Chapter 16

Green Chemistry of Recoverable Catalysts

Rasmi P. Bhaskaran and Beneesh P. Babu

1 Introduction

The recovery of catalysts after the completion of a reaction is of great importance in green chemistry [1]. Green chemistry addresses the impact of any process on the environment, and it is primarily concerned about preventing pollution [2]. Catalysis plays a vital role in the chemical industry [3]. The waste generated in chemical synthesis is mainly due to the usage of stoichiometric reagents, especially the metal-based reagents [4]. For example, stoichiometric reducing agents, both metals (Na, Mg, Zn, Fe) and metal hydrides ($LiAlH_4$, $NaBH_4$, etc.), oxidizing agents such as permanganate, manganese dioxide, and chromium(VI) reagents are the commonly used ones. Reactions such as sulfonation, nitration, halogenation, diazotization, and Friedel–Crafts acylation employ stoichiometric amounts of mineral acids (H_2SO_4, HF, H_3PO_4) and Lewis acids ($AlCl_3$, $ZnCl_2$, BF_3) [5].

The broad classification of catalysis is heterogeneous and homogeneous catalysis. In heterogeneous reactions, the phase of the catalyst is different from that of the reactants, and hence, the separation of the catalyst from the reaction medium is relatively easy. On the other hand, in homogeneous reactions, the catalyst and other reactants are in the same phase and are miscible with one another [6]. Solvent extraction, [7] filtration, nanofiltration, [8] catalyst leaching, chemical precipitation, [9] magnetic recovery, [10], and adsorption are catalyst recovery techniques typically employed in industrial and pharmaceutical processes. Nanofiltration is a relatively new membrane filtration technique used only in the homogenous process, and the catalysts are immediately reused. Materials such as activated carbon and ion exchange resins are used

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G. Anilkumar and S. Saranya (eds.), *Green Organic Reactions*, Materials Horizons: From Nature to Nanomaterials, https://doi.org/10.1007/978-981-33-6897-2_16

in the adsorptive recovery techniques and can include the recovery of either homogeneous catalysts or homogeneous ligands/catalysts. Magnetic regeneration of the catalysts allows the easy retrieval of catalysts with minimal loss.

2 Classification

Catalyst recovery can be broadly classified based on the recovery techniques used, and the choice of method for the catalyst separation is dependent on the nature of the catalysts. The separation techniques are time-consuming and have the limitations of cost, efficiency, generation of secondary wastes, etc. [11].

2.1 Metallodendrimers-Dendrimers Supported Catalysts

A widely used method for the easy recovery of the catalyst is the attachment of the metal catalysts to a solid support [12]. Generally used supports include the organic, inorganic, and hybrid, which work through heterogeneous catalysis. The solid support silica is the universal inorganic support used because of its chemically inert nature and physical strength. But the catalyst efficiency in this type of heterogeneous catalysis is inferior due to the very slow diffusion of the catalyst into the reaction medium, which decreases the rate of mass transfer and also the generally less activity of heterogeneous catalyst compared to the homogeneous ones. These limitations focus on the development of soluble catalyst support, which makes the reaction medium seamless. Dendrimers are such types of soluble catalyst supports used. The globular macrostructure of such supports enables the catalyst recovery effortless, and it is suited for membrane filtration [13]. The first example of a recoverable metallodendritic catalyst was reported in 1997 by Reetz for the Heck reaction using Pd dendrimers derived from the dendritic phosphines [14]. Potentially speaking, a dendrimer can be considered as a homogenous catalytic system as it is a combination of a large number of monomeric units with active sites. The total catalytic features such as selectivity, stability, and recyclability depend on the dendritic architecture of the metallodendrimers [15] (Fig. 1).

A copper-free recoverable dendritic palladium catalyst for the Sonogoshira reaction was reported in 2003 by Heuze and co-workers [16]. The catalyst prepared bears two cyclohexyl substitutions on the phosphorous atom, and the catalyst is quickly recovered and reused by a simple precipitation method. They have developed three generations of the dendritic palladium complexes by treating $Pd(OAc)_2$ with aminophosphines. The catalytic activity of the synthesized compounds was tested on the coupling between phenylacetylene and iodobenzene or bromobenzene in a copper-free Sonogashira procedure (Scheme 1). The first two generations of the complex showed excellent catalytic activity. Still, for the third generation complex, the activity was less because of the increased steric effect of the dendrimer branch.

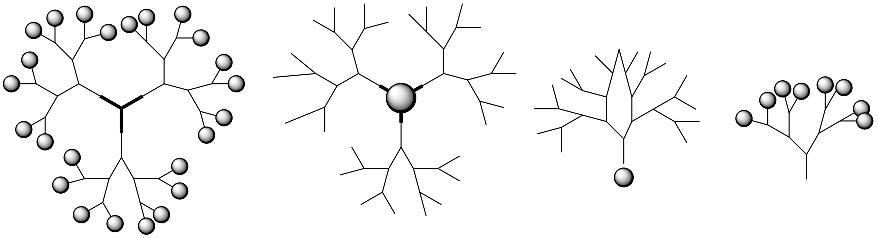
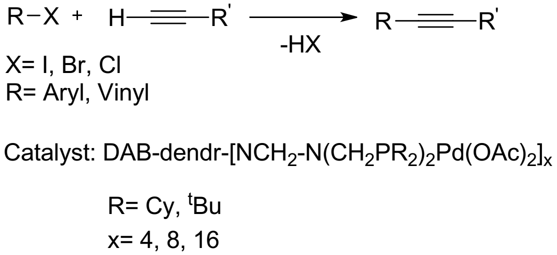
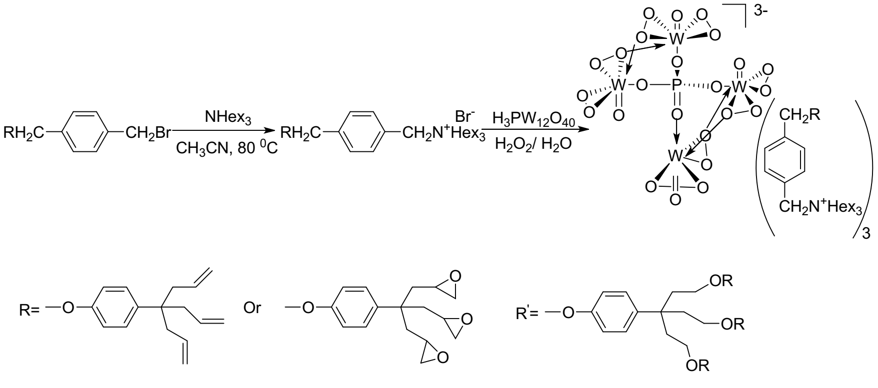


Fig. 1 Dendrimer architectures

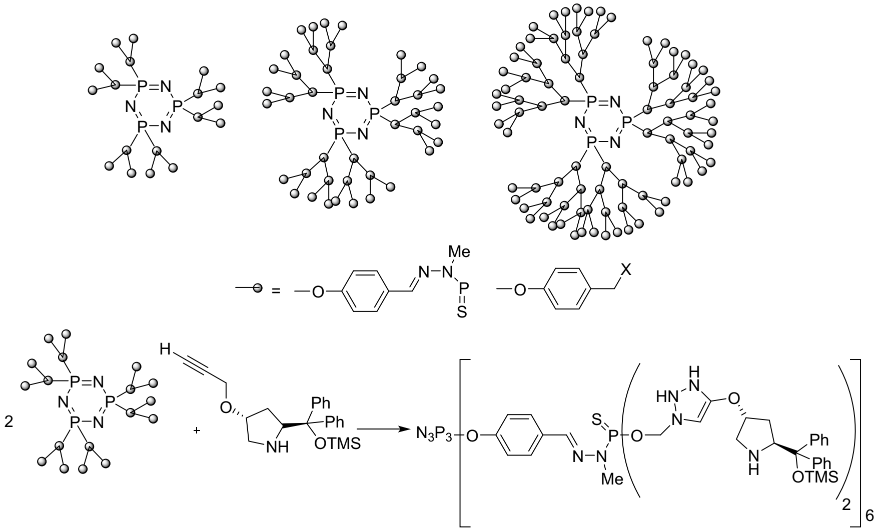
Scheme 1 Dendritic Pd catalyzed Sonogoshira reaction



In the year of 2004, Nlate and co-workers synthesized a stable polyoxometallate (POM) centered dendrimer and studied its catalytic activity in different oxidation reactions [17]. The core present in the dendritic catalyst was peroxophosphotungstate and was developed by the ionic bonding approach (Scheme 2). The application of this catalyst lies in the oxidation reactions using peroxides, and they were found to be highly air-stable and recoverable. The catalyst was efficient for performing the epoxidation of the alkene, selective oxidation of sulfide to sulfone, and also on the oxidation of cyclohexanol to cyclohexanone. The bulkier branches surrounding



