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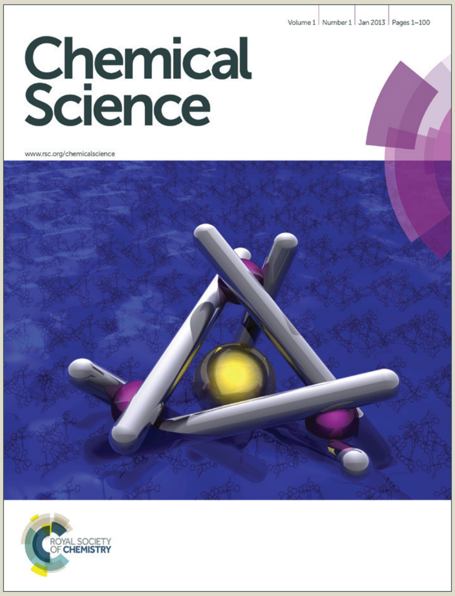

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Water-Medium Organic Synthesis over Active and Reusable Organometal Catalysts with Tunable Nanostructures

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Water-medium organic synthesis on reused heterogeneous organometal catalysts represents an important trend in green chemistry owing to the absence of pollution from both toxic organic solvents as reaction media and heavy metallic ions leached from the catalysts. However, heterogeneous organometal catalysts usually display lower activities than their corresponding homogeneous ones due to the decreased dispersion and unmatched microenvironment of the active sites, together with the enhanced diffusion limitation. The great efforts have been made to develop active heterogeneous organometal catalysts by adusting composion, engineering surface chemistry, tailoring morphology and pore structure. In this Minireview, we summarized recent progress in designing heterogeneous organometal catalysts with high efficiency and strong durability in various water-medium organic reactions and the discussion on the structure-performance relationship. It might be beneficial for the developments of both the powerful immobilized homogeneous catalysts and green chemical transformations.

Introduction

Today, the chemical enterprise has provided a power to support our living needs such as foods, medicines and energy resources.[1] However, increasing concerns about environmental pollution and public health have posed new challenges because traditional chemical synthesis exhibits in general low efficiency and high pollution.[2] One major drawback in modern chemical production processes is the use of massive toxic and flammable organic solvents in most organic synthesis.[3] However, tremendous biochemical reactions in nature occur actively and selectively in aqueous medium with the help of enzymes.[4] Learning from the living system, there has been a growing interest in the development of water-medium organic synthesis since water is safe, renewable, nontoxic and nonflammable.[5] To date, most studies are focused on simulating enzymes by using homogeneous catalysts.[6, 7] Several research groups recently have summarized the results of homogeneous catalytic systems in a number of excellent reviews.[8] Although the high activity and selectivity, homogeneous catalysts usually can not be recycled and reused,[9] which inevitably adds cost and also causes pollutions in both environment and products by heavy metallic ions leaching.[10] Moreover, homogeneous catalysts are not designed to fit into continuous-flow reactors, which are economically attractive to many industries.[11]

