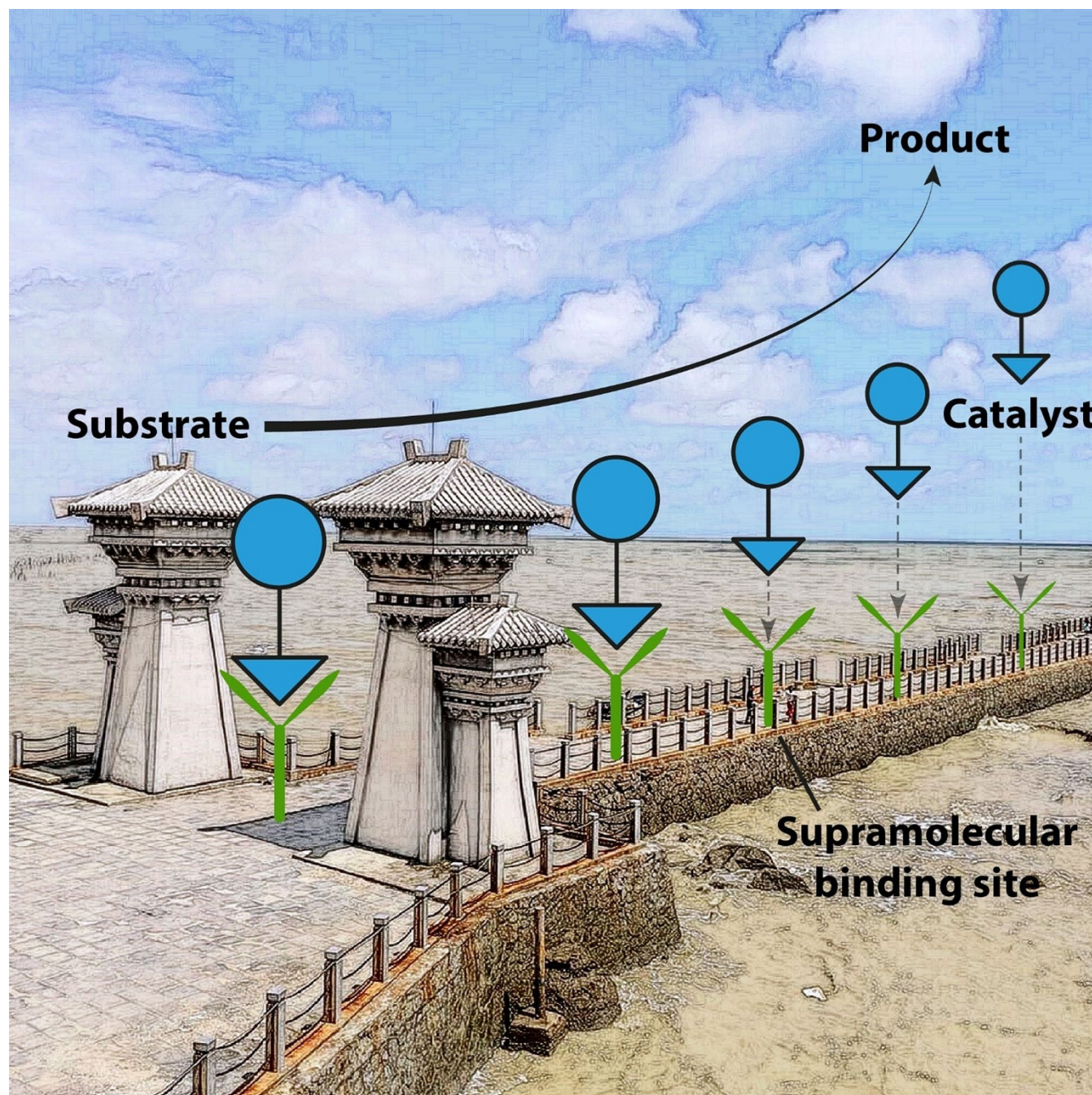Special Collection

# Supramolecular Strategies for the Recycling of Homogeneous Catalysts

Bo Zhang and Joost N. H. Reek*[a]

**Abstract:** Supramolecular approaches are increasingly used in the development of homogeneous catalysts and they also provide interesting new tools for the recycling of metal-based catalysts. Various non-covalent interactions have been utilized for the immobilization homogeneous catalysts on soluble and insoluble support. By non-covalent anchoring the supported catalysts obtained can be recovered via (nano-) filtration or such catalytic materials can be used in continuous flow reactors. Specific benefits from the reversibility of catalyst immobilization by non-covalent interactions include the possibility to re-functionalize the support material and the use as "boomerang" type catalyst systems in which the catalyst is captured after a homogeneous reaction. In addition, new reactor design with implemented recycling strategies becomes possible, such as a reverse-flow adsorption reactor (RFA) that combines a homogeneous reactor with selective catalyst adsorption/desorpion. Next to these non-covalent immobilization strategies, supramolecular chemistry can also be used to generate the support, for example by generation of self-assembled gels with catalytic function. Although the stability is a challenging issue, some self-assembled gel materials have been successfully utilized as reusable heterogeneous catalysts. In addition, catalytically active coordination cages, which are frequently used to achieve specific activity or selectivity, can be bound to support by ionic interactions or can be prepared in structured solid materials. These new heterogenized cage materials also have been used successfully as recyclable catalysts.

## 1. Introduction

Catalysis plays a crucial role in chemical process industry, as it generally leads to economically beneficial and sustainable chemical processes. As market demand for new products is continuously changing and the feedstock is changing from fossil to biobased, the demand for new catalysts is huge. Whereas homogenous catalysts can have specific advantages, typically high selectivity and activity under relatively mild conditions, the separation of catalyst from product needs to be addressed. Such separation should lead to a clean product and possible reuse of the catalyst, which is especially important when using valuable metal complexes in order to end with an economically effective process. As a result, multiple catalyst recycling strategies for homogeneous catalyst have been developed over the years, of which some are now commercially applied.[1–8] One popular strategy involves multiphase catalysis,[9–11] in which the catalysts and the substrate/product reside in different phases, and as such they can be separate based on their difference in solubility in immiscible liquids. Most popular is aqueous phase catalysis in which water-soluble catalysts are used in combination with an organic phase that contains the substrate, and this has for example resulted in commercial hydroformylation of propene. Also intensively studied is the immobilization of the catalysts to support material such as silica,[12–16] which enables the recycling by filtration of the supported catalyst or using the solid material in a continuous-flow reactor. Typically, immobilization is achieved by attaching a linker to the ligand that can be used to graft the complex to the support. Leaching of metal complexes from the ligand supported system, as well as general catalyst life-time are important properties to achieve high turnover numbers with the supported catalysts. Next to the covalent anchoring of catalysts, supramolecular anchoring has been explored. For these systems catalyst leaching and stability are also important issues, and as the catalyst is non-covalently attached this may be subject to the conditions applied. The reversible nature of non-covalent anchoring also allows release of the catalysts under certain conditions.[17] Next to the non-covalent anchoring of catalysts, the rapid development of supramolecular chemistry brings more opportunities for developing recyclable homogeneous catalysts. Larger well-organized structures are accessible by self-assembly strategies, such as metal organic cages (MOCs), metal organic frameworks (MOFs) and supramolecular gels, and such structure provide handles for new concepts in catalysis. The application of MOFs in catalysis is growing into a new field and has been reviewed by several groups,[18–24] and as such it will not be covered in this review. Supramolecular gels have a wide variety of potential applications and also have been used in the context of catalysis.[25,26] Typically, the formation of supramolecular gels is dominated by non-covalent interactions between low-molecular-weight gelators (LMWGs) to drive hierarchal self-assembly processes. The self-assembled soft materials can be used as carriers for catalytical active species like enzymes or metallic nanoparticles.[27–31] Also composite materials have been made by using building blocks that contain catalytic sites and these materials can be used as heterogeneous catalysts.[32–38] Also the field of supramolecular cages has grown enormously, and a huge variety of cage structures have been reported. Among the diverse set of applications, catalysis hold a prominent position.[39–43] Supramolecular cages can be used as catalyst or host a catalyst, and such systems can display higher activity, selectivity and stability as demonstrated for several different reactions, providing an interesting new tool in the development of catalytic processes. Because of the potential of these systems, caged catalysts have recently also