Scheme 2 POM-centered dendrimer synthesis



Scheme 3 Preparation of Azido terminated phosphorous dendrimers

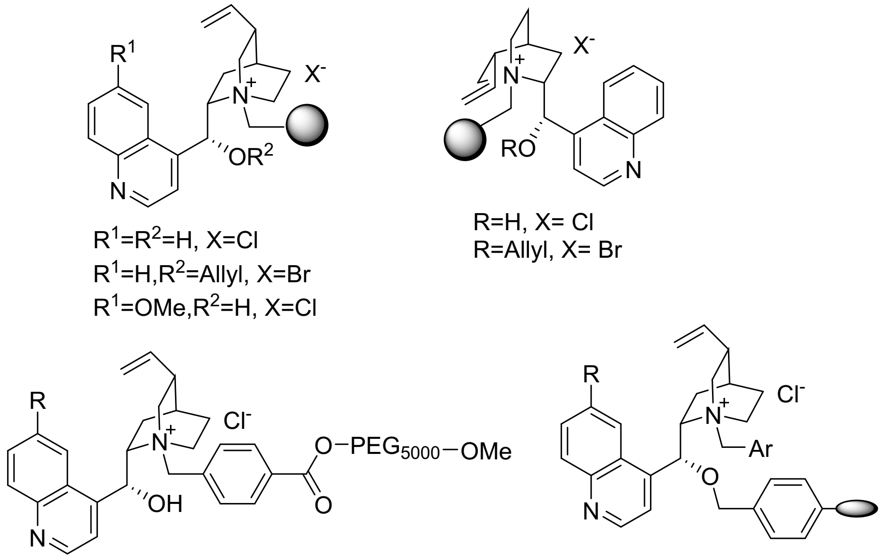
the POM center increase the stability of the catalyst, which prevents it from the degradation.

An efficient catalyst supported on phosphorous dendrimers and nanobeads of Co/C for the Michael addition of aldehydes to nitro olefins was developed by Keller and co-workers in 2013 [18]. The dendritic catalyst was a combination of Jorgensen-Hayeshi organocatalyst grafted via triazole linkers on phosphorus dendrimers (Scheme 3). A comparative study on the catalytic performances of dendrimer supported and magnetic nanoparticle supported organocatalysts on Michael addition was carried out. The dendrimer supported catalyst was efficient with maximum conversion at a reasonable time. It showed excellent recycling ability via precipitation method and were reused up to seven consecutive catalytic cycles.

2.2 *Fluorous Biphasic Catalyst-PTC*

Phase transfer catalyst (PTC) allows the transfer of reagents from one phase and creates suitable conditions for the reaction to happen. Generally, organic salts with fluorinated anions act as phase transfer catalysts in organic transformations [19].

In the year of 2004, several cinchona derived alkaloids were anchored to different polystyrene supports by Chinchilla et al., resulting in the formation of chiral polymeric ammonium salts (Scheme 4) [20]. The catalyst prepared was used for the asymmetric alkylation of *N*-(diphenyl methylene) glycine esters. The best *S*-enantiomer

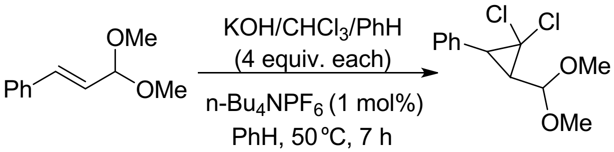


Scheme 4 Polystyrene anchored cinchona ammonium salts

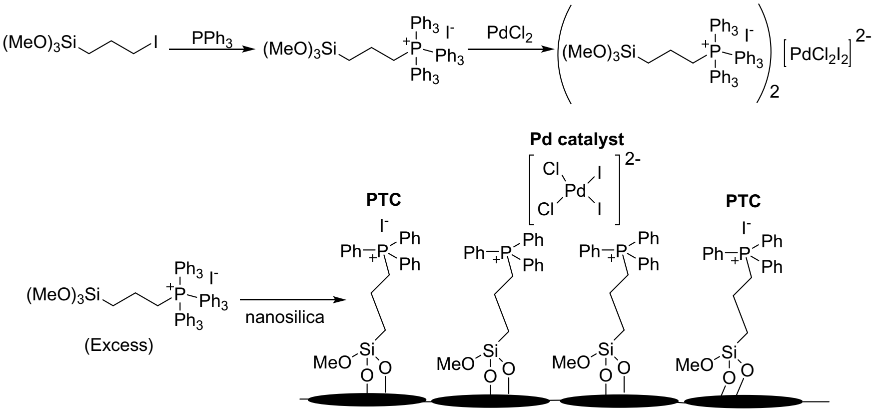
selectivity was found for the Merrifield resin supported cinchonidium salt, and the *R*-selectivity was observed for the cinchonine derived salts. Simple filtration techniques were used to separate the catalysts after the reaction and were reused.

Tetraalkyl ammonium salts containing PF_6- and BF_4- anions were developed by Kryshtal and co-workers and have used as efficient PTC for the trichloromethylation and dichlorocyclopropanation reactions of alkenes and aldehydes (Scheme 5) [21]. The fluorinated PTCs were readily recovered from the reaction medium and washed with H_2O and Et_2O. The catalyst retained its activity over several cycles of reactions.

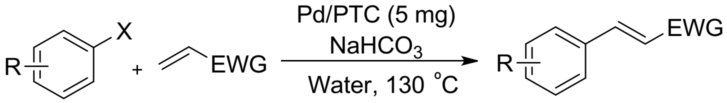
A silica nanoparticle supported phosphonium-palladium phase transfer catalyst matrix was reported by Hajipour et al. The application of this catalyst in the Heck reaction in neat aqueous media was studied [22]. The palladium complexes along with the quarternary phosphonium cations were covalently immobilized on a silica support. The catalyst was synthesized by a complex formation of quaternary phosphonium iodide with palladium chloride, which resulted in the formation of $[PdCl_2I_2]^{2-}$, and it was reacted with SiO_2 nanoparticles (Scheme 6). The activity of Pd/PTC was tested in the coupling reaction of iodobenzene and methyl acrylate, using pure water as the



Scheme 5 Cyclopropane synthesis using fluorinated PTCs



Scheme 6 Immobilization of Pd/PTC on silica



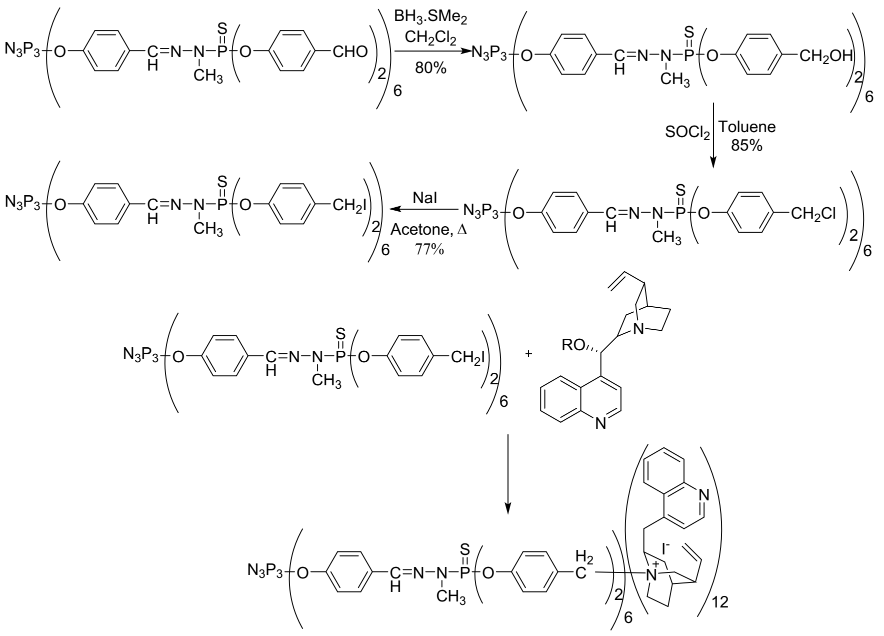
Scheme 7 Heck reaction catalyzed by immobilized Pd/PTC on silica

solvent (Scheme 7). The catalytic recyclability was also checked in the same reaction conditions. Catalyst recovery from the medium was done expertly by centrifugation method and reused after washing it with ethanol and acetone. The synthesized catalyst exhibited better reactivity in terms of turnover numbers.

Commercially available cinchona alkaloids were used for the synthesis of different dendrimeric phase transfer catalysts by Rull et al. The quaternization of the quinuclidine nitrogen resulted in the formation of PTC, and they catalyzed asymmetric organic transformations [23] (Scheme 8). The catalytic activity was checked on the asymmetric alkylation of the glycinate Schiff base with benzyl bromide. The recovery and reusability of the catalyst were valid for five consecutive cycles, maintaining the activity. The enantioselectivity of the catalyst was observed to reduce slightly during the runs.

2.3 Magnetically Recoverable Metal Nanoparticles

Magnetically recoverable catalysts are green chemistry aspects as they enable the environmentally friendly catalytic approach. Various strategies, like grafting, surface modification, and self-assembly, etc., provide a wide range of scope for the preparation of metal nanoparticles (MNPs). The separation of the catalyst from the reaction



Scheme 8 Synthesis of benzyl chloride/iodide functional phosphorous dendrimers

medium is also cheap, feasible, and straightforward. Most of the Fe-, Ni-, Co-based MNPs enhance the reaction in both homogenous and heterogeneous media [24].

