaded nanoporous polymers were successfully used as catalysts in the Suzuki–Miyaura cross-coupling of a variety of substrates in aqueous environments. Only slight leaching of the metal species was observed. A critical issue in this context is the exact qualitative and quantitative determination of the coordinated metal species. Both types of polymers were synthesized by either Fe- or Ni-catalyzed coupling reactions. Though, no quantification of a residual metal species was presented, as partial coordination of

these species seems feasible and should, thus, be considered for catalytic testing.

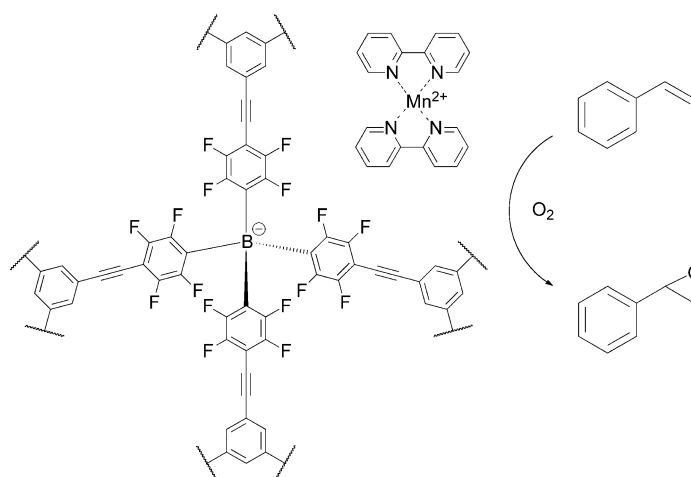
This issue could be avoided by applying transition-metal-free non-catalyzed coupling reactions such as the organolithium route. By this approach, two groups simultaneously reported the synthesis of a poly(biphenylene phosphine) EOF (Scheme 10c).<sup>[27]</sup> Minimal differences in the synthesis parameters resulted in different properties. On the one hand, a porous polymer with a specific surface area of  $450 \text{ m}^2 \text{ g}^{-1}$  that could be increased to  $640 \text{ m}^2 \text{ g}^{-1}$  by drying with supercritical  $\text{CO}_2$  was obtained that contained phosphine oxide or phosphonium moieties in addition to the phosphine connecting groups.<sup>[27b]</sup> On the other hand, a less porous material with an external surface area of  $135 \text{ m}^2 \text{ g}^{-1}$  was obtained with phosphine groups exclusively.<sup>[27a]</sup> The first material was proven to coordinate  $\text{PdCl}_2$  as well as  $\text{RhCl}(\text{PPh}_3)_3$  from solution. The as-synthesized catalyst was then successfully applied in the transfer hydrogenation of cyclohexanone with 2-propanol. By hot filtration, no leaching of an active species was observed, which thus proved the heterogeneity of the catalyst. However, a significant decrease in the yield of the product from 80 to 40% within three runs was observed, which

emphasizes the need for further investigation of the structure–activity relationship. In contrast, the less porous polymer was loaded with  $\text{Pd}(\text{dba})_2$  (dba = dibenzylidene acetone) as well as with  $\text{Pd}(\text{acac})_2$  (acac = acetylacetonate). Whereas  $\text{Pd}(\text{dba})_2$  easily decomposed and formed elemental Pd nanoparticles,  $\text{Pd}(\text{acac})_2$  remained as a coordinated molecular species mainly as a biphosphine complex, although it formed metal nanoparticles as well after the catalytic test reaction. As such, the telomerization of 1,3-butadiene with phenol and with glycerol was investigated. In the latter case, the polymeric phosphine catalysts showed superior activity than molecular triphenylphosphine as a ligand. Additionally, it was shown that by increasing the phosphine-to-metal ratio the product selectivity as well as the metal leaching could be improved presumably as a result of a higher dispersion of the active sites.