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been heterogenized with the aim to recycle catalytic supramolecular cages.[44–47]

In this review we discuss supramolecular strategies for catalysts recycling, without aiming to be comprehensive, but to demonstrate that new tools become available when catalysis and supramolecular chemistry are combined in a smart fashion (Figure 1). First, catalysts immobilization using supramolecular methods will be discussed, and this section is organized according to the type of interaction used for the non-covalent immobilization, including hydrogen bonding, electrostatic interactions, π-π stacking, and fluorine-fluorine interactions. In the second section self-assembled structures with catalytic functions are discussed. This includes the use of catalytically active gels and heterogenized supramolecular cages, which facilitate recycling of the catalysts and lead to enhanced stability. The recyclability of a catalyst system can be simply evaluated by the yield obtained in subsequent reactions, however this provides limited insight. For a comprehensive assessment reaction rates in subsequent reactions should be compared, in combination with retention/leaching of catalyst, and maximum cumulative TON. In most papers this data is not provided, but when available we will comment on this in the context of the evaluation of the recyclability.
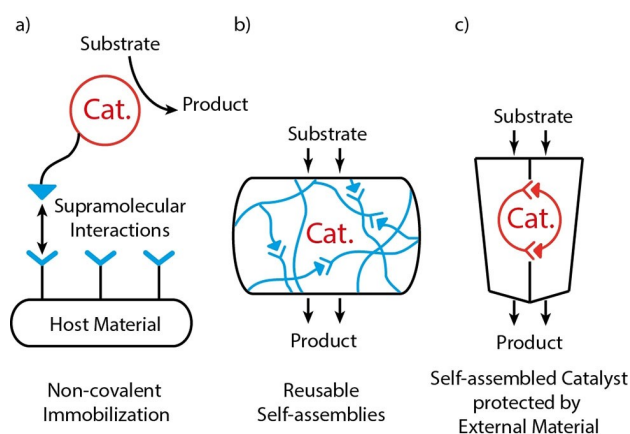


**Figure 1.** Supramolecular strategies for catalysts recycling; a) Non-covalent anchoring of catalysts; b) Catalyst immobilization in self assembled gel structures; c) Heterogenization of self-assembled caged catalysts.

## 2. Immobilization via non-covalent interactions

Immobilization of homogenous catalysts by anchoring it to a support is a generally employed strategy that allows recycling of homogeneous catalysts by filtration. In most reported examples the catalyst is covalently linked to the support. Supramolecular approaches in which the catalyst is anchored via non-covalent interactions are less frequently applied. Proper design of the supramolecular anchoring motif leads to sufficient binding strength to use the material as heterogeneous catalyst under the proper conditions. Meanwhile, non-covalent immobilization offers additional advantages. The immobilized catalysts can be released into the solution under certain conditions, allowing for example the replacement of catalyst when deactivated. Also, the catalyst can be released during the reaction to profit from the selectivity and reactivity of the homogeneous catalyst, to capture it on support after the reaction for recycling purposes.[48–51] The binding strength can be adjusted depending on the actual requirements imposed by the application.[48,52] Interestingly, relatively simple, or in some examples even no additional modifications, are needed to realize efficient supramolecular immobilization.

### 2.1. Catalyst anchoring by hydrogen bonding interactions

In 2001 a supramolecular approach was reported in which a palladium complex was non-covalently immobilized to a soluble dendrimer using a combination of multiple hydrogen bonds and acid-base interactions.[53] The urea adamantyl functionalized poly(propylene imine) dendrimer **1** was used in CHCl₃ as host to bind triphenylphosphine ligands that were functionalized with the complementary motif based on urea and carboxylic acid **2** (Figure 2). The supramolecular complex showed similar reactivity and selectivity as the unbound monomeric catalyst in an allylic amination reaction. The self-assembled catalyst system, with the palladium complexes **3** strongly bound to the dendrimer **1** were applied in a

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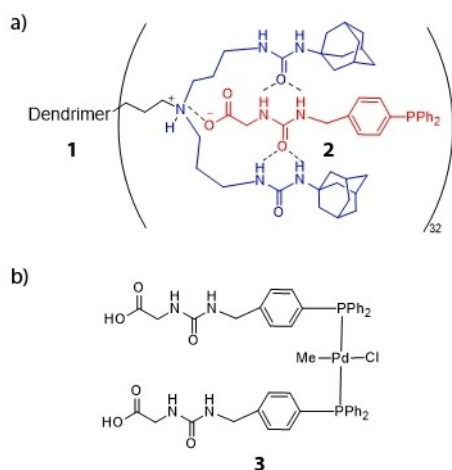
**Figure 2.** a) A functionalized triphenylphosphine ligand anchored to a dendrimer support via supramolecular interactions; b) The palladium catalyst based on the functionalized ligand that was used in a continuous flow reactor.

continuous-flow membrane reactor. Over 99% retention of palladium complex was observed after pumping 13 reactor volumes of solvent through the reactor and there was only little loss of catalytic activity after 10 h (1 h operational mode equals 1–2 reactor volumes being pumped through the reactor). These experiments demonstrate that supramolecular anchoring lead to sufficiently stable structures for application in continuous-flow reactors and as such it provides a valuable strategy for catalyst recycling.