Considering the photocatalytic application of magnetically recoverable catalysts, Boruah and co-workers synthesized Fe_3O_4/reduced graphene oxide catalysts [25]. The synthesis was carried out following eco-friendly solution chemistry. The performance of the prepared nanoparticle was checked on the dye degradation. Carcinogenic and mutagenic dyes such as methyl green, methyl blue, and rhodamine B were effectively degraded by Fe_3O_4/rGO (Scheme 9). The catalytic application was

$$Fe_3O_4 + h\nu \longrightarrow Fe_3O_4\,(e^- + h^+)$$

$$\text{Dyes} + h\nu \longrightarrow (\text{Dyes})^*$$

$$Fe_3O_4/\,\text{rGO} + h\nu \longrightarrow Fe_3O_4\,(h^+) + \text{rGO}\,(e^-)$$

$$\text{rGO}\,(e^-) + O_2 \longrightarrow \text{rGO} + O_2^{\bullet\,-}$$

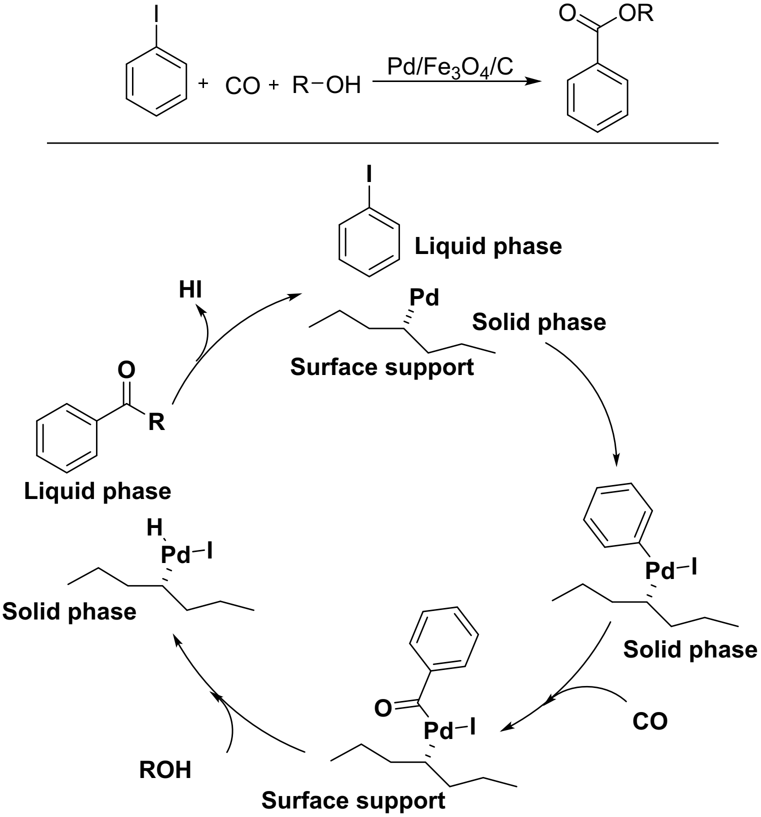
$$Fe_3O_4\,(h^+) + OH^- \longrightarrow Fe_3O_4 + \dot{O}H$$

$$\text{Dye Molecules} + \dot{O}H \longrightarrow \begin{array}{c}\text{Degraded products}\\ (Cl^-,\ NO_3^-,\ SO_4^-,\ CO_2 \text{ and } H_2O)\end{array}$$

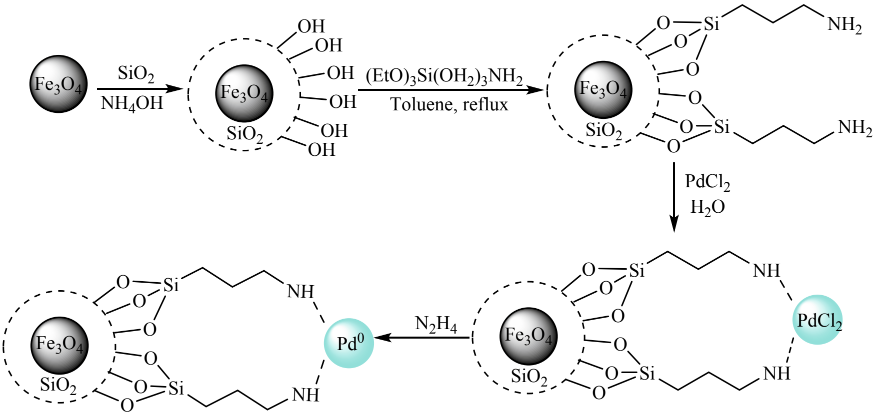
Scheme 9 Photo dye degradation using Fe_3O_4/reduced graphene oxide extended to the photoreduction of mutagenic aqueous Cr (VI) to nontoxic Cr (III) solution under sunlight. The activity was found to be valid up to ten reaction cycles and was stable enough.

Vavasori et al. synthesized a new magnetically recoverable Pd catalyst by depositing 1% palladium on Poly-(1-oxo-trimethylene) with a 15% magnetite [26]. Alkoxycarbonylation of iodobenzene to benzoic esters was catalyzed using synthesized metal nanoparticles under phosphine free conditions (Scheme 10). The conversion was found to reach up to 100% within 3 h. The catalyst was recovered and recycled for about five times.

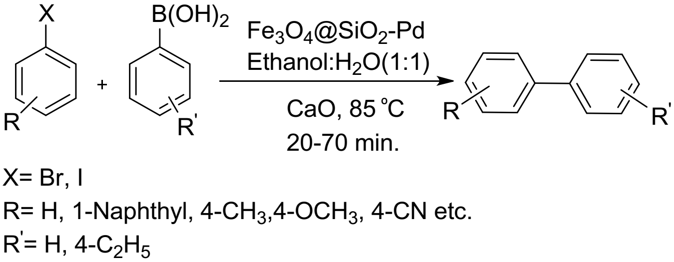
Later, in 2017, a Pd(0)-based magnetically recoverable nanocatalyst supported on nano Fe_3O_4–SiO_2 was developed by Khazaei et al. (Scheme 11) [27]. The prepared catalyst was used for the Suzuki coupling reaction (Scheme 12). Eggshell was utilized as a low-cost solid base for the reaction. The catalyst was characterized using SEM, EDS, XRD, TEM, etc. and confirmed the formation of Fe_3O_4@SiO_2–Pd. An external



Scheme 10 Alkoxy carbonylation catalyzed by Pd/Fe_3O_4 with the mechanism



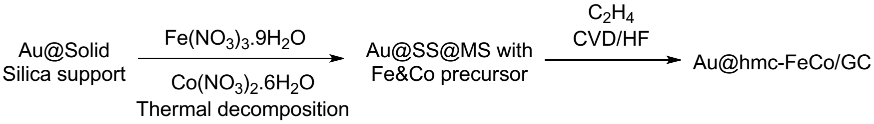
Scheme 11 Preparation of Pd-magnetic nanoparticles



Scheme 12 Suzuki coupling in the presence of Fe_3O_4@SiO_2-Pd

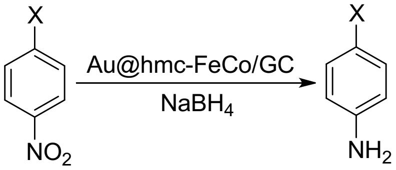
magnet recovered the nanoparticles and was further used certain times without losing the catalytic activity.

A catalytic reduction of nitroaromatic compounds using magnetically separable nanoparticles was reported by Hong et al. in 2018 [28]. The catalyst synthesized was a combination of 13 nm Au nanoparticles enclosed in a hollow mesoporous carbon. The nanocatalyst Au@hmc-FeCo/GC was prepared from the thermal decomposition of Fe and Co on silica support containing Au nanoparticles (Scheme 13). Au@hmc-FeCo/GC showed superparamagnetism at room temperature. Catalytic reduction of 4-nitrophenol, 4-nitrotoluene, etc. was carried out, and the results were confirmed to



Scheme 13 Synthesis of Au@hmc-FeCo/GC

Scheme 14 Au@hmc-FeCo/GC catalyzed nitroarene reduction



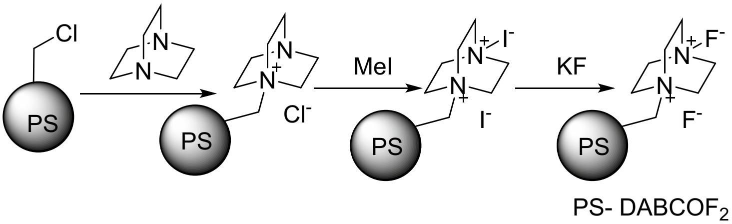
be better (Scheme 14). The same reaction cycle can be repeated at least five times without losing the initial catalytic properties.