The use of heterogeneous catalysts in water-medium organic synthesis is of considerable current interest. The obvious advantage for heterogeneous catalytic system is the ease of recovery and recycling and is readily amenable to continuous processing, which substantially decrease the production cost and chemical waste. Meanwhile, it could reduce the final product contamination by metal and organic residues, which is especially critical for the pharmaceutical and fine chemical industries. More interestingly, the synergistic catalytic effects that generated from the active species and the solid support provide catalytic activity and selectivity superior to what can be obtained from homogeneous catalysts.[12] Until now, a large number of heterogeneous catalysts with different active species such as solid acids,[13] bases,[14] and metal particles,[15] together with the immobilized organometals[16] and organic molecules,[17] have been successfully employed in a wide range of water-medium organic synthesis. Among various heterogeneous catalytic systems, immobilized organometal catalysts attract a lot of interest owing to their diversified active centers, high catalytic efficiencies and mild reaction conditions, especially for asymmetric synthesis.[18] However, heterogeneous organometal catalysts usually exhibited poor activity and selectivity comparing to their corresponding homogeneous ones due to several inherent drawbacks. Firstly, the active sites in heterogeneous catalysts are not as accessible as those in homogeneous catalysts.[19] Moreover, the unmatched chemical microenvironment of active species was usually observed due to the uncontrollable negative interactions between the supports and the organometal complex.[20] Furthermore, mass transfer limitation in the heterogeneous catalytic systems was more pronounced owing to the spatial hindrance of solid matrix as well as the low solubility of organic reactants in water.[21] To overcome these barriers, a variety of novel strategies have been developed to design powerful organometal catalysts *via* controlling morphology and porous structure, adjusting the location and interaction of the active sites with the supports, and engineering surface chemistry. Recent developments in nanoscale supports such as mesoporous materials and nanoparticles supply a promising way for designing the powerful heterogeneous organometal catalysts.[22] The high surface and suitable pore channels facilitated the reactant diffusion and adsorption. Meanwhile, the dispersion and location of active sites could also be improved by controlling materials shape and size. In addition, the surface chemistry and the microenvironment of active sites could be engineered *via* functionalizing with organic groups. Furthermore, some bifunctional organometal catalysts have also synthesized and used in "one-pot" cascade reactions, which could simplify operation steps and thus reduce the production of pollutant and byproducts. The purpose of this review is to describe some of the most important and recent developments for the design and synthesis of highly active and reusable heterogeneous organometal catalysts and summarize their performances in water-medium organic reactions. In particular, this review will emphasize the preparation methods including the post-grafting and self-assembly approaches, which effectively govern the structural and compositional properties of heterogeneous organometal catalysts. Meanwhile, we will also endeavor to analyze the relationship between the catalytic performances of heterogeneous organometal catalysts and their physio-chemical characteristics including particle morphology and size, pore structure and shape as well as surface chemistry.

Grafted Organometal Catalysts

The most common method for preparing immobilized organometal catalysts is to graft the active organometal complex onto or into the desired supports through covalent binding or non-covalent binding protocols (e.g. physisorption, encapsulation and electrostatic interaction). In general, the supports functionalized with chelated ligands could easily capture organometal and thus obtained the immobilized organometal active species *via* forming new coordination bonds. Obviously, the morphology and pore structure, composition and surface chemistry of the supports inevitaly play critical roles in determining the catalytic efficiencies in water-medium organic synthesis.

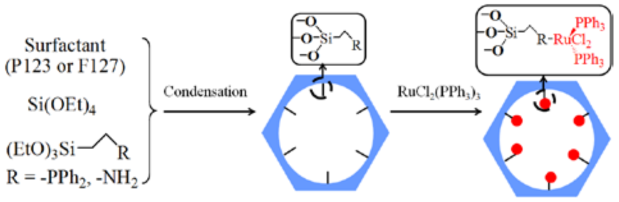


Figure 1 Illustration of preparing Ru(II) organometal catalysts terminally bonded to ordered mesoporous silica by grafting method.