The strategy was further extended to generate homogeneous catalyst that were anchored on insoluble silica support to be applied as heterogeneous catalyst.[52] A silica material functionalized with **4** containing similar binding motifs as dendrimer **1** was used as the host for anchoring of transition metal catalysts (Figure 3b). Various phosphine ligands able to
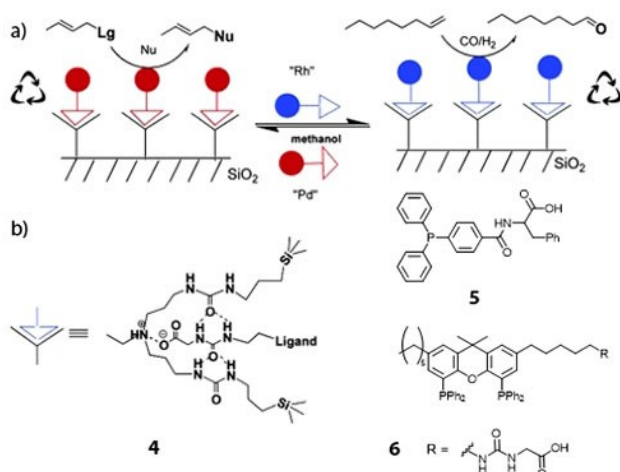


**Figure 3.** a) Supramolecular anchoring enables immobilization of transition-metal catalysts and reversible functionalization of support material; b) Functionalized silica supporting material and phosphine ligands. Adapted with permission from Ref. [52].

interact with the silica via hydrogen bonds and acid-base protonation were synthesized. Palladium and rhodium catalysts were investigated for allylic amination and hydroformylation respectively, after non-covalent grafting on the functionalized silica. The silica-supported catalysts generally showed lower catalytic activity compared to homogeneous system, which is typically observed for immobilized catalysts. The transition-metal catalysts were simply recycled after a reaction through a filtration procedure, allowing the use of the catalyst for multiple times. For example, a Pd catalyst based on functionalized ligand **5** could be reused four times with only a slight decrease in activity. As no leaching of the Pd catalyst was observed, decomposition of the palladium catalyst is likely responsible for the decrease in activity. The Rh complex based on functionalized bidentate ligand **6** was reused for 11 times without any loss of activity nor any leaching was observed. In addition, the silica support could be defunctionalized by washing with MeOH and subsequently the next set of catalysts could be installed by just mixing the components (Figure 3a).

The reversibility of the supramolecular anchoring also allows to use these materials in new reactor concepts. As such, the supramolecularly functionalized silica material was applied in a reverse-flow adsorption (RFA) reactor.[48] In such a reactor, a homogeneously catalyzed reaction is combined with a selective adsorption of the catalyst on a bed. Once the bed is saturated, the flow of the substrate feed is reversed and the adsorbed catalyst is fed back in the reactor, and adsorbed on the second bed. For this reversible adsorption the binding constant between absorbent and catalysts should be around $1 \times 10^3 \, \text{M}^{-1}$ to have maximum adsorption with sufficient reversibility. For this purpose, the binding affinity was adjusted by changing the number of hydrogen bonds. The base/acid interaction can also be modified, and the polarity of the solvent can be changed to further optimize the binding for this RFA reactor. Functionalized silica material **7** was utilized as absorbent for recycling of the catalysts formed by a rhodium precursor and the chiral ligand **8**. During the RFA experiment the reaction was catalyzed by complex **8** in homogeneous phase in the reactor, while the product flow passed through the adsorption bed II to separate transition-metal complexes from the product. Meanwhile, catalysts anchored on the adsorption bed I was desorbed by the substrate flow and started next round of reaction in the reactor (Figure 4a). The flow direction was changed after every certain period to enable recovery and recycling of transition-metal catalyst. Modelling of the system shows that in this reactor concept about 50% of the complex is at the adsorption bed, while 50% is in the reactor and involved as catalyst in the reaction. In this experimental set up, the rhodium catalyst was used for asymmetric hydrosilylation of acetophenone with comparable selectivity and activity as found for the homogeneously catalyzed batch reaction, and it was recycled up to 9 times (adsorbed and desorbed). The same catalyst could also be used in the asymmetric hydrogenation of methyl acetamidoacrylate, however, a decrease in activity was observed partly due to catalyst leaching under these conditions. In line with this, after five runs of adsorption/desorption, 6% of rhodium catalysts leached in the fifth cycle as confirmed by UV/Vis
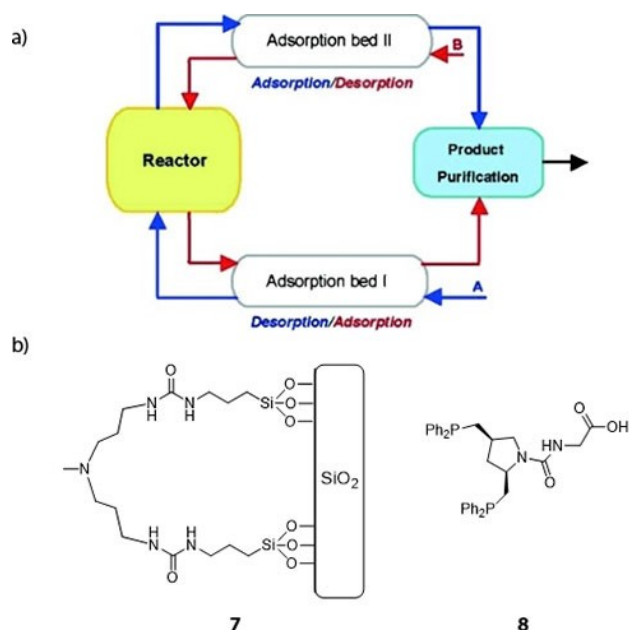
**Figure 4.** a) Schematic picture of a set-up of a Reverse-Flow Adsorption reactor; b) Silica absorbent and chiral phosphine ligand that was used in this reactor. Adapted with permission from Ref. [48].

analysis. In previous application of RFR's the metal and the ligand have been adsorbed separately, which in some cases leads to decomposition as the metal is not stable in absence of the ligand. By adsorbing the catalyst as a whole using supramolecular interactions this problem can be avoided demonstrating the benefit of the supramolecular approach.

**2.2. Immobilization based on electrostatic interactions**

In 2012 the synthesis of a pyridinium-tagged Ru-NHC-complex **9** (Figure 5) was reported, which is able to interact with sulfonated silica material **10** via an ion-exchange process.[54] The composite material **11** was applied in the metathesis reaction as a recyclable heterogenized catalyst. In a batch reaction, the heterogeneous catalyst **11** performed well and could be separated by filtration and reused multiple times. However, an obvious decrease in activity has been reported after running two cycles of RCM (ring-closing metathesis) reaction in continuous flow mode due to leaching of the ruthenium catalyst,
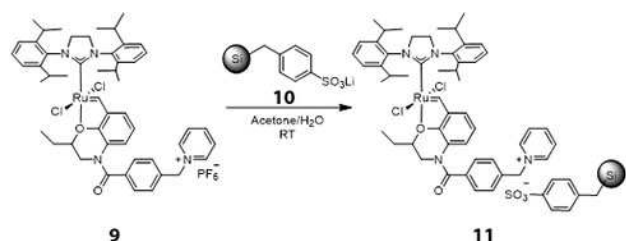
most likely via metathesis induced detachment of the ruthenium from the carbene anchor. The "split test" revealed that no catalytic reaction happened in the supernatant. After the reaction 0.03–4.6% of Ru residue was found in the product, depending on the type of solvent that was used, which indicates that the non-covalent interactions were sufficient for immobilization. Currently, the stability of the catalyst limits the use of the material in subsequent reactions.