2.4 Organic Resin and Polymer-Supported Recoverable Catalysts

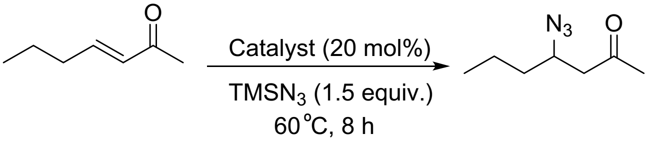
Insoluble organic resins and polymers such as polystyrene-based cross-linkers have been used as supports in heterogeneous catalysis, which allows the active recovery and reuse of many metal catalysts by simple methods. Organic polymer supports provide improved catalytic stability, surface activity, and high selectivity for the reaction.

Angelini et al. reported the conjugate addition of an N-nucleophile for the synthesis of β-amino carbonyl compounds catalyzed by polystyryl-DABCOF$_2$ (Scheme 15) [29]. The reaction was carried out in an aqueous medium. The porous polymeric materials were found to be more compatible with the conditions. DABCO, a diamine moiety carries high loading fluoride as the counter ions and efficient than the commercially available fluoride catalysts. The catalyst was used in the β-azidation of enones (Scheme 16). The reaction was carried out in a continuous flow method, and it helps for the recovery of the catalyst used.

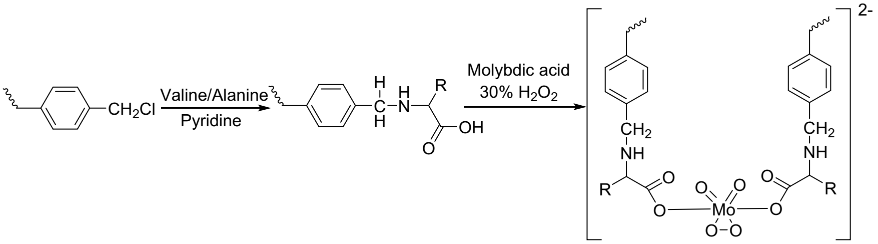
Merrifield resin supported peroxomolybdenum (VI) compounds for the selective oxidation of organic sulfides was developed by Boruah et al. in 2013 [30]. The catalyst was prepared by the immobilization of dioxomonoperoxomolybdenum (VI) on amino acid-functionalized Merrifield resins (Scheme 17). The catalyst showed excellent activity and selectivity for the oxidation of thioethers and dibenzothiophene to sulfoxides/sulfones by peroxides (Scheme 18). H_2MoO_4 reacted with 30%



Scheme 15 Preparation of PS-DABCOF$_2$

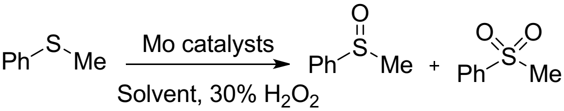


Scheme 16 β-Azidation in the presence of PS-DABCOF$_2$ based catalysts



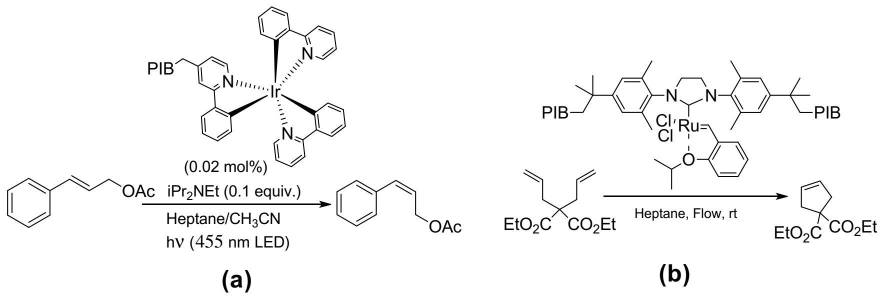
Scheme 17 Synthesis of Merrifield resin supported PMO complexes

Scheme 18 Selective oxidation of methyl phenyl sulfide

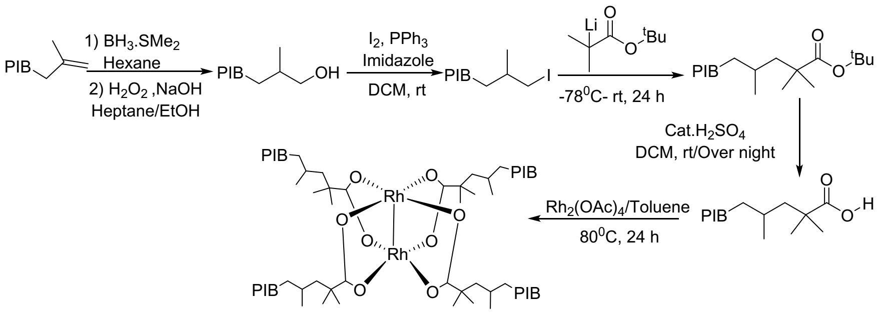


H_2O_2, and amino acid-functionalized resin at neutral pH resulted in the catalyst $[MoO_2(O_2)L_2]^{2-}$MR, L = Valine/Alanine; MR = Merrifield resin. The straightforward synthetic route, clean and safe reaction conditions, commercially cheap starting materials, easy recovery and reusability of the catalyst for several cycles, etc. are the compelling features of the catalyst.

Liang and co-workers studied soluble polymer supports for homogenous continuous flow reactions [31]. The transition metal entrapped polyisobutylene, and poly(4-dodecylstyrene) catalyzes the cyclopropanation, ring-closing metathesis, and nucleophilic catalysis. Reactions were carried out in the heptane phase, saturated with acetonitrile (Scheme 19a). The catalyst was finally separated via gravity-based liquid/liquid separation. Leaching helps the recovery of the catalyst after the reaction. The desired products were obtained in moderate to good yields, and the reaction outputs were compatible with the prior results obtained with the same phase insoluble catalyst. The utility of heptane soluble polymer-supported catalyst was first studied in a batch reaction of rhodium-catalyzed cyclopropanation. Heptane soluble PIB (Polyisobutylene)-bound Rh (II) carboxylate catalyzes cyclopropanation (Scheme 20) was reported. A commercially available PIB-bound iodide was used as the starting material. In the same way, a ruthenium-based PIB-bound Hoveyda-Grubbs catalyst affected in the ring-closing metathesis of diene substrates



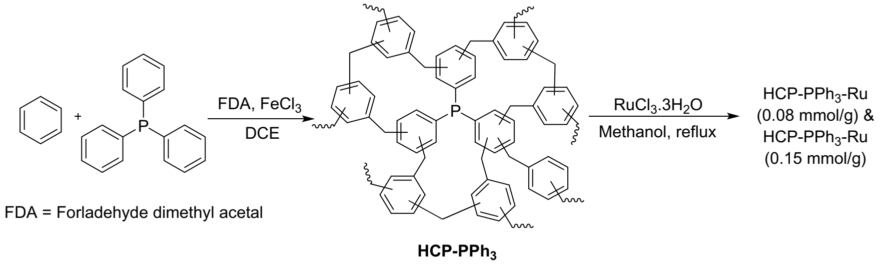
Scheme 19 **a**) Photo *E/Z* isomerization using PIB-Ir complex, **b**) reaction catalyzed by PIB-bound Hoveyda-Grubb's catalyst



Scheme 20 Synthesis of PIB-Rh (II) Carboxylate

(Scheme 19b). The constant recovery and reuse of the catalyst were achieved because of the phase selectivity of PIB.

An efficient, recyclable catalyst based on ruthenium complexes immobilized on hyper cross-linked polymers for organic transformations was reported by Jia et al. (Scheme 21) [32]. The synthesized catalyst was characterized by employing physicochemical methods. It was observed to possess high thermal stability, chemical stability, and low synthetic cost. Organic synthesis of 2,4-diaryl substituted pyridine