Tailoring grafted organometal catalysts on the nanoscale offers great potentials for making all active sites on solid supports accessible to a reaction, so as to achieve catalytic reactivity similar to that of the homogeneous catalyst. Mesoporous silicas are frequently used as the supports owing to its high surface area and uniform pore size distribution which faciliate the diffusion and accessiblility of reactant molecules toward active sites.[23] Li group developed a serious of mesoporous Ru(II) catalytsts by grafting $RuCl_2(PPh_3)_3$ organometal complex into PPh_2- or NH_2-functionalized mesoporous silicas such as SBA-15 and FDU-12 through coordination reaction (Figure 1). During homoallylic alcohol isomerization reactions in water, they usually displayed much higher activity and selectivity than their corresponding partners grafted onto traditional silica supports. The PPh_2-functionalized SBA-15 supported Ru(II) organometal catalyst (Ru-PPh_2-SBA-15) exhibited almost the same efficiecy (73% yield) as the corresponding $RuCl_2(PPh_3)_3$ homogeneous catalyst (75% yield) for 1-phenyl-3-buten-1-ol isomerization in aqueous solution.[24] An important advatage was that it could be recycled and reused for more than seven times without significant deactivation. Meanwhile, amine-functionalized SBA-15 can also be used for grafting Ru(II) organometal complex *via* forming Ru(II)-NH_2 coordinating bond (Ru-NH_2-SBA-15) and such a catalyst also displayed good activity and durability in water-medium organic reactions.[25] In addition, the Ru(II) organometal catalytst can also be immobilized onto PPh_2-functionalized FDU-12 silica with three-dimensional cubic mesoporous structure (Ru-PPh_2-FUD-12), which could further improve the catalytic performance in water-medium isomerization of 1-phenyl-3-buten-1-ol. Obviously, large-sized pore entrances and pore cages facilitated the diffusion, the adsorption and the transformation of organic substrates including both either reactants and products.[26] Furthermore, Tu et al reported the synthesis of mesoporous silica MCM-41 and SBA-15 supported Ru-TsDPEN catalysts (Figure 2), which exhibited high efficiencies (both activity, selectivity and ee value) in asymmetric hydrogenation of various aromatic ketones in water.[27] Particularly, the catalyst could be readily recovered and reused in 11 consecutive catalytic runs. The authors also mentioned that this catalytic system in aqueous media showed a distinct "acceleration effect" in comparison with the reaction in organic solvent such as CH_2Cl_2. Nevertheless, this system must have the aid of phase transfer catalyst such as tetrabutylammonium bromide to decrease the reactant mass transfer limitaion in water.

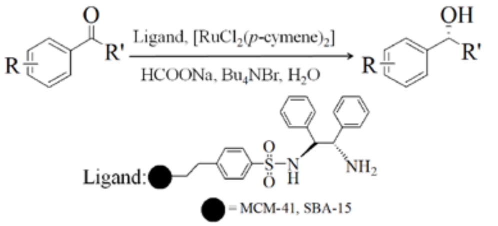


Figure 2 Asymmetric transfer hydrogenation in water using mesoporous silica supported Ru-TsDPEN catalyst.

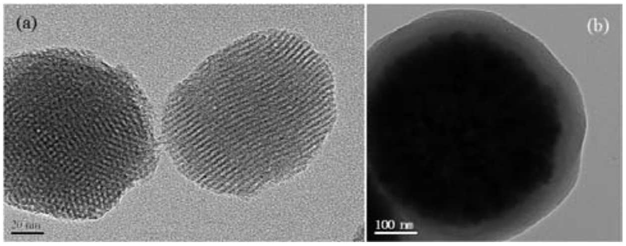


Figure 3 TEM images of mesoporous nanospherical Pd-PPh_2-MSN (a) and magnetic mesoporous core-shell Pd-PPh_2-MCM-41@SiO_2@Fe_3O_4 (b) prepared by grafting protocol.