In 2014[55] a Grubbs-Hoveyda ruthenium catalyst equipped with a quaternary ammonium group was reported and this complex was immobilized on the surface of siliceous mesoporous molecular sieves by electrostatic interaction (Figure 6). The activity of the heterogeneous catalyst related to the porous size of supporting material and the type of counterion of the ammonium group of the Ru complex. After optimization of the reaction conditions, a Ru complex **12** with Cl⁻ as counterion supported on SBA-15 was applied in the RCM, CM (cross metathesis), and enyne metathesis reaction. 2.6% of Ru leaching was observed in test reactions after 5 h. The stability of the heterogeneous composite material was demonstrated later to increase significantly by using the steric more bulky Ru catalyst **13**, immobilized on the same material.[56] The complex **13** supported on SBA-15 provided almost 5 times higher cumulative TON in RCM reactions than **12**/SBA-15 in a reusing experiment and has been also applied in a continuous flow reactor.

A series of silica materials grafted with imidazolium-based ionic liquid film has been developed by Gruttadauria's lab.[57–59] The catalysts, equipped with compatible functional groups were immobilized efficiently to the supported ionic liquid phase via electrostatic interactions. Taking the advantage of the unique physical property of ionic liquid, biphasic catalytical reactions were performed without requiring a large amount of expensive ionic liquid. Catalysts recycling and reuse was reported. These strategies have been successfully applied in proline-catalyzed asymmetric Aldol reaction[57,58] and TEMPO-catalyzed alcohol oxidation.[59]

In 1999 an approach was reported in which homogenous catalysts were anchored on $Al_2O_3$ support using heteropoly acid (HPA) as anchoring agents.[60] Since then, this strategy has been intensively studied to non-covalently support transition-metal catalysts with the aim to recycle and reuse.[61–65] The strategy has been extended to the use of mesoporous silica **14** (KIT-6-
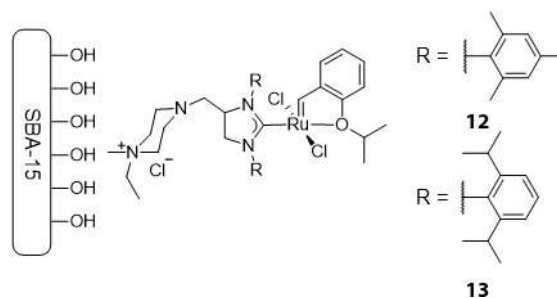


**Figure 5.** Immobilization of a pyridinium-tagged Ru catalyst on a sulfonate functionalized silica support, using ionic interactions.



**Figure 6.** Immobilization of quaternary ammonium-tagged Ru catalyst on siliceous mesoporous molecular sieves SBA-15 for the application in metathesis reactions.

NH$_2$) as support that was functionalized with Brønsted base on the surface (Figure 7).[66] The acid base interactions were supposed to offer decent stability by salt formation to keep the heteropoly acid (HPA, in this work silicotungstic acid was used) on the surface. Positively charged catalytic complexes were absorbed to HPA via electrostatic interactions. Various chiral Rh catalysts were immobilized on the silica-HPA composite and applied to a continuous-flow reactor for asymmetric hydrogenation reaction. Excellent activity and enantioselectivity for a broad substrate scope were obtained. No loss in activity or leaching of the rhodium complex was observed after operating the reactor for 90 h.

## 2.3. Anchoring using π-π stacking

Catalyst immobilization using π-π stacking has been explored for various applications in recent years. Without much modification, carbon-based materials like carbon nanotubes[51,67–69] or graphene[50,70–76] can be applied as the support. It has demonstrated that pyrene-tagged Ru catalyst **15** could be adsorbed to the surface of single-walled carbon nanotubes (SWCNTs, Figure 8).[51] The binding strength by π-π stacking is
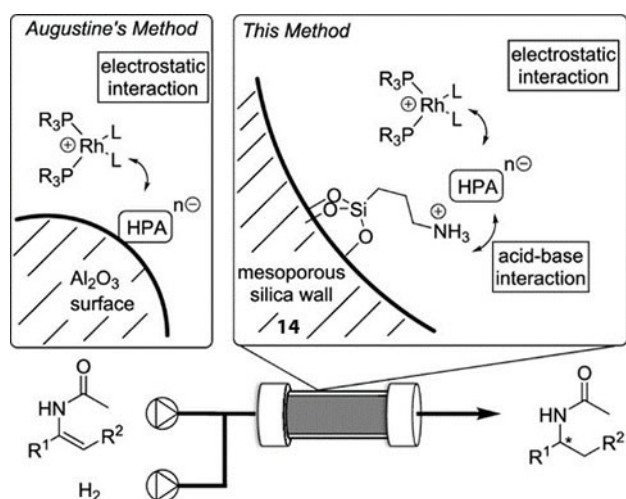
**Figure 7.** Immobilization of Rh catalysts to mesoporous silica materials using heteropoly acid to anchoring cationic complexes by ionic interactions. Adapted with permission from Ref. [66].
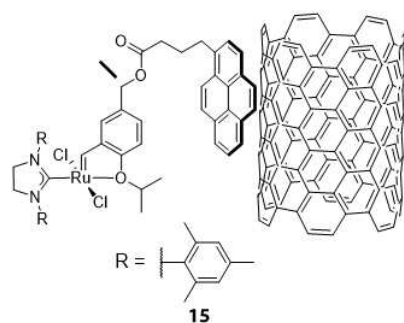
highly dependent on the solvent and temperature. When acetone is used as the solvent, no desorption of catalyst was observed below 25 °C after 20 h, while around 80% of the Ru complex was in solution after heating at 56 °C for 24 h. For the catalyst recycling studies, a series of RCM reactions were performed at 35 °C. After the reaction, the catalyst is re-adsorbed by stirring the system at 0 °C for 30 min. The **15**-SWCNTs catalyst was isolated by filtration and was reused up to 7 times. However the recyclability of the catalyst system was far from ideal as, generally, a much longer reaction time was required in subsequent reactions in order to reach a similar yield, indicating a decrease of catalytic activity. Interestingly, because the catalyst is non-covalently anchored, the SWCNTs as supporting material can also be recycled by removing the decomposed catalyst by just washing with THF. The recovered SWCNTs can be refunctionalized with catalyst and with similar properties as the original material.

The temperature dependence of binding strength using π-π stacking was further expored using Co-nanoparticles on graphene as support.[50] Pyrene-tagged Pd complex **16** was anchored to the Co/C nanoparticles at 25 °C in water. The complex could be desorbed at 100 °C to catalyze the hydroxycarbonlyation of aryl halides in homogeneous solution. In this way, grafting and releasing of the palladium catalyst was controlled by the temperature (Figure 9). This release-capture strategy was coined a "boomerang" catalyst system, in which the supramolecular anchoring enabled the reversible binding of the catalyst by just changing the conditions. The magnetic properties of the Co/C nanoparticles allowed the NHC-Pd complexes able to be separated by magnetic decantation at room temperature and the catalyst was reused for more than 16 times. The system revealed decent recyclability, with 30% loss of palladium content from material **17** was observed after 10 runs, as confirmed by ICP-AES analysis (initial content: 0.1 mmol/g, content in the 10$^{th}$ run: 0.07 mmol/g). No significant catalyst deactivation was observed in the first seven reactions.