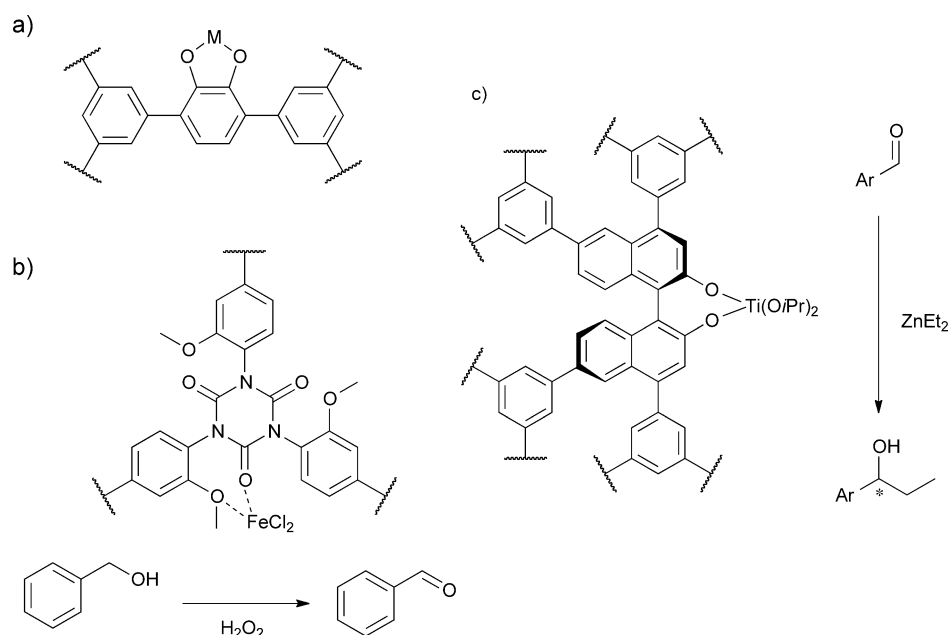
Another possibility is provided by ion exchange of charged framework species such as a nanoporous polymer that consists of quaternary phosphonium ions as connection species between the aromatic linkers (Scheme 10d).<sup>[54]</sup> The halide counterions in the pores were exchanged by complex metal ions in solution, in that case  $\text{PdCl}_4^{2-}$ , to yield a homogeneous dispersion of the metal precursor. Upon chemical reduction with  $\text{NaBH}_4$ , the molecular precursor was converted into uniform Pd nanoparticles. Catalytic activity in the Suzuki–Miyaura cross-coupling reaction was proven for various substrates. High conversions of >95% were reported. It was shown that the catalyst provides exceptionally high activity, as even fluorobenzene with low reactivity was coupled with a product yield of 87%.

The same approach for metal immobilization by ionic interactions was used for nanoporous polymers containing boron instead of phosphorus as the connecting element.<sup>[69]</sup> Therefore, a tetraphenylborate anion was used as the building block, and it was cross-linked by Sonogashira–Hagihara coupling.  $\text{Li}^+$  as the counterion was afterwards exchanged with  $\text{Mn}^{2+}$ . Additional molecular bipyridine (bpy) forms a  $[\text{Mn}(\text{bpy})_2]^{2+}$  complex cation, which is immobilized within the anionic framework by strong ionic interactions in combination with sterically shielded ions (Scheme 11). This complex is known to show catalytic activity in oxidation reactions. Thus, this material was tested in the oxidation of styrene with molecular oxygen to the corresponding epoxide. The immobilized complex showed a significantly higher conversion than the molecular species or the pure  $\text{Mn}^{2+}$  within the porous framework. The conversion remained nearly constant over three runs. Overall, this approach poses great potential for the immobilization of catalytically active metal complexes provided that suitable ionic porous organic frameworks are available.

Further versatile functional moieties for the immobilization of molecular metal species by covalent or coordinative bonds are catechol groups. The opportunity for loading them post-synthetically with different metal species such as magnesium, copper, and manganese was proven for a porous polymer containing a catechol derivative as the co-monomer in the cyclotrimerization of ethynyl-functionalized building blocks (Scheme 12a).<sup>[70]</sup> Recently, a combined density functional theory and spectroscopic study provided insight into the



**Scheme 11.** Immobilization of an ionic molecular Mn complex by electrostatic interaction within a borate-based framework used in the epoxidation of styrene.<sup>[69]</sup>