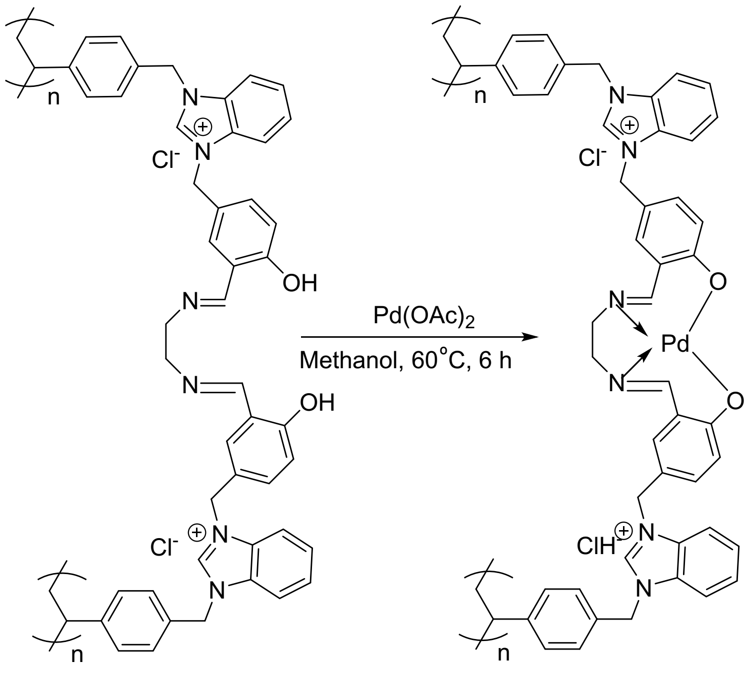


Scheme 21 Preparation of HCP-PPh_3-Ru catalyst

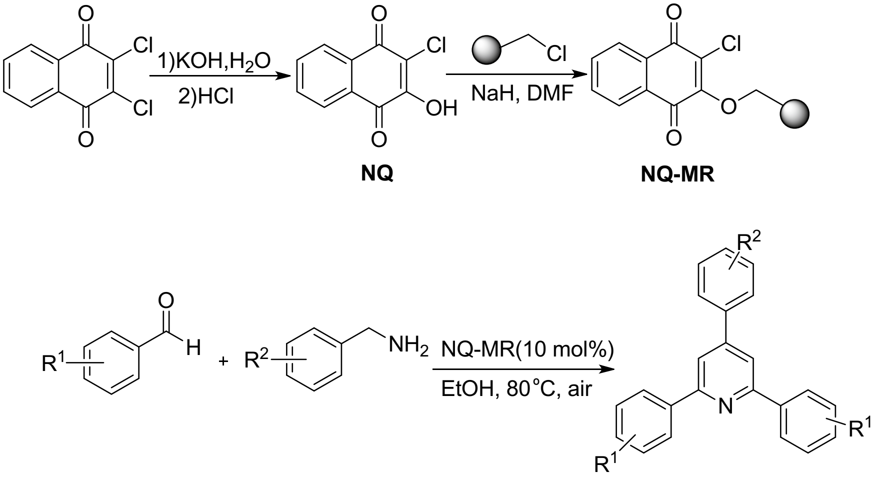
was carried out from acetophenones, NH_4OH, and DMF using ruthenium catalysts, and it also catalyzed the formation of dihydrofurans via cycloaddition reaction of diazodicarbonyl compounds with olefins. After the reaction, the HCP-PPh_3-Ru catalyst was recovered and reused without significant loss in reactivity. The study indicates that the PPh_3-Ru catalyst immobilized on external cross-linked HCP materials are quite robust for the organic transformations.

A highly recoverable polymer-supported ionic salen-Pd complex (PS-Pd-salen) was developed by Balinge et al. for the Suzuki- Miyaura cross-coupling reactions (Scheme 22) [33]. The catalytic activity was checked on the coupling of phenylboronic acid with different aryl halides using water as a solvent, under 20% catalyst loading. The PS-Pd-salen complex was found to be thermally stable, and it showed excellent reusability for five consecutive runs.

Very recently, Yang et al. developed a heterogeneous system in which chloride quinones supported on an organic resin was used for the synthesis of trisubstituted pyridines (Scheme 23) [34]. Recoverable Merrifield resins were used as organic support. The synthesized catalyst was characterized using FTIR, XPS, EDX techniques. The chemoselective synthesis of 2, 4, 6-trisubstituted pyridines offered good yields under mild conditions. The proposed mechanism was well established by the successful capture of the intermediate during the reaction pathway. The catalyst was



Scheme 22 Synthesis of polymer-supported Pd-Salen complexes



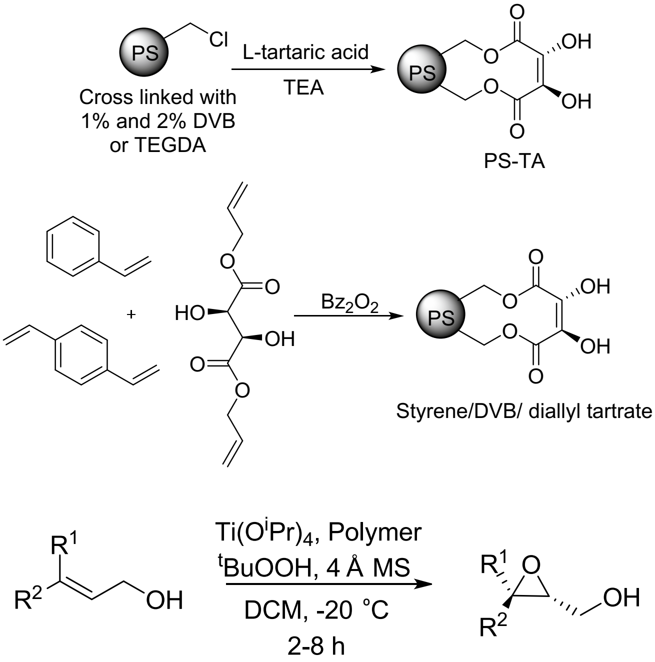
Scheme 23 Supported NQ-MR catalyzed pyridine synthesis

recovered by simple centrifugation techniques, washed with water, dried, and used further for the synthesis.

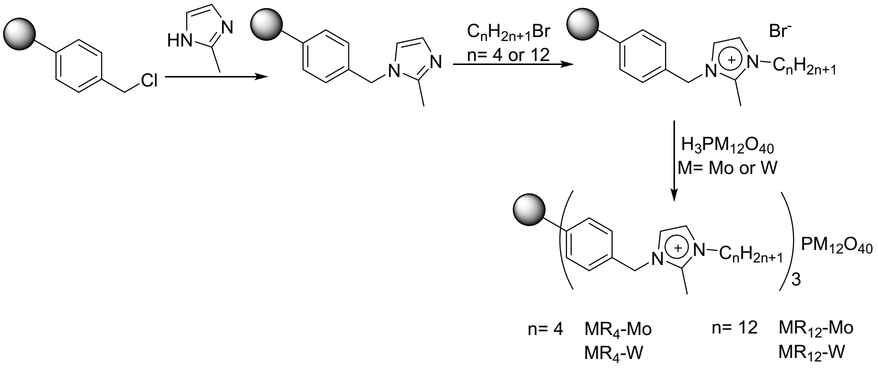
Bartacek reported a heterogeneous catalyst for enantioselective Sharpless epoxidation in 2019 (Scheme 24) [35]. The metal present in the catalyst was Ti (IV). The titanium complexes were supported on cross-linked polystyrene beads with ethyl-(4-vinyl benzyl)-*L*-tartrate/ethyl-(2*R*,3*R*)-2,3-dihydroxy-4,5-oxo-5-(4-vinyl phenyl) pentanoate using suspension polymerization. The catalytic activity was checked on the cinnamyl alcohol epoxidation, and high conversion and enantioselectivity were observed for the reaction.

Pisk and co-workers synthesized adipic acid via oxidation reaction using Molybdenum/Tungsten-based Keggin polyoxometallates (Scheme 25) [36]. The POM was surrounded by organic cations or functionalized Merrifield resins. Aqueous H_2O_2 (30%) was used as the oxidizing agent, and the starting materials used were cyclohexene, epoxy cyclohexane/cyclohexane diol. The catalyst loading was very low, about 0.001%- 0.007% for the POM, and adipic acid was obtained in excellent yields. The resin was finally isolated at the end of the catalytic cycle, washed with diethyl ether, dried, and used further.

Very recently, Chen et al. demonstrated the fabrication of thermoresponsive polymer-based TEMPO nanoreactors [37]. The application of the catalyst lies in the selective oxidation of alcohols in aqueous media. Catalyst synthesis was carried out initially using an amphiphilic co-polymer NHS-P(MMA_{25}-b-$OEGMA_{75}$) consisting of PMMA and poly(oligo ethylene glycol) methyl ether methacrylate with terminal NHS (Scheme 26). Then, TEMPO was introduced to the terminal of the hydrophobic part. The self-assembly of the amphiphilic co-polymer in water is resulted in the

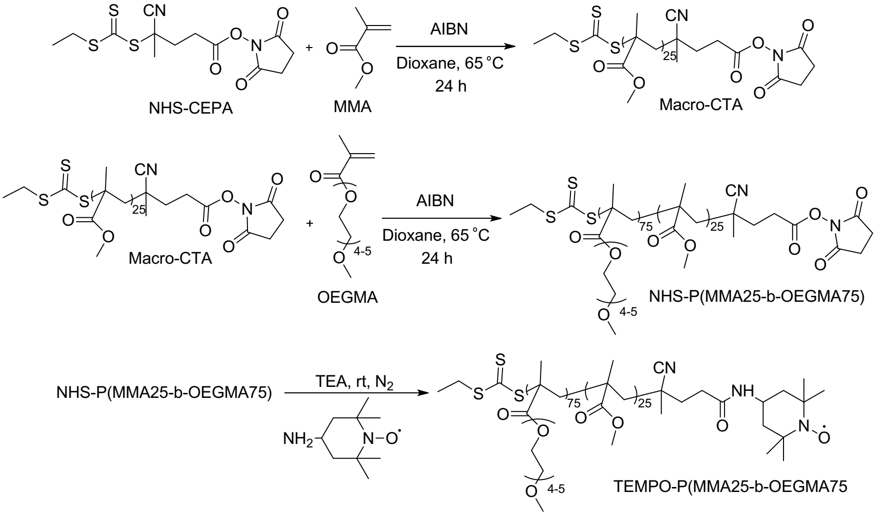


Scheme 24 Synthesis and application of *L*-(+)-tartaric acid esters immobilized on styrene on Sharpless epoxidation