Immobilization of pyrene functionalized NHC-Pd and NHC—Ru complexes was explored using reduced graphene oxide **20** (rGO, Figure 10) as the support material.[70] In contrast to SWCNTs and graphene support, the binding strength based on stacking between the transition-metal complexes and rGO **20** is not influenced by solvent and temperature. Interestingly,
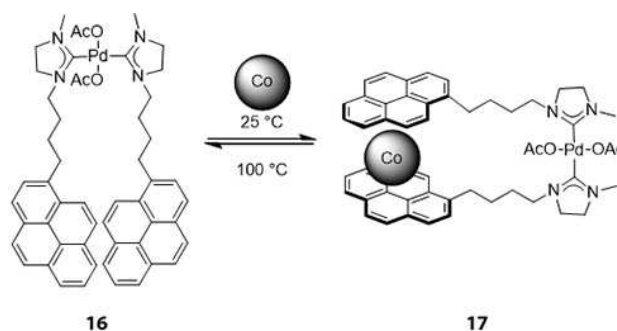
**Figure 8.** Pyrene-tagged Ru catalyst that is anchored to SWCNTs via π-π stacking.

**Figure 9.** Reversible graphing of Pd complex to Co/C nanoparticle.
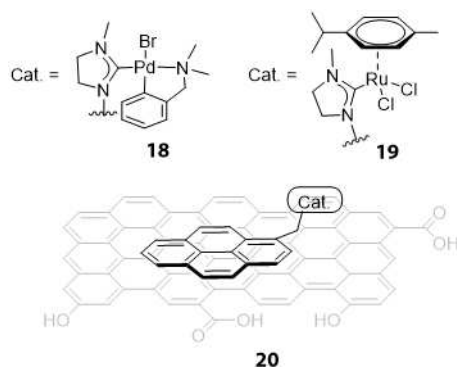
**Figure 10.** Immobilization of pyrene functionalized NHC catalysts on rGO **20**.



**Figure 11.** Immobilization of perfluoro-tagged Pd complexes (**22**) to fluorous reversed-phase silica gel **21**.

the hybrid materials generally revealed a higher activity compared to their parent catalysts in solution. A possible reason could be that the rGO promote the interaction between the catalysts and substrates. The heterogeneous catalyst **18**-rGO was used for hydrogenation and nitro reduction. The formation of Pd nanoparticles on the surface of rGO **20** was observed, which might be the real catalytical active species. **19**-rGO was applied as catalyst material for alcohol oxidation reactions. Both Pd and Ru attached materials were separated by filtration after the reaction and were reused for up to 10 times in small-scale experiments (1 mol% catalyst loading for hydrogenation and 2 mol% for alcohol oxidation) and 3 times in large-scale experiments (0.01 mol% of **18**-rGO and 0.03 mol% of **19**-rGO) without loss of catalytic activity. In 2015, the same group has reported hydrodefluorination catalyzed by a catalyst material in which both **18** and **19** are immobilized on rGO.[71] In addition, bimetallic catalyst equipped with two pyrene moieties were further developed for different types of catalytic reactions.[72,74]

## 2.4. Immobilization of perfluoro-tagged catalysts

Perfluoro compounds or heavily fluorinated molecules exhibit both hydrophobic and oleophobic features and display a preference to dissolve in fluorous solvent like perfluoroalkanes and perfluorodialkyl ethers. Taking advantage of these properties, several methods have been reported that allow recycling of catalysts, such as fluorous biphasic catalysis,[77,78] separation using fluorous solid-phase extraction (FSPE),[79–81] or immobilization of perfluoro-tagged catalyst using F–F binding.[82–84] While biphasic catalysis requires expensive perfluorinated solvents, the immobilization using fluor-fluor interactions does not and as such provide an alternative for catalysts recycling. Along these lines, the immobilization of bis(triphenylphosphane)-palladium complex **22**, which is functionalized with perfluoroalkyl chains, to fluorous reversed-phase silica gel **21** as support material has been reported (Figure 11).[82] The composites were applied in Suzuki and Sonogashira coupling reactions. The Pd catalyst was collected after the reaction by decantation. The catalyst were able to be reused up to 3 times and a palladium leaching of 1.6% was reported.
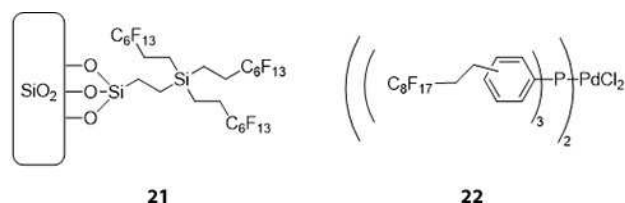
In 2005, a fluorinated analogue of polyglycerol ester-based dendrimer (**23**) was synthesized aiming for the binding of the perfluoro-tagged Pd catalyst **24** in DMF (Figure 12).[83] The supramolecular complex **25** was used as catalyst for the Suzuki coupling reaction and provided a significantly higher yield compared to the parent catalyst. The explanation provided is the enhancement of the solubility of the fluorous catalyst by binding to the dendrimer. Recycling of the catalyst was enabled by precipitation with a mixture of DEM (dimethoxyethane) and water followed by filtration. The composite **25** was reused 3 times without significant decrease in activity providing over 96% yield of the product with 0.5 mol% catalysts loading.

Comparing to other non-covalent interactions, fluor-fluor interactions have been less applied in catalyst immobilization.

## 2.5. Anchoring via other supramolecular interactions

The initially reported Revers-Flow Adsorption (RFA) reactor in which catalyst recovery is based on reversible non-covalent immobilization to the adsorption bed, required further optimization due to limitation in terms of adsorption kinetics.[48] For this reason, the same group explored other supramolecular interactions, and also explored these materials in batchwise reactions.[49] These new materials were explored in the rhodium catalyzed hydroformylation reaction. A XantPhos-based ligand functionalized with a pyridine moiety was synthesized. Three types of materials were explored as support materials to which the catalyst can be bound via the pyridyl function; 1) Brønsted acid-tagged silica; 2) neutral γ-alumina (Lewis acid), and
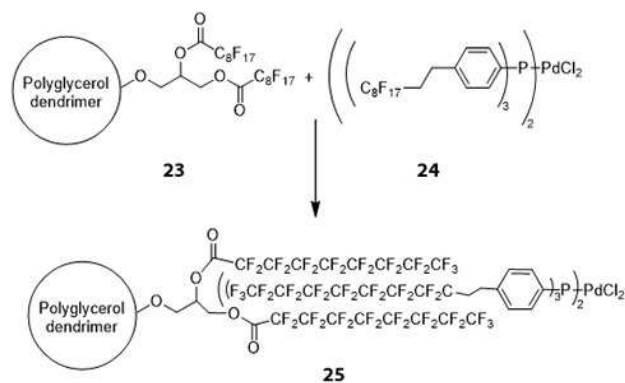


**Figure 12.** Supramolecular anchoring of perfluoro-tagged Pd complexes to the fluorinated polyglycerol ester based dendrimer as support.