**Scheme 12.** Oxygen donor groups can be used to immobilize molecular metal species such as a) catechol,<sup>[70]</sup> b) neighboring isocyanurate and methoxy groups<sup>[18]</sup>, and c) BINOL units<sup>[72]</sup> by post-synthetic metalation.

metal coordination environment within the nanoporous catechol-containing polymers.<sup>[71]</sup> Catalytic activity was shown for a microporous polyisocyanurate that was synthesized from bifunctional isocyanate linkers by a cyclotrimerization reaction catalyzed by a NHC (Scheme 12b).<sup>[18]</sup> Although the material does not contain catechol moieties, the methoxy group containing linker in close proximity to the carbonyl groups of the isocyanurate connector was shown to coordinate  $\text{FeCl}_2$ . The material was investigated in the oxidation of benzyl alcohol to benzaldehyde by using an aqueous solution of hydrogen peroxide. Molecular  $\text{FeCl}_2$  in solution as well as  $\text{Fe}_2\text{O}_3$  nanoparticles gave selectivities of 51 and 35–97% and TONs of 29 and 12–32, respectively, whereas the Fe-containing porous polymer

showed TONs of up to 100 with 98% selectivity towards the desired product. The catalyst was recycled up to eight times without any loss in activity or selectivity.

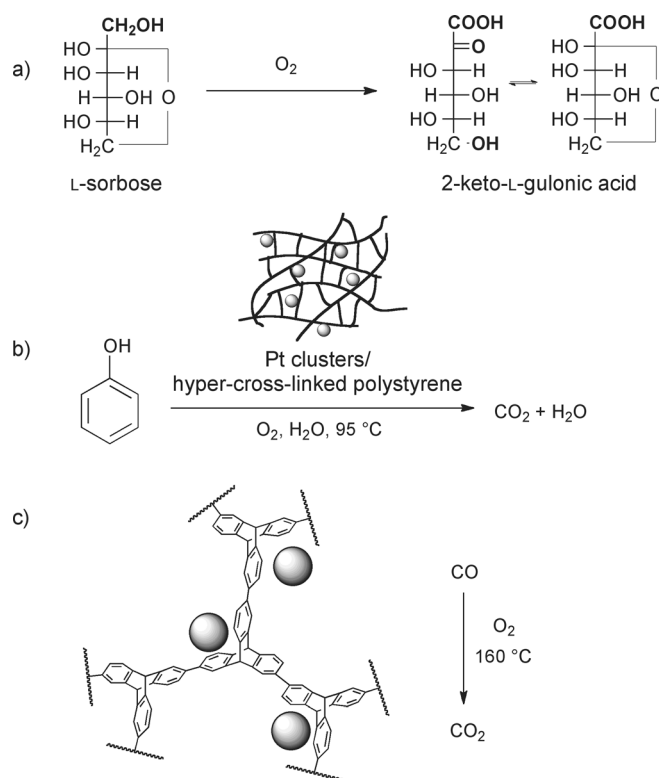
Similar to catechol moieties, also 1,1'-binaphthol (BINOL) units have been used for post-synthetic metalation with Ti(OiPr)<sub>4</sub> by covalent bonds for the production of a chiral catalyst (Scheme 12c).<sup>[72]</sup> For polymer production, tetrafunctional BINOL derivatives of different sizes were cross-linked by cyclo-trimerization of terminal ethynyl groups. As an asymmetric catalytic test reaction, the addition of diethyl zinc to aldehydes was used. Enantioselectivities of 55–81%*ee* were achieved, which turned out to be slightly lower than those obtained with the respective molecular species as well as with comparable MOF catalysts. However, the catalysts were successfully recycled up to 10 times with constant activity and selectivity. In another example, a chiral vinyl-substituted 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) was co-polymerized with divinylbenzene to yield a mesoporous cross-linked polymer.<sup>[73]</sup> Subsequently, a molecular Ru species was coordinated to the phosphine moieties of the chiral building block. The resulting catalyst was successfully used in the asymmetric hydrogenation of  $\beta$ -keto esters. For nine different substrates, the catalysts showed full conversion with >99.5% selectivity to the targeted product and 90–99%*ee*. No change in activity was observed over six runs.