Both experimental results and theoretical predictions confirmed that the irregular shape with long pore channels in traditional mesoporous silicas like MCM-41 and SBA-15 are harmful to the catalytic performances due to the unignored diffusion resistance.[28] Recently, Li et al reported an immobilized Pd(II) organometal catalyst (Pd-PPh_2-MSN) synthesized by chelating $PdCl_2(PPh_3)_2$ organometal complex with PPh_2-ligands grafted on the nanospherical mesoporous silica support (PPh_2-MSN).[29] Such a catalyst was present in uniform nanospheres with diameter about 100 nm and ordered mesoporous channels with diameter around 2.0 nm (Figure 3a). In water-medium Barbier and Sonogashira reactions, this catalyst displayed comparable catalytic efficiencies with the homogeneous $PdCl_2(PPh_3)_2$ catalyst. As a reference, the Pd-PPh_2-MCM-41 catalyst in irregular shape with average diameter bigger than 1.5 μm was also syntheized, which showed remarkable lower catalytic activity than that of Pd-PPh_2-MSN. For example, Pd-PPh_2-MSN exhibited 97% yield in the water-medium Sonogashira reaction with phenyl acetylene and iodobenzene while Pd-PPh_2-MCM-41 exhibited only 85% yield. The promoting effect of the the uniform nanospheres with short mesopore channels in Pd-PPh_2-MSN could be attributed to the decreased mass transfer resistance of reactant molecules toward active sites. This was supported by the adsorption test of Rhodamine B in aqueous solution, which demonstrated that the Pd-PPh_2-MSN displayed higher saturated adsorption capacity and faster adsorption rate than the Pd-PPh_2-MCM-41**.** Moreover, the Pd-PPh_2-MSN catalyst also exhibited longer lifetime than the Pd-PPh_2-MCM-41 during aqueous organic reactions owing to the enhanced stability against both the leaching of Pd(II) active sites and the damage of ordered mesoporous structure.

More recently, Li and co-workers also synthesized magnetic mesoporous microsphere supported organometal catalysts by anchoring $PdCl_2(PPh_3)_2$ or $RhCl(PPh_3)_3$ organometal onto MCM-41 thin layer coating Fe_3O_4 microsphere (M-PPh_2-MCM-41@SiO_2@Fe_3O_4, M = Pd or Rh).[30] The M-PPh_2-MCM-41@SiO_2@Fe_3O_4 was comprised of a superparamagentic Fe_3O_4, an amorphous silica with around 20 nm thickness and an outer layer of M-PPh_2 organometal functionalized MCM-41 with about 40 nm thickness and radial ordered mesopore channels (Figure 3b). These two catalysts exhibited comparable activities with their corresponding homogeneous organometal catalysts in various water-medium organic reactions including Sonogashira reactions and Miyaura-Michael reactions. Interestingly, Pd-PPh_2-MCM-41@SiO_2@Fe_3O_4 catalyst even displayed slightly higher activity than homogeneous $PdCl_2(PPh_3)_2$ catalyst in water-medium Sonogashira reaction with phenylacetyltlene and iodobenzene. Moreover, in comparison with the traditional Pd-PPh_2-MCM-41 catalysts with irregular shape and the Pd-PPh_2-SiO_2@Fe_3O_4 catalyst directly coating on the Fe_3O_4 core without ordered mesoporous structure, it also exhibited much higher catalytic reactivities. This excellent catalytic behavior could be ascribed to the high dispersion of active sites and the uniform microsphere with short-vertical ordered mesopore channels favoring reactant diffusion and adsorption. More importantly, the authors showed that the Pd-PPh_2-MCM-41@SiO_2@Fe_3O_4 catalyst was easily separated from the reaction system by simply applying an external magnet and meanwhile it could be used repeatedly 8 times without significant decrease in activity. The detailed characterizations demonstrated that the strong durability could be attributed to the preservation of the chemical microenvironment of the Pd active sites, the high stability of the microspheres against agglomeration, and the inhibition of Pd leaching. However, the control catalyst Pd-PPh_2-MCM-41 catalyst without Fe_3O_4 core was difficult to separate due to the extremely broad particle size distribution. Moreover, Pd-PPh_2-SiO_2@Fe_3O_4 catalyst without mesoporous structure displayed a rapid decrease in activity from the second run, which could be attributed to the remarkable Pd active sites leaching.