Scheme 25 Merrifield supported heterogeneous catalysts- synthetic route

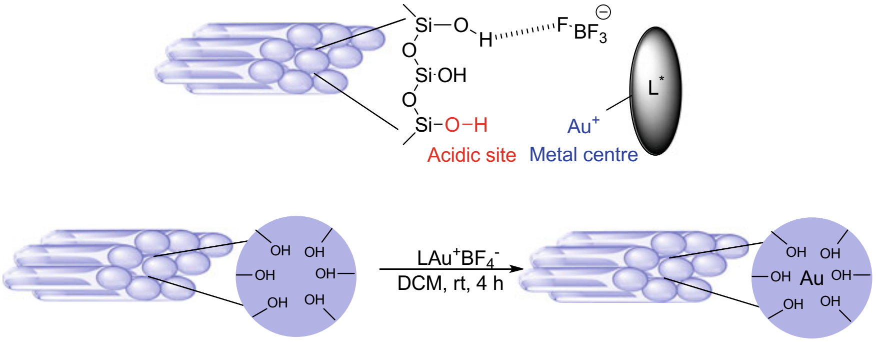
core-shell type of polymeric nanoreactors, which catalyzed the selective oxidation of the alcohol and yielded excellent amounts of aldehydes and ketones. The thermoresponsive character of the catalyst helps for its easy recovery by precipitation.



Scheme 26 Synthesis of TEMPO-(PMMA$_{25}$-b-OEGMA$_{75}$)

2.5 Silica-Supported Organocatalysts

An efficient synthesis of silica-supported gold (I) complexes were developed by Shu et al. [38]. The catalyst was used for the regio- and enantio-selective lactonization reactions. The preparation of the catalyst was carried out by stirring silica materials in a CH_2Cl_2 solution of Ph_3PAuBF_4 at room temperature for 4 h (Scheme 27). Catalytic activity was observed on the nucleophilic addition reaction of allenes. High enantioselectivities for the lactonization were obtained using heterogeneous catalysts. The catalysts were quickly recovered and reused up to 11 consecutive cycles without loss in the enantioselectivity.

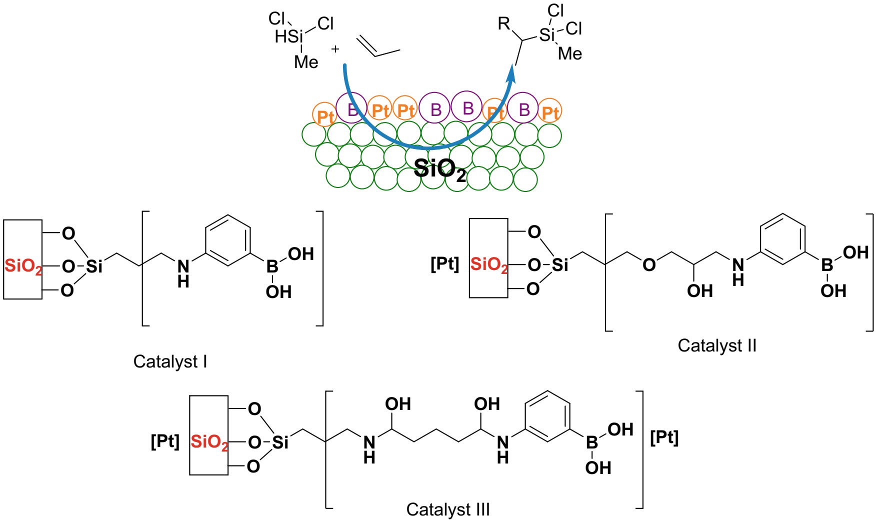


Scheme 27 One-step synthesis of heterogenous gold@SiO$_2$ catalysts

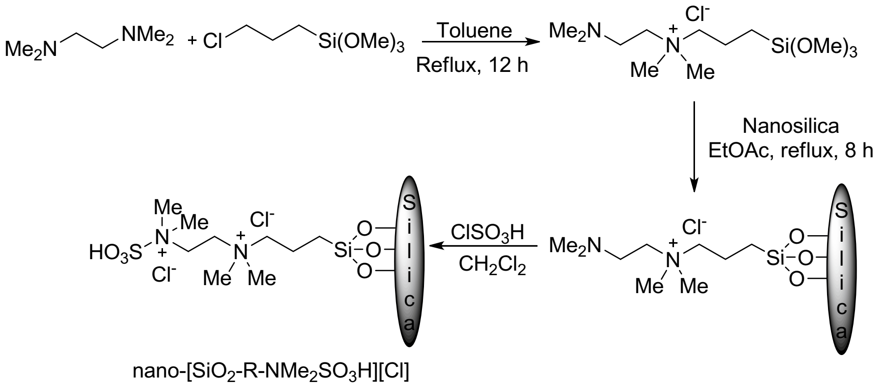
A novel and efficient boronic acid substituted silica-supported Pt was synthesized by Li et al. in 2019 [39]. The boronic acid-functionalized silica gel complex (SiO_2- BA) was prepared by grafting silica gel and 3-aminophenyl boronic acid using 3-chloropropyltrimethosilane, γ-glycidoxypropyltrimethoxysilane, and 3-aminopropyl tri methoxysilane as complexing agents. Further, Pt nanoparticles were dispersed on the complex using a solution of $H_2PtCl_6.6H_2O$ in ethanol. The catalytic activity of the synthesized compounds was investigated by the hydrosilylation of olefins with methyl dichlorosilane (Scheme 28). The substrate scope was explored for a wide range of terminal aliphatic olefins and methyl dichlorosilane. The recycled catalyst was found to be useful up to 10 catalytic cycles without any noticeable loss in catalytic activity.

Mesoporous recoverable silica-based nanomaterials for the synthesis of substituted pyridodipyrimidines were reported by Kohzadian and co-workers [40]. The catalyst preparation was straightforward and cost-effective (Scheme 29). The nanocatalyst [SiO_2-R-NMe_2SO_3H]Cl was detached from the reaction medium via centrifugation and decantation. Further, it was washed with methanol and reused. Synthetic protocol carried out for the preparation of pyrido[2,3-*d*: 2,3-*d*']dipyrimidine was a one-pot multicomponent reaction of aryl aldehydes, 2-thiobarbituric acid, and NH_4OAc in the presence of the synthesized catalyst. The reaction time, yield, as well as the condition were better compared to the reported methods.

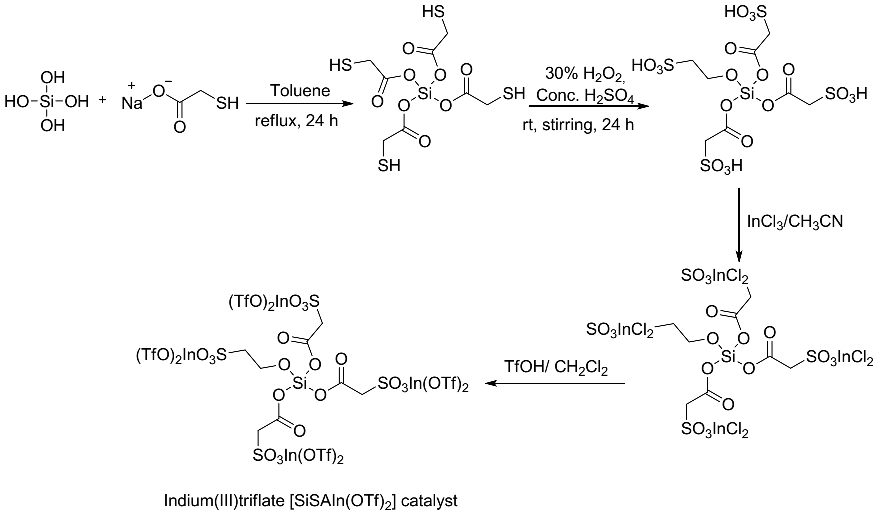
Post-transition metal triflates as solid catalysts are being used in heterogeneous green catalysis. An indium (III) triflate [SISAln$(OTf)_2$] supported on sulfoacetate modified silica for the synthesis of tetrasubstituted imidazoles was established by Vaid et al. (Scheme 30) [41]. 1,2,4,5-Tetrasubstituted imidazoles were obtained by the



Scheme 28 Boronic acid substituted Pt@SiO_2 catalyzed reaction



Scheme 29 Preparation of nano-[SiO$_2$-R-NMe$_2$SO$_3$H][Cl]



Scheme 30 Multi-step synthesis of Sulfoacetate modified silica-supported indium (III) triflate [SiSAIn(OTf)$_2$]