### Supported metal nanoparticles and clusters

Molecularly well-defined functional groups within nanoporous polymers provide certain advantages over conventional porous support materials such as activated carbons, zeolites, metal oxides, and ceramics. Especially, advanced immobilization of metal nanoparticles or defined nanoclusters seems feasible; thus, a high dispersion of catalytically active centers in combination with good stabilization against agglomeration and sintering is provided. Activated carbons often provide a heterogeneous surface that is tunable only to a certain extent by parameter variation of the activation process or post-synthetic chemical treatment. In contrast, ceramic supports such as metal oxides or nitrides often provide insufficient specific surface area, which is required for high dispersion, as well as limited possibilities for tuning of the transport pore systems. Also, the surface chemistry is predominantly controlled by the composition of the materials. Thus, adding functional groups is often only possible by using certain grafting methods. The advantageous properties of nanoporous polymers pose great potential to overcome most of the aforementioned limitations. By the modular building block approach, they possess surface chemistry that is a well tunable by all means of organic chemistry.

Additionally, post-synthetic functionalization enables high density and dispersion of functional groups. These properties in combination with accessible and tunable pore systems for enhanced transport properties and very high specific surface areas provide numerous opportunities for advanced catalysis engineering. An example of the importance of a combined transport pore system with high surface area was reported for

a hyper-cross-linked polystyrene.<sup>[74]</sup> This material was used as a support for platinum nanoclusters that were derived by impregnation with dissolved hexachloroplatinic acid and subsequent drying under mild conditions. A mixture of highly dispersed Pt<sup>0</sup>/Pt<sup>II</sup>/Pt<sup>IV</sup> was observed, despite the absence of additional coordinating moieties. The material was used as a catalyst in the oxidation of L-sorbose to 2-keto-L-gulonic acid by using molecular oxygen (Scheme 13a). Comparison of an ex-



**Scheme 13.** a, b) Supported Pt nanoparticles on a HCP and c) Pd nanoparticles on polytriptycene have been successfully used as oxidation catalysts for a) sugar conversion,<sup>[74]</sup> b) total oxidation of phenol in water,<sup>[75]</sup> and c) CO oxidation.<sup>[76]</sup>

clusively microporous material with a micro-/macroporous material revealed that the latter showed increased activity. This effect was ascribed to enhanced mass transfer in the hierarchical porous material, whereas the micropores with a maximal diameter of 2 nm and additionally filled with metal clusters 1.3 nm in size showed hindered diffusion of the sterically demanding substrate and product. This example emphasizes the importance of mass transfer in solid catalysts and the convenient tunability within nanoporous polymers. A similar catalyst was investigated in the total oxidation of phenol in aqueous solution (Scheme 13b).<sup>[75]</sup> Under these relatively harsh reaction conditions, the polymeric catalyst showed exceptional stability. Additionally, the catalyst performance was compared to that of commercial Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/AC and was found to exceed them in terms of productivity and selectivity. A third example of a polymer-based oxidation catalyst was published recently. The