The similar concept of the utility of nanoscale mesoporous support for immobilizing organometal catalysts was also demonstrated by Liu group.[31] They synthesized a flower-like mesoporous silica-supported chiral organorhodium catalyst through coordinating bis[(pentamethylcyclopentadienyl)dichloro-rhodium] complex ($[Cp^*RhCl_2]_2$) with chiral diamine (DPEN) that originally grafted onto the silica support. The obtained Cp*RhTs-FFMS catalyst displayed uniformly distributed three-dimensional mesoporous spherical flowers constructed by the stacking of leaf-shaped nanoflake. This unique structure endowed the excellent catalytic activity and high enantioselectivity in the asymmetric transfer hydrogenation of aromatic ketones in water medium. Taking acetophenone as an example, it exhibited 99% conversion and 97% ee of (S)-1-phenyl-1-ethanol product, in which the conversion was even higher than its corresponding homogeneous counterpart (88%). In addition, it could be recovered easily and reused repeatedly for more than ten times without significantly affecting either conversion or ee value.

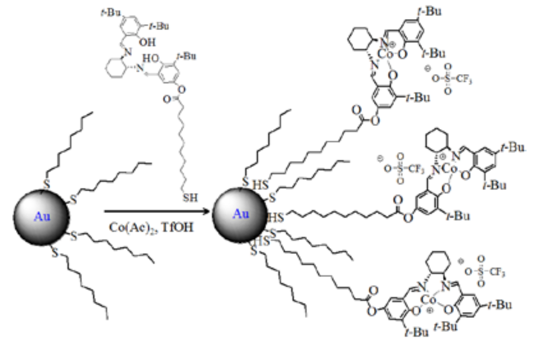


Figure 4 Illustration of preparing [(salen)Co(II)] chiralcatalyst terminally bonded to gold nanoparticles.

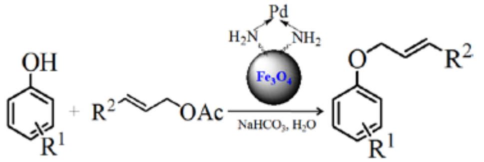


Figure 5 Water-medium *O*-Allylation of phenols on a Fe_3O_4-dopamine-Pd catalyst.

The other way to overcome the accessibility problem for heterogeneous organometal catalysts is to immobilize organometal complexes onto tiny nanoparticles, which might guarantee the high dispersion of organometal active sites and also avoid the diffusion resistance in the porous channels of these organometal catalysts deposited onto big-sized supports.[32, 33] Jacobsen group designed a chiral [(salen)Co(II)] organometal catalyst deposited on the Au nanoparticles.[34] They introduced salen-terminated thiols on the surface of 3.4 nm-sized gold nanoparticles through place-exchange reaction with n-octane thiol.

Then, $Co(OAc)_2$ catalyst was immobilized *via* the coordination reaction with salen-terminated thiol (Figure 4). Such a catalyst was highly active in the hydrolytic kinetic resolution of racemic hexane-1-oxide, which displayed the complete kinetic resolution with 99.9% ee of epoxide within 5.0 h. It could be recycled conveniently by filtration and used repetitively for more than seven times without affecting ee value, but the reactivity decreased by 50% after the sixth recycle. Laska et al reported that Fe_3O_4 nanoparticle could be directly used for anchoring $[Rh(TPPTS)_3Cl]$ complex (TPPS: tri(m-sulfophenyl)phosphine) owing to the surface hydroxyl groups.[35] The NP-$[Rh(TPPTS)_3Cl]$ catalyst successfully promoted water-medium hydrogenation of olefins and addition reaction of arylboronic acids to dimethyl itaconate. The catalyst could be reused for up to ten consecutive cycles. Varma group developed a very good method using dopamine functionalized Fe_3O_4 nanoparticle to anchor $PdCl_2$ as an easily recyclable catalyst for the water-medium O-allylation of phenols with allylic acetates in aqueous solution with yields up to 85% under ambient conditions (Figure 5).[36] The catalyst was easily recovered by magnetic separation and could be reused for more than six times without significant decrease in activity.