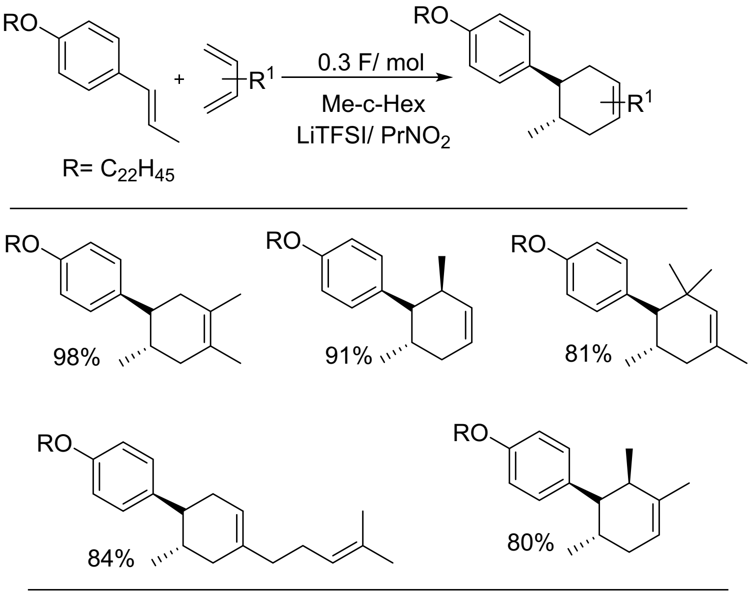
reaction of aromatic aldehydes, benzyl, aromatic amines, and ammonium acetate. To investigate the stability and recyclability, the catalyst was separated from the reaction mixture by simple filtration. The catalytic activity was found to be stable up to five consecutive runs.

2.6 Thermomorphic Catalysts

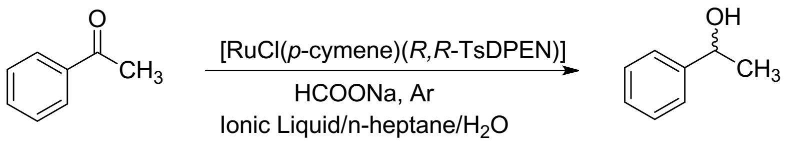
Thermomorphic catalysts are separated from the reaction mixture by varying the temperature of the system. This helps in the phase separation based on their temperature-dependent solubility behavior. The separation strategies include (i) cooling (for the catalysts which are soluble under elevated temperatures)—catalysts separate by lowering the temperature, (ii) temperature-dependent miscibility of solvent mixtures.

A novel thermomorphic system for the electrolytic Diels-Alder reaction was reported by Imada et al. [42]. They replaced the polar $LiClO_4/CH_2NO_2$ solution with a less polar LiTFSI/1-nitropropane solution (Scheme 31). During the electrochemical response, methylcyclohexane forms a monophasic condition with LiTFSI/1-nitropropane at rt. After the completion of the reaction, at −50 °C, it turns into a biphasic system. Cycloadducts move into the upper methylcyclohexane phase, and in the lower phase, $LiTFSI/PrNO_2$ gets separated, which can be used for further cycles.

Heijazifar et al. proposed the use of thermomorphic ionic liquid microemulsion applied for the Ru-catalyzed asymmetric transfer hydrogenation of ketones (Scheme 32) [43]. $[C_{12}mim][(^iC_8)_2PO_2]$ and $[C_{12}dmim][(^iC_8)_2PO_2]$ were found to be the best thermomorphic ionic liquids for the reaction (Fig. 2). Use of water-soluble ligands improve the immobilization of the catalyst, and it minimizes the chances of leaching into the organic layer during extraction. The catalytic system was found to be more effective for aromatic ketones than the aliphatic ones in terms of conversion



Scheme 31 Electrocatalytic Diels-Alder reaction under thermomorphic conditions



Scheme 32 Asymmetric *trans* hydrogenation of ionic liquid microemulsion

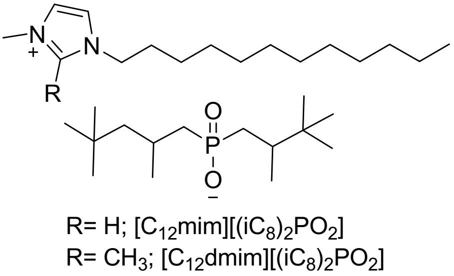
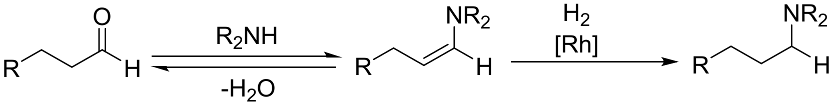


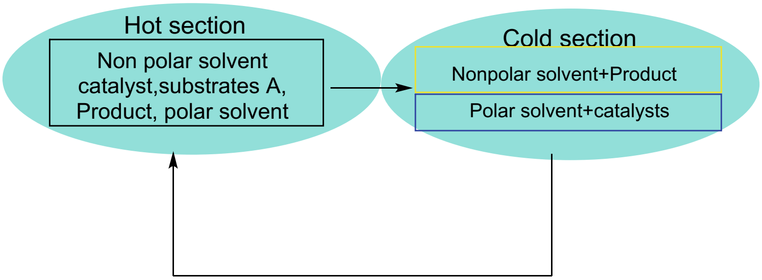
Fig. 2 Surface active ionic liquids

and enantioselectivity. Moderately good yields were obtained during the recyclability study, and the reuse of the catalyst was effective.

Homogenously catalyzed reductive amination in a thermomorphic system was first reported very recently by Künnemann and co-workers (Scheme 33) [44]. Thermomorphic multiphase system was established for the recovery and reuse of the catalyst (Scheme 34). Commercially available PPh_3 ligand and Rh(acac)(cod) catalyst precursor were used for the reaction. The researchers have scaled up the reaction



Scheme 33 Thermomorphic Rh complex catalyzed reductive amination



Scheme 34 Representation of thermo multiphase system

into a continuous system that recycles the catalyst inflow over 70 h. The overall reaction possessed above 90% yield and meager percentage of catalyst leaching, 1%/h.

3 Conclusion

The development of a recoverable catalyst is a rapidly growing area in catalysis. Effective recycling of the catalyst from the reaction medium can be performed using various methodologies. Depending on the nature of the catalyst used, different recovery methods are applied. Significant progress has been observed in the preparation of solid-supported catalysts—both dendritic and silica-supported, magnetically supported, and also organic resin supported catalysts. In most of the methods, the effective recovery of the catalysts is done without altering its efficiency. Moderate to high reaction rates can be sustained over multiple consecutive cycles.

Magnetically recoverable metal nanoparticles enhance the catalytic activity because of its increased surface area. The advantages of metallodendritic catalysts extend to both homogenous and heterogeneous catalysis, and these can be separated employing simple techniques such as precipitation, filtration, and centrifugation. These modified recoverable catalysts could benefit from the additional active supports (dendrimers, organic resins, silica, polymers, etc.), which helps in the catalyst formation and reaction. Ease of synthesis, the serenity of the reaction, recyclability, and cost-effectiveness make these methods more sustainable toward green chemistry approach.

Acknowledgements B.P.B. acknowledges the Department of Science and Technology (DST), Government of India, for an INSPIRE Faculty Award (IFA-13 CH-98). B.P.B. and R.P.B. thank NITK, Surathkal, for providing laboratory facility and research fellowship for R.P.B.

References

1. a) Gladysz JA (2002) Introduction: recoverable catalysts and reagents—perspective and prospective. Chem Rev 102:3215–3216; b) Kirchhoff MM (2003) Promoting green engineering through green chemistry. Environ Sci Technol 37:5349–5353
2. a) Glaser JA (2012) Green chemistry with nanocatalysts. Clean Techn Environ Policy 14:513–520; b) Sheldon RA (2016) Green chemistry and resource efficiency: towards a green economy. Green Chem 18:3180–3183. www.rsc.org/greenchem. 23 Feb 2020
3. Schmidt F (2004) The importance of catalysis in the chemical and non-chemical industries. Springer, Berlin, Heidelberg
4. Sheldon RA, Arends IWCE, Hanefeld U (2007) Green Chemistry and Catalysis Wiley, Germany
5. Liu F, Hung K, Zheng A et al (2018) Hydrophobic solid acids and their catalytic applications in green and sustainable chemistry. ACS Catal 8:372–391