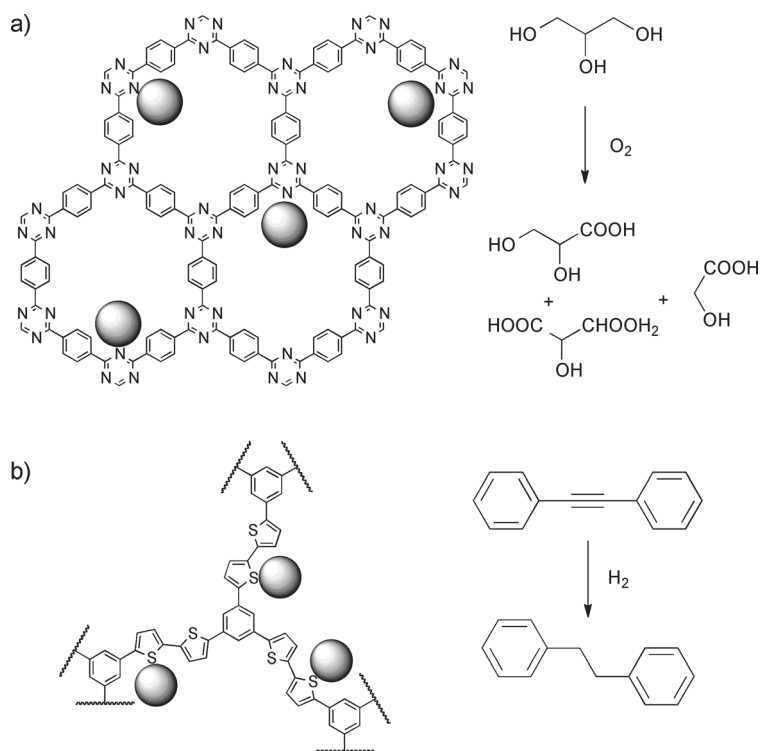
porous polymer used as the support was prepared by Yamamoto coupling of triptycene building blocks (Scheme 13 c).<sup>[76]</sup> A  $\text{PdCl}_4^{2-}$  species was impregnated into the framework and subsequently reduced by means of the gas bubbling assisted membrane reduction method. At different metal loadings, varying particle sizes ranging from 2.7 to 5 nm were obtained with varying activity in the oxidation of CO. Low temperatures of 160 °C for full CO conversion were obtained for this active and stable catalyst. Recently, the aforementioned divinylbenzene-based porous polymer derived by nanocasting of oxides was used as a convenient support for highly dispersed Pt nanoparticles.<sup>[77]</sup> In the aerobic oxidation of ethanol and glycerol in an aqueous phase, they showed improved activity and selectivity compared to Pt supported on carbon- and alumina-based catalysts. Thus, the advantageous properties of liquid-phase and even aqueous-phase reactions were proven.

For several examples, an additional stabilization effect for metal nanoparticles by heteroatom-containing building blocks with Lewis basic properties and, thus, strongly coordinating effects was reported. This effect can be regarded as a porous polymer-specific strong metal-support interaction. CTFs are one example: they possess a high content of aromatic nitrogen atoms ideally suited for additional stabilization of well-dispersed metal nanoparticles. Preformed Pd nanoparticles with a diameter of approximately 3 nm were impregnated into the porous material by a sol immobilization technique (Scheme 14 a).<sup>[78]</sup>

This catalyst was then investigated in the oxidation of glycerol by using molecular oxygen. Its activity was compared to that of the same nanoparticles supported on an AC as a nitrogen-free porous solid. In comparison, the Pd/CTF catalysts exhibited a higher initial reaction rate as well as increased selectivity to glyceric acid. Whereas Pd/AC showed a maximal conversion of only 30% after 1 h, Pd/CTF achieved full conversion after 3 h. With the fourth cycle a slightly decreased activity was observed. The fast deactivation of Pd/AC was proven to be a result of immediate particle aggregation, as shown by TEM imaging. In contrast, Pd/CTF showed basically no aggregation owing to the stabilization effect of the coordinating nitrogen moieties within the framework structure.

In another example, monodisperse  $\text{Pd}^0$  nanoparticles with a diameter of 1.5 nm were supported on a porous poly(thienylene arylene) by impregnation of a  $\text{PdCl}_2$  solution and subsequent reduction (Scheme 14 b).<sup>[79]</sup> The monodisperse particle size distribution was stated to be a result of stabilizing effects of the sulfur atoms incorporated within the framework. This material was tested in the hydrogenation of diphenylacetylene to 1,2-diphenylethane. After a reaction time of 2 h, full conversion and 100% selectivity of the main product were obtained.

An alternative method for impregnation of molecular metal species to achieve a dispersion as high as possible before the reduction was shown for a CMP material.<sup>[80]</sup> Thereby, supercritical  $\text{CO}_2$  was used as the impregnation solvent for a  $\text{Pd}^{\text{II}}$  species.