3) silica-alumina (contains both Brønsted and Lewis acid sites). While the first two support materials showed poor adsorption ability, silica-alumina material was able to offer a binding constant of $4 \times 10^5$ to XantPhos-Rh-catalyst **26**. The strength of binding was decreased by adding THF or by using support materials with capped silanol groups using dimethyldimethoxysilane as reagent for the support functionalization. The end-capped silica-alumina was used as the adsorbent in RFA as this required a lower affinity. After using the catalyst in a homogeneous phase batch reaction, the catalyst was scavenged by the capped silica-alumina and separated from reaction products. Subsequently, the absorbent bed was washed in reversed flow using THF for desorption to reintroduce the catalysts in the reactor for the next batch wise reaction (Figure 13). In order to maintain the selectivity, an additional equivalent of ligand was added to each batch reaction, to compensate for ligand loss or decomposition (hydroformylation reactions are always executed in excess of ligand). The catalyst was recycled successfully four times.

Along the same lines, a combination of Zn-porphyrin functionalized silica **27** and amine-functionalized Xantene-based bidentate diphosphine ligand **28** were studied for supramolecular anchoring and subsequent use as supported transition-metal catalysts (Figure 14).[52] Pd or Rh complexes
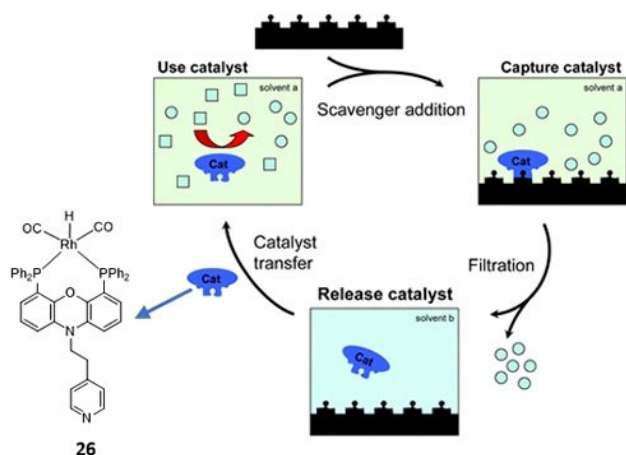
based on ligand **28** were anchored to the Zn-porphyrin functionalized silica **27** via pyridine coordination to the zinc. A decrease in reactivity was observed for the heterogenized Pd-**28** compared to the homogenous analogue when applied in the allylic alkylation reaction. The heterogenized palladium catalyst was separated by filtration and the catalyst was recycled to perform two more reactions. The heterogeneous Rh catalyst was applied in the hydroformylation of 1-Octene, and this catalyst showed a similar activity compared to the catalyst immobilized via hydrogen-bonding *vide infra* (Figure 3).[52] The catalyst could be recycled by filtration and reused for 4 reactions, however, a loss in activity after each run was observed. The reason for the loss in activity was the desorption of the catalyst caused by conversion of the amine on the ligand **28** into the imine via a condensation reaction with the aldehyde product (nonanal), lowering the affinity for the zinc. By washing the Zn-porphyrin functionalized silica with MeOH, the non-covalently anchored catalyst could be removed, and as a result the Zn-porphyrin functionalized support material could be reused by binding a new catalyst.

# 3. Catalysts recycling based on supra-molecular self-assemblies

Catalysis is a central research topic in supramolecular chemistry,[85–89] however, generating self-assembled supramolecular structures with catalytic functions that allow separation an recycling is still challenging. One of the major challenges involves the stability of the self-assembled structure during catalytic or recycling process. In this part of the review, we highlight a few examples in which catalysts were immobilized within self-assembled structures with the aim to provide recoverable catalyst systems.

## 3.1. Reusable supramolecular gels

Supramolecular gels can be generated by coordination chemistry using multidentate ligands, and such materials have been used for catalytic purposes.[25–26] As coordination bonds can be relatively strong, the resulting gels are likely to have good mechanical stability.[32–33] Further enhancement of the stability has been realized by post-modification.[37] In contrast, the gels formed by pure organic building blocks are normally too fragile for catalysis application and such materials could rarely be reused.[38]

A metallogel **28** formed by coordination of a *C*3-symmetric triphosphine building block **27** and Pd(CH$_3$CN)$_4$Cl$_2$ via self-assembly (Figure 15). The gel was used as catalyst in the Suzuki-Miyaura reaction using aryl halide and arylboronic acids as the substrates, under atmospheric condition in aquaous solution.[32] The palladium complexes have a dual role, they are part of the network to form the gel and are the catalytic active sites. The supramolecular material was demonstrated to be highly

**Figure 13.** Catalyst recycling in batchwise reaction realized by reversible supramolecular adsorption. Adapted with permission from Ref. [49].
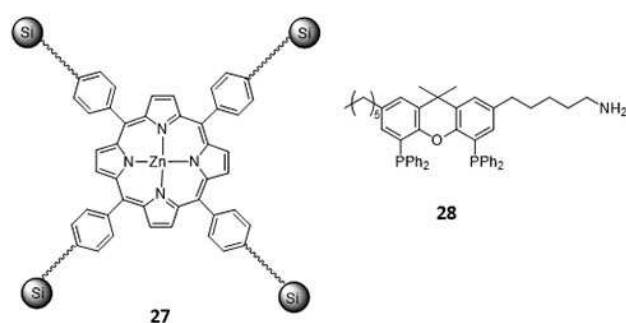
**Figure 14.** Zn-porphyrin functionalized silica support material (**27**) that can bind Xantene-based bidentate diphosphine functionalized with amine group (**28**).
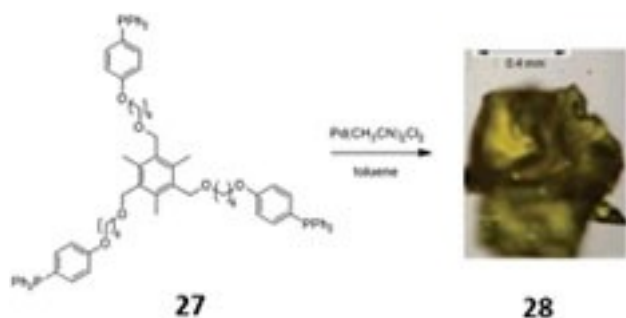
**Figure 15.** Metallogel (**28**) formation formed via coordination driven self-assembly of tridentate **27** and a palladium precursor. Adapted with permission from Ref. [32].

catalyst was used in five subsequent reactions providing similar product yields. However, the individually time to finalize each run of the reaction has not been reported, therefore the change on catalytic activity after recycling cannot be evaluated. In addition, the novel material was applied as catalyst in a Diels-Alder reaction, again displaying much better catalytic activity in terms of substrates conversion compare to the homogeneous phase reaction. The kinetically favorable endo isomer was the major product in this reaction, which might also be the result of the preorganization of the guests inside the cavity.

Zhang and coworkers have synthesized a porphyrin-based ligand functionalized with amine groups (**31**) and reported gelation via a condensation reaction with glyoxal (GO) (Figure 17).[33] In order to enhance the stability and reusability of the gel **32**, the imine group was further reduced by post-modification. After metalation with various metal ions, the porphyrin-based gels were able to absorb $CO_2$ and catalyze cycloaddition of epoxides. The Zn analogue **34** exhibited the best performance. The post-modified Zn-porphyrin gel could be reused 5 times without a significant change in structural and catalytic features. Interestingly, the imine analogue, the material before modification, was also used but showed a decrease in product yield after 3 runs.

reactivity and could be used in four consecutive reactions offering over 90% product yields in 3 hours.