Due to the rare functionality in pure nanoparticle surface, the application of nanoparticles as supports for immobilizing organometal catalysts was quite limited.[37] The core-shell structured nanoparticles provide a new promising way to generate more grafted organometal catalysts since the outer-shell could be easily modified with various chelated ligands. In this context, the silica shell attracted a lot of attention owing to the plenty of surface hydroxyl groups for derivatization with different functional groups and the protection of the nanoparticle core by outer silica-shell under harsh condition.[38] One excellent sample was demonstrated by Lee group. Commercially available Fe_3O_4 nanoparticles with an average diameter of 20 nm were coated with silica thin layer using a sol-gel process to generate $SiO_2@Fe_3O_4$. Then, (β-oxoiminato)(phosphanyl)palladium complex was immobilized onto $SiO_2@Fe_3O_4$ through simlple silane-coupling reaction (Figure 6).[39] This catalyst exhibited excellent catalytic reactivity and selectivity in the water-medium Suzuki, Sonogashira and Stille coupling reactions with 57 different unreactive aryl chlorides under mild conditions. Most reactions displayed high yields around 90% and the catalyst could be reused for more than 10 consecutive times without significant loss of catalytic activity. ICP-AES analysis confirmed that less than 0.06% of the stating palladium catalyst had leached out from the catalyst surface. Also, no obvious agglomeration of Pd(0) to form visible nanoparticles was observed on the support surface after the tenth reaction owing to the robust nature of this palladium complex, resulting in the high durability of this $SiO_2@Fe_3O_4$ supported Pd(II) catalyst. Recently, Rezaeifard and co-workers immobilized Cu(II) phthalocyanine-tetrasulfonic acid tetrasodium complex (CuPcS) onto silica-coated magnetic nanoparticles through ion-pair strategy to form heterogeneous Cu(II) organometal catalyst, which also showed excellent activity and selectivity in water-medium sulfide oxidation to sulfones.[40] Moreover, this catalyst could be reused for seven successive cycles and FT-IR spectrum showed that the catalyst was strongly anchored on the magnetite nanoparticles

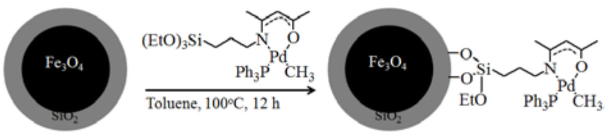


Figure 6 Illustration of preparing Pd(II) organometal catalyst terminally bonded to $SiO_2@Fe_3O_4$ nanoparticles.

Liu group developed a convenient method for preparing a magnetically recoverable chiral rhodium organometal catalyst through directly coordinating $[Cp^*RhCl_2]_2$ with (S, S)-TsDPEN-ligand that originally grafted on the SiO_2 layer coating Fe_3O_4 nanoparticle (TsDPEN: N-(p-toluenesulfonyl)-1,2-diphenylethylenediamine)). SEM and TEM imgaes (Figure 7a-b) revealed that this catalyst presented in uniform core-shell microspheres with the average diameter around 400 nm and the silica shell thickness was about 30 nm. The high magnetization ensured the rapid separation using a small external magnet (Figure 7c-d). Meanwhile, this catalyst exhibited excellent catalytic activities (up to 99%) and enantioselectivities (up to 97% ee) for asymmetric transfer hydrogenation of various aromatic ketones in aqueous solution. In particular, such a chiral catalyst could be recovered easily and used repetively for more than 10 times without obviously affecting either the activity or the enantioselectivity.[41]

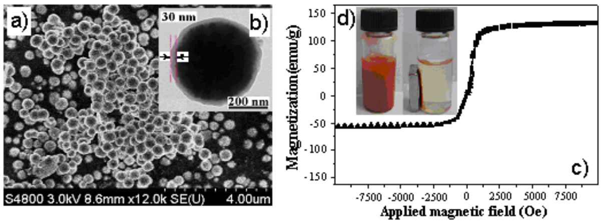


Figure 7 SEM (a) and TEM (b) images, magnetization curve (c) and separation process (d) of the $[Cp^*RhCl_2]_2$ chiral catalyst terminally bonding to TsDPEN-modified SiO_2 coated Fe_3O_4 nanoparticles.