**Scheme 14.** Supported Pd nanoparticles in porous frameworks providing enhanced stabilization and dispersion as a result of heteroatoms such as a) nitrogen in CTFs<sup>[78]</sup> and b) sulfur in a poly(thienylene arylene).<sup>[79]</sup>

It offers negligible surface tension and thus provides excellent wetting properties to penetrate all pores and homogeneously distributes the metal precursor. By thermal decomposition, monodisperse Pd nanoparticles with a diameter of 1–3 nm were obtained. In a similar approach, highly disperse Pd nanoclusters 2.4 nm in diameter were incorporated in COF-102 by gas-phase infiltration and subsequent photodecomposition of  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)]$ .<sup>[81]</sup>

Recently, the formation of a CMP by the Pd-catalyzed cyclo-trimerization of 1,3,5-triethynylbenzene was used to incorporate in situ formed and covalently stabilized Pd nanoclusters within the porous framework structure.<sup>[82]</sup> As in the previous example, this material also exhibited high catalytic activity for the Suzuki–Miyaura cross-coupling reaction. Main advantages are the short reaction times, high yields, as well as high TONs and TOFs in aqueous media under aerobic conditions. Agglomeration and leaching of the metal clusters were inhibited by the covalent stabilization strategy.

### Challenges in characterization

Compared to conventional nanoporous materials, novel polymeric catalysts exhibit some significant issues in terms of characterization, which are briefly addressed in the following. Nearly all issues typical for nanoporous polymers are attributed to the quite high chemical stability of most of the 3D highly cross-linked frameworks in combination with the lack of long-range ordered structural motives. Even determining the

degree of cross-linking by measuring the amount of unconverted functional groups poses a great challenge for many materials. As soon as elements are contained within the framework structure, which cannot be analyzed by combustion elemental analysis, as typically used for C, H, N, and S, the analysis of the composition has to be performed carefully. Using special digestion methods, one has to make sure that the respective compounds are dissolved quantitatively before analyzing the respective elements.

Characterizing supported metal nanoparticles and clusters by means of electron microscopy with high magnification also poses a challenge. Despite the large conjugated  $\pi$ -electron systems in many of the materials, they are often rather insulators made of light elements. Thus, high-resolution electron microscopy images are difficult to obtain, as high voltages are required. They often result in instantaneous decomposition of the organic materials and prohibit determination of the size of the metal nanoparticles. Accompanying electron microscopy, energy-dispersive X-ray spectroscopy is a valuable tool for element mapping of immobilized metal species in the form of particles as well as molecular species. Especially in the latter case, a qualitative statement on the dispersion of the coordinated species can be obtained.

Characterizing coordinated molecular metal species in amorphous non-soluble frameworks is definitely the greatest challenge. Solid-state NMR spectroscopy, especially of amorphous materials, is often of limited use for comprehensive characterization as a result of signal broadening. However, measuring NMR spectra of dissolved metal complexes can be used for comparative studies, for example, as in the case of coordinated Pd ions in bipyridyl moieties within a PIM.<sup>[37a]</sup> Whereas oxidation states of metals are accessible by X-ray photoelectron spectroscopy, even more specialized X-ray absorption methods such as extended X-ray absorption fine structure and X-ray absorption near-edge structure by using synchrotron radiation are required to obtain detailed information on the chemical environment of the coordinated metal species.

The porosity of nanoporous polymers can be investigated with gas physisorption analysis, although certain effects occur, such as hysteresis over a broad pressure region. They are attributed to dynamic behavior of the flexible and amorphous polymeric frameworks. In recent years, a few reports have been published in which these effects were investigated by applying methods such as small-angle X-ray scattering and NMR spectroscopy of  $^{129}\text{Xe}$  as a probe molecule aside conventional gas physisorption.<sup>[83]</sup> Regarding catalytically active metal centers, chemisorption is a versatile tool, although conventional methods might have to be adjusted by taking the different chemical natures of the nanoporous polymers into account.