6. Cole-Hamilton DJ (2003) Homogeneous catalysis—new approaches to catalyst separation, recovery, and recycling. Science 299:1702–1706
7. a) Sun PP, Lee MS (2011) Separation of Pt from hydrochloric acid leaching solution of spent catalysts by solvent extraction and ion exchange. Hydrometallurgy 110: 91–98; b) Lee JY, Raju B, Kumar BN et al (2010) Solvent extraction separation and recovery of palladium and platinum from chloride leach liquors of spent automobile catalyst. Separ Purif Tech 73:213–218; c) Gürsel IV, Noël T, Wang Q et al (2015) Separation/recycling methods for homogeneous transition metal catalysts in continuous flow. Green Chem 17: 2012–2026
8. a) Nair D, Luthra SS, Scarpello JT et al (2002) Homogeneous catalyst separation and re-use through nanofiltration of organic solvents. Desalination 147:301–306; b) Dijkstra HP, Klink GPMV, Koten GV (2002) The use of ultra- and nanofiltration techniques in homogeneous catalyst recycling. Acc Chem Res 35:798–810
9. Dloumaev VK, Bullock RM (2003) A recyclable catalyst that precipitates at the end of the reaction. Nature 424:530–532
10. a) Polshettiwar V, Luque R, Fihri A et al (2011) Magnetically recoverable nanocatalysts. Chem Rev 111:3036–3075; b) Shylesh S, Schünemann V, Thiel WR (2010) Magnetically separable nanocatalysts: bridges between homogeneous and heterogeneous catalysis. Angew Chem Int Ed 49:3428–59; c) Shifrina ZB, Bronstein LM (2018) Magnetically recoverable catalysts: beyond magnetic separation. Front Chem 6:1–6; d) Rossi LM, Costa NJS, Silva FP et al (2014) Magnetic nanomaterials in catalysis: advanced catalysts for magnetic separation and beyond. Green Chem 16:2906–2933
11. Vono LLR, Damasceno CC, Matos JR et al (2018) Separation technology meets green chemistry: development of magnetically recoverable catalyst supports containing silica, ceria, and titania. Pure Appl Chem 90:133–141
12. a) Munnik P, de Jongh PE, de Jong KP (2015) Recent developments in the synthesis of supported catalysts. Chem Rev 115:6687–6718; b) Wang D, Astruc D (2013) Dendritic catalysis-basic concepts and recent trends. Coord Chem Rev 257:2317–2334
13. Van Heerbeek R, Kamer PCJ, Van Leeuwen PWNM et al (2002) Dendrimers as support for recoverable catalysts and reagents. Chem Rev 102:3717–3756
14. Reetz MT, Lohmer G, Schwickardi R (1997) Synthesis and catalytic activity of dendritic diphosphane metal complexes. Angew Chem Int Ed 36:1526–1529
15. Méry D, Astruc D (2006) Dendritic catalysis: major concepts and recent progress. Coord Chem Rev 250:1965–1979
16. Heuzé K, Mery D, Gauss D et al (2003) Copper-free, recoverable dendritic pd catalysts for the sonogashira reaction. Tetrahedron 22:74–75
17. Nlate S, Astruc D, Neumann R (2004) Synthesis catalytic activity in oxidation reactions, and recyclability of stable polyoxometalate-centred dendrimers. Adv Synth Catal 346:1445–1448
18. Keller M, Perrier A, Linhardt R et al (2013) Dendrimers or nanoparticles as supports for the design of efficient and recoverable organocatalysts? Adv Synth Catal 355:1748–1754
19. a) Dobbs AP, Kimberley MR (2002) Fluorous phase chemistry: a new industrial technology. J Fluor Chem 118:3–17; Pozzi G, Shepperson I (2003) Fluorous chiral ligands for novel catalytic systems. b) Coord Chem Rev 242:115–124; c) Hejazifar M, Pálvölgyi ÁM, Bitai J, Lanaridi O, Bica-Schröder K (2019) Asymmetric transfer hydrogenation in thermomorphic microemulsions based on ionic liquids. Org Process Res Dev 23(9):1841–1851
20. Chinchilla R, Mazón P, Nájera C (2004) Polystyrene-anchored cinchona ammonium salts: easily recoverable phase-transfer catalysts for the asymmetric synthesis of α-amino acids. Adv Synth Catal 346:1186–1194
21. Kryshtal GV, Zhdankina GM, Zlotin SG (2008) Recoverable phase-transfer catalysts with fluorinated anions: generation and reactions of dichlorocarbene and CCl_3 anion in the heterogeneous system $KOH(s)/CHCl_3/nBu_4NPF_6$. Eur J Org Chem 1777–1782
22. Hajipour AR, Azizi G (2014) Simultaneous immobilization of a matrix containing palladium and phase transfer catalyst on silica nanoparticles: application as a recoverable catalyst for the heck reaction in neat water. RSC Adv 4:20704–20708

23. Rull J, Jara JJ, Sebastian RM et al (2016) Recoverable dendritic phase-transfer catalysts that contain (+)-cinchonine-derived ammonium salts. Chem Cat Chem 8:2049–2056
24. Baig RBN, Varma RS (2013) Magnetically retrievable catalysts for organic synthesis. Chem Commun 49:752–770
25. Boruah PK, Borthakur P, Darabdhara G et al (2016) Sunlight assisted degradation of dye molecules and reduction of toxic Cr(VI) in aqueous medium using magnetically recoverable Fe_3O_4/reduced graphene oxide nanocomposite. RSC Adv 6:11049–11063
26. Vavasori A, Calgaro L, Quartarone G et al (2016) New magnetically recoverable palladium-based catalysts active in the alkoxycarbonylation of iodobenzene. Pure Appl Chem 88:445–455
27. Khazaei A, Khazaei M, Nasrollahzadeh M (2017) Nano-Fe_3O_4@SiO_2 supported Pd(0) as a magnetically recoverable nanocatalyst for suzuki coupling reaction in the presence of waste eggshell as low-cost natural base. Tetrahedron 73:5624–5633
28. Hong Y, Choi IA, Seo WS (2018) Au Nanoparticle@hollow mesoporous carbon with FeCo/graphitic shell nanoparticls as a magnetically recyclable yolk-shell nanocatalyst for catalytic reduction of nitroaromatics. Sci Rep 8(1)-7469
29. Angelini T, Lanari D, Maggi R et al (2012) Preparation and use of polystyryl-DABCOF2: an efficient recoverable and reusable catalyst for β-azidation ofα, β- unsaturated ketones in water. Adv Synth Catal 354:908–916
30. Boruah JJ, Das SP, Ankireddy SR et al (2013) Merrifield resin supported peroxomolybdenum(vi) compounds: recoverable heterogeneous catalysts for the efficient, selective and mild oxidation of organic sulfides with H_2O_2. Green Chem 15:2944–2959
31. Liang Y, Watson C, Malinski T et al (2016) Soluble polymer supports for homogeneous catalysis in flow reactions. Pure Appl Chem 88:953–960
32. Jia Z, Wang K, Tan B et al (2017) Ruthenium complexes immobilized on functionalized knitted hypercrosslinked polymers as efficient and recyclable catalysts for organic transformations. Adv Synth Catal 359:78–88
33. Balinge KR, Khiratkar AG, Bhagat PR (2018) a highly recoverable polymer-supported ionic salen-palladium complex as a catalyst for the suzuki-miyaura cross coupling in neat water. J Organomet Chem 854:131–139
34. Yang Q, Zhang Y, Zheng W et al (2019) Merrifield resin-supported quinone as an efficient biomimetic catalyst for metal-free, base-free, chemoselective synthesis of 2,4,6-trisubstituted pyridines. Green Chem 21:5683–5690
35. Bartáček J, Drabina P, Váňa J et al (2019) Recoverable polystyrene-supported catalysts for sharpless allylic alcohols epoxidations. React Funct Polym 137:123–132
36. Pisk J, Agustin D, Poli R (2019) Organic salts and merrifield resin supported $[PM_{12}O_{40}]_3-$ $(M = Mo$ or $W)$ as catalysts for adipic acid synthesis. Molecules 24:783
37. Chen T, Xu Z, Zhou L et al (2019) Highly efficient polymer-based nanoreactors for selective oxidation of alcohols in water. Mol Catal 474:110422
38. Shu XZ, Nguyen SC, He Y et al (2015) Silica-supported cationic gold(I) complexes as heterogeneous catalysts for regio- and enantioselective lactonization reactions. J Am Chem Soc 137:7083–7086
39. Li L, Li Y, Wang H et al (2019) Preparation and evaluation of a novel and high efficient boronic acid-substituted silica supported Pt catalyst colloids. Surf A Physicochem Eng Asp 570:322–330
40. Kohzadian A, Zare A (2019) Effective and rapid synthesis of pyrido[2,3-d:6,5-d′]dipyrimidines catalyzed by a mesoporous recoverable silica-based nanomaterial. Silicon 12:1407–1415
41. Vaid R, Gupta M, Kour G et al (2019) Sulfoacetate modified silica supported indium(III) triflate $[SiSAIn(OTf)_2]$: a novel solid acid nano-catalyst and investigation of its catalytic potential for one-pot synthesis of 1,2,4,5-tetrasubstituted imidazole derivatives. Chem Sel 4:9179–9184
42. Imada Y, Shida N, Okada Y (2019) A novel thermomorphic system for electrocatalytic diels-alder reactions. Chin J Chem 37:557–560
43. Hejazifar M, Pálvölgyi AM, Bitai J et al (2019) Asymmetric transfer hydrogenation in thermomorphic microemulsions based on ionic liquids. Org Process Res Dev 23:1841–1851

44. Künnemann KU, Bianga J, Scheel R et al (2020) Process development for the rhodium-catalyzed reductive amination in a thermomorphic multiphase system. Org Process Res Dev 24:41–49