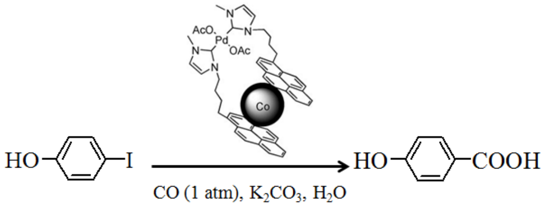


Figure 8 Hydroxycarbonylation of 4-iodophenol with CO in water over Co@C nanomagnet supported Pd(II) NHCs catalyst.

Reiser and co-workers demonstrated that Pd-NHCs catalyst with pyrene tags (NHCs: N-heterocyclic carbene) could attach to Co/C nanoparticle *via* noncovalent binding approach (Figure 8).[42] This catalyst was used in water-medium hydroxycarbonylation of six different aryl halides under an atmospheric pressure of CO and obtained satisfory yields. Interestingly, when the reaction reached to 100°C, the Pd(II) complex could dissociate from the carbon shell to allow Pd(II) organometal catalyst acted as a homogeneous catalyst and when the system cooled to room temperature after reaction, the pyrene-modified Pd NHCs complex could be re-immobilized onto the carbon shell surface.

The high magnetic remanence of Co nanoparticle permitted rapid and efficient separation of the catalyst. Correspondingly, this catalyst could be conveniently recycled and used repetitively for more than 16 times.

In nature, enzymes generally make use of a compartmentalized hydrophobic cavity with a hydrophilic outer shell. This unique structure endows the high reactivity and selectivity of enzymes for various organic and biochemical reactions occurred in aqueous solution.[43] Learning from this concept, immobilized organometal catalysts for water-medium organic reactions are usually modified with organic groups to enhance surface hydrophobocity. Initially, the hydrophobic organic moieties such as polyethylene glycol (PEG), phenyl and ethane groups were introduced into the pore channels of mesoporous silica supports by grafting approach, which showed great improvement on both the catalytic reactivity and the selectivity. Xiao group developed a palladium catalyst ($Pd(PPh_3)_4$) anchored on the PEG-functionalized mesoporous silica (Figure 9),[44] which exhibited high activity and selectivity in water-medium Suzuki coupling reactions. Moreover, this catalyst remained highly active after exposure to air for up to 6 weeks. An aqueous suspension of the catalyst was reused five times by simple extraction of the aqueous reaction mixture, indicating that the PEG organic layer on the catalyst pore surface inhibited the leaching of Pd organometal active sites.

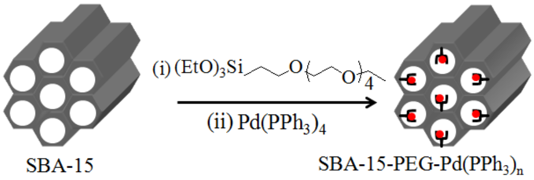


Figure 9 Illustration of preparing SBA-15-PEG-$Pd(PPh_3)_n$ catalyst by grafting method.

Taking into account that the organic groups terminally bonded to the silica pore surface blocked pore channels and even destroyed ordered mesoporous structure,[45] periodic mesoporous organosilicas (PMO)[46] with organic groups uniformly embedded in silica walls were used as the supports for immobilizing organometal catalysts. Li et al used PPh_2-functionalized ethyl-bridged PMOs to coordinate $PdCl_2(PPh_3)_3$ complex, which exhibited high activity in water-medium carbon-carbon coupling reactions including Barbier and Sonogashira reactions and could be reused for many times.[47] Control experiments demonstrated that the enhance surface hydrophobicity due to the ethyl- and PPh_2-modification faciliated the diffusion and adsorption of organic reactant molecules, which promoted the organic reactions and also prevented the leaching of active sites or the damage of ordered mesoporous structure.[48] Meanwhile, Liu et al reported chiral Rh organometal catalyts immobilized on ethane-, ethylene- and benzene-bridged PMOs (Figure 10) and found that