The group of Ma has developed a supramolecular gel based on Co(II) metal-metalloporphyrin **30** (Co-MMPG).[37] The gel was supposed to be formed through two steps: first, the carboxylic acid group of Co-porphyrin **29** coordinates to Al to form a porphyrin-Al cluster. Subsequently, π-π stacking between porphyrin layers leads to aggregation of the clusters. Within the network, two units of Co-porphyrins, connected by the Al—O—Al moieties, form a binding pocket, which could be utilized for catalytical purposes (Figure 16). The Co-MMPG **30** was first used as catalyst material for acryl-transfer reactions with pyridine or imidazole functionalized compounds as substrates, to demonstrate the effect of the binding pocket by catalysis via guest encapsulation. A significant increase in the conversion and reaction rate compared to the homogeneous phase reaction with Co-TPP or the MOF analogue was observed. The preorganization of substrates inside of the binding pocket was proposed be the reason for the enhanced performance in catalysis. The gel **30** was sufficiently stable for recycling and the
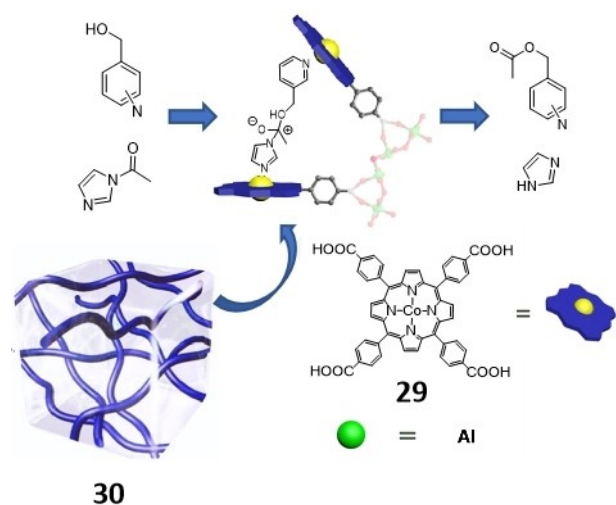
Recycling of supramolecular gels formed by purely organic building blocks is challenging, as they usually exhibit mechanical fragility. A organic hydrogel was produced in 2009,[38] based on the self-assembly of the L-proline-based building block **35** using a combination of hydrogen bonds and hydrophobic interactions (Figure 18). Under optimized reaction conditions, the hydrogel **36** could be applied as catalyst in the asymmetric aldol reaction providing excellent yield and stereoselectivity. Interestingly, the gel was sufficiently stable for recycling and as such was used for at least two runs. Moreover, given the thermal reversibility and pH responsiveness, the supramolecular gel could be regenerated when it was mechanically broken.



**Figure 16.** Schematic picture of Co-MMPG **30** gel material and the catalytic acyl transfer reaction performed in the cavity. Adapted with permission from Ref. [37].
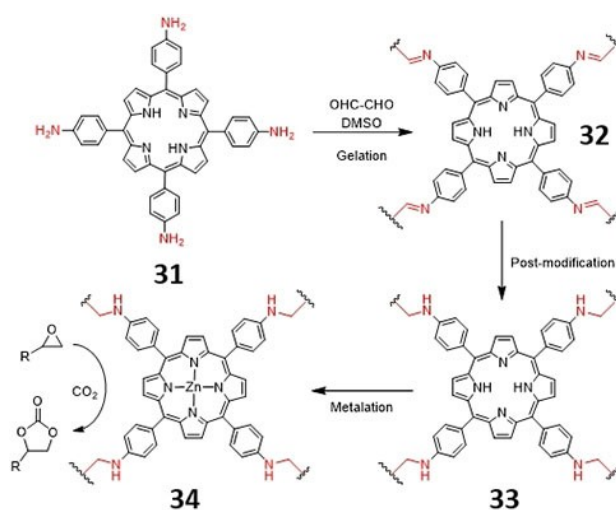


**Figure 17.** Synthesis of porphyrin-based supramolecular gel **34** via condensation and post-modification.
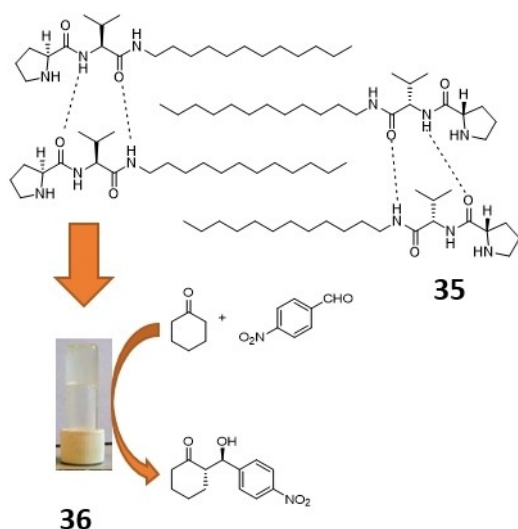
**Figure 18.** Gelation of L-proline-based building block **35** based on hydrophobic effects, and it application in the Aldol reaction. Adapted with permission from Ref. [38].



**Figure 19.** Immobilization of negative charged tetrahedral cage **36** onto catanionic polymer via electrostatic interactions. Adapted with permission from Ref. [49].

### 3.2. Enhanced stability of catalytic self-assemblies with external support

Supramolecular cages provide unique objects to control catalytic reactions by second coordination sphere effects as a special environment within these cages is created. By encapsulation of reactants into the cavity, sometimes next to an active site, supramolecular cages can accelerate reactions by preorganization,[90,91] by stabilization of transition states,[92] or can control the (regio)selectivity.[93] Whereas, there are many examples of applications of such supramolecular cages in catalysis, the recovery and recycling is rarely reported. Many of these supramolecular cages that are prepared by coordination chemistry are charged, and it was recently demonstrated that this charge could be used to immobilize such systems onto polymeric support.[46] In addition, porous materials have also been applied on supramolecular organogel and coordination driven self-assemblies for increasing their recylability.[35,47,94]