## Outlook

Nanoporous polymers have emerged in the last decade as an independent class of new materials with huge potential for catalytic applications. Thus far, various proof-of-concept studies have been reported that deal with all kinds of model reactions. Mainly materials of scientific interest have been developed and

investigated. To facilitate the focused development of catalysts suitable for new processes, several issues summarized in the following have to be taken into account and must be addressed in future studies:

- 1) Selected challenges concerning the characterization of the materials were described above. However, whether metals from catalyzed cross-linking reactions are coordinated aside the targeted metal species has to be addressed in detail.
- 2) Regarding the heterogeneity of catalysts in liquid-phase processing, on the one hand, "hot filtration" tests should be performed to verify the leaching of catalytically active species. On the other hand, leaching should also be checked by investigating the reaction solution for the molecular species derived from the catalyst.
- 3) Upon addressing stability and recyclability, often only a few runs are performed, which is sufficient for proof-of-principle but not for an overall statement in terms of process development. Additionally, these tests in batch reactions should neither be performed at 100% conversion nor in the reaction equilibrium, because the catalyst could still be deactivating without being recognized. Such experiments should rather be performed at a conversion level significantly below the full or equilibrium conversion.
- 4) Another issue of great importance that has to be addressed is the shaping of the materials, which often occur as fine powders. For most industrial applications, shaped bodies of catalysts are required. However, conventional shaping procedures used for activated carbons, zeolites, and other inorganic materials might not be suitable. The different chemical nature of the polymeric materials thus necessitates further and detailed research and development.

In established processes, nanoporous polymers presumably pose no competition for conventional catalysts, owing to availability and pricing issues as well as significantly different materials properties. However, as a result of well-defined functional moieties and catalytically active sites, mainly applications in new processes seem feasible, in which conventional catalysts and support materials reach their limits. Nanoporous polymers combine the advantages of the modular construction of MOFs with the high stability of polymers because of covalent bonds. Three main strategies can be differentiated:

- 1) Utilization as organocatalysts by chemically well-defined organic functional groups to incorporate molecular catalytically active species within porous framework structures, which thus enables organocatalytic process development on the industrial scale.
- 2) Immobilization of molecular metal species by covalent or coordinative bonds to Lewis basic moieties within the linker or connector species.
- 3) Support of metal nanoparticles and clusters by strong metal-support interactions resulting from the high amount of coordinating groups; this prevents or delays aggregation of the particles and thus catalyst deactivation.

All concepts result in well-dispersed catalytically active sites within easily accessible framework structures and additionally provide permanent porosity and high specific surface areas. The most important advantage of nanoporous polymers is the opportunity of including molecularly defined catalytically active species as well as versatile functional groups. Thus, heterogenization of molecular catalysts, for example, for asymmetric reactions, facilitates numerous possibilities for joining the concepts of homo- and heterogeneous catalysis. In terms of immobilized metal particles, significantly stronger stabilization of small metal clusters seems feasible and thus might enable the development of catalysts that perform at the interface of molecular and solid active species.

Application oriented, nanoporous polymers offer the potential for various highly specialized catalytic transformations mainly in fine-chemical synthesis. Future prospects on the industrial scale might be their utilization in catalytic transformation of renewable resources derived from biogenic feedstock. Owing to often polar compounds, various processes have to be developed for liquid-phase and often aqueous-phase processing. Therefore, high chemical stability in combination with tunable catalytically active sites of nanoporous polymers could be of great importance for a vast number of novel catalytic processes. Still a lot of work is required to comprehensively investigate the potential and especially understand the structure–property–activity relations with a different focus than for inorganic support materials. Future work should especially focus on the unique properties of these catalysts for certain challenges rather than treating them as conventional supports in well-known reactions. Thus, nanoporous polymers could contribute significantly to a greener and sustainable future by enabling the development of efficient new processes and by bridging the gap and unifying the concepts of classical homogeneous and heterogeneous catalysis.

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**Keywords:** immobilization · molecular catalysts · organic frameworks · polymers · solid catalysts

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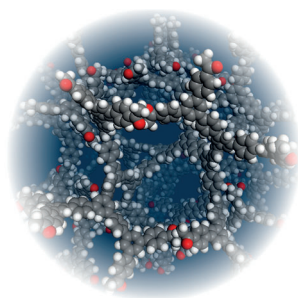
## MINIREVIEWS

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M. Rose\*

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**Nanoporous Polymers: Bridging the Gap between Molecular and Solid Catalysts?**



**Poring over polymers:** Nanoporous polymers pose great potential for the future development of catalytic processes. They unite the advantages of homogeneous and heterogeneous processing by providing solid organocatalysts, immobilized molecular metal species, and stabilized metal nanoparticles and clusters. Recent developments in these three main areas are summarized.

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