The Raymond group has developed a unique tetrahedral cage **36** formed by coordination of bis-catecholate ligands to Ga (III) corner stones. This supramolecular cage is negatively charged, which enabled encapsulation of positively charged substrates into the well-defined cavity for catalysis.[95–100] Lately, Toste and Raymond have attempted to pack the cage **36** in cross-linked polymers via electrostatic interactions (Figure 19).[46] The ammonium cations functionalized on polymer chains were interacting with the exterior of the cage and left the cavity empty for catalytic reactions. The performances of the resulting heterogeneous catalysts were evaluated in the Aza-Prins and Aza-Cope reaction. Compare to the original soluble coordination cage **36**, the heterogeneous version provided a higher yield in the case of Aza-Cope reaction under optimized reaction conditions and, importantly, the catalyst material could be reused 18 times in batch reactions. In addition, it was used as catalyst material for 60 h in a
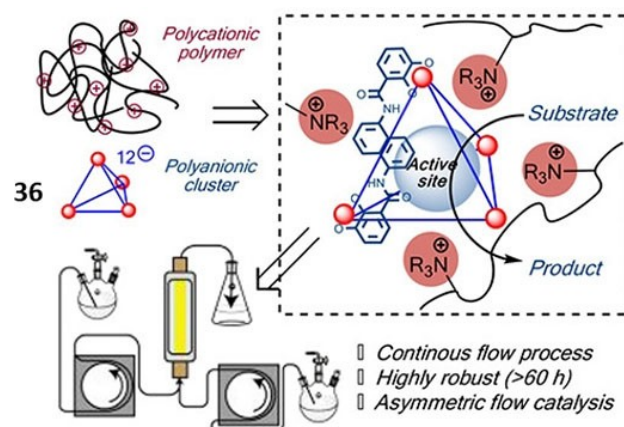
continuous flow mode, with neither significant loss of activity, nor detectable leaching of Ga (III). Interestingly, after immobilization, the reactions could be carried under ambient atmosphere and degassed solvents were not required, while the cage homogeneous phase trends to be oxidized under these conditions. Furthermore, the enantiopure cages were loaded to the polymer material as catalyst for asymmetric Aza-Cope reactions. Evidence shows that the polymer supported catalyst is less prone to racemization of the cage.

Jierry and coworkers described a novel approach to significantly improve the mechanical stability of a supramolecular organic hydrogel with the help of porous material.[35] A water-soluble bis-phosphorylated heptapeptide was chosen as the precursor of the gelator **37** (Figure 20). Upon addition of alkaline phosphatase (AP), the formation of a hydrogel was observed immediately. This enzyme-mediated gelation was then applied in an open-cell polymer foam, where AP was immobilized on the inside wall of the porous material. By passing through a solution of the bis-phosphorylated peptide, the catalytically active supramolecular hydrogel was
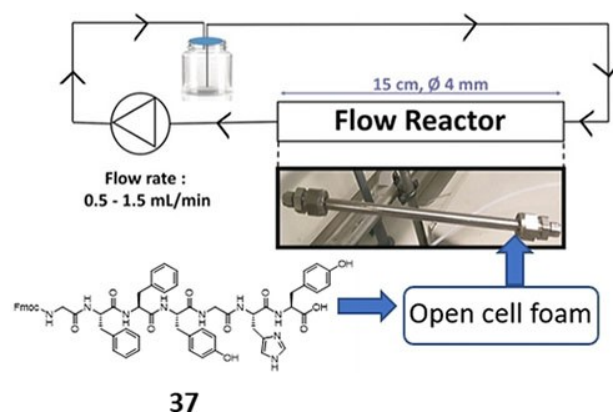


**Figure 20.** Catalytic hydrogel formed by heptapeptide **37** in open cell foam and applied on continuous flow reactor. Adapted with permission from Ref. [35].
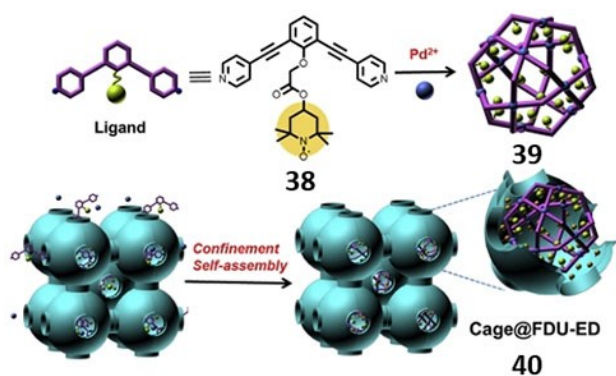
**Figure 21.** Self-assembly of coordination cage **39** inside the porous material. Adapted with permission from Ref. [47].

successfully grown inside the polymer. The gels presented esterase-like catalytic activity in hydrolysis and several (unactivated) esters were successfully converted to the corresponding carboxylic acids. In addition, the hydrogels could also be used for kinetic resolution. While the non-supported gel could only be used once for a catalytic reaction, the foam material was sufficiently stable to be used in the flow reactor to catalyze the hydrolysis of esters in five subsequent reactions without significant loss of activity.

A similar strategy was used to generate coordination assemblies in porous materials.[47] $[Pd_{12}L_{24}]^{24+}$ cage **39**,[101] which is endohedrally functionalized with TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxyl), was assembled in the cavity of amino-functionalized mesoporous carbon FDU-ED foam (Figure 21). As the structure characterization of cage that was prepared inside the porous material was difficult, a series of experiments was carried out to provide indirect evidence of cage formation. The heterogeneous catalyst Cage@FDU-ED **40** was studied for a one-pot two step reaction: first, oxidation on 4-nitrobenzyl alcohol was promoted by TEMPO using $PhI(OAc)_2$ as co-oxidant generating the corresponding aldehyde. This reaction was followed by a Knoevenagel condensation of the oxidized product with malononitrile promoted by the amino moieties. Comparing to the free ligand or cage in solution, Cage@FDU-ED **40** was able to accelerate the first step of the reaction. The heterogeneous catalyst could be recycled and reused at least 5 times with similar catalytic activity and over 90% yield. The catalyst system was further used for various substrates and revealed decent activity. This work is an interesting extension of work the same group who reported also the self-assembly of catalytically active metallacycles prepared within mesoporous carbon.[94] The confinement helped to increase the stability and thus the recycle-ability of the macrocycle, next to the improved performance in the catalytic reactions.

## 4. Conclusion and Perspectives

Supramolecular chemistry has provided many new tools for catalysis, including possibilities for catalysts recovery and recycling. Supramolecular immobilization of homogeneous

catalysts to a solid (or soluble) support presents a general strategy and several different types of non-covalent interactions have been used for this purpose. Typically, catalysts functionalized with binding motifs complementary to that of the support are used. The supramolecularly anchored catalysts materials allow recycling of the catalysts via filtration or such materials can be used in continuous flow reactor. For these applications the binding strength should be sufficiently strong, as otherwise catalyst leaching will occur during the recycling. The reversibility of supramolecular immobilization also provides new recycling concept such as reverse flow reactors in which the catalyst is captured after application in homogeneous phase, and re-introduced by desorption upon reversing the direction of the flow. The binding strength can also be dependent on the conditions such as solvent and temperature, and this is the basis for catalyst recycling via boomerang concepts, i.e. catalysis in a homogeneous phase under conditions that are different from those during recycling when the catalyst is back on the support. The binding strength between the catalyst and support is crucial in these concepts, and can be controlled by design of the motif. An additional interesting advantage of the reversible binding of the catalyst to the support, is that the catalyst can be replaced when it is deactivated and as such the support material can be reused, which is hardly possible with covalent strategies.

Next to supramolecular attachment of catalyst to support, support materials can also be made by self assembly, a research field that is still at the early stage. The stability of materials generated by self-assembly, such as gels, is still the main challenge. Supramolecular gels have been used as catalyst materials and mainly metallogels that are formed by coordination chemistry displayed sufficient stability for catalyst recycling purposes. In addition, new concepts have been reported such as the application of coordination cages that are incorporated to porous support. Although so far these supramolecular catalyst recovery strategies are merely out of academic interest, we believe it is a matter of time before these concepts turn into application.

## Conflict of Interest

The authors declare no conflict of interest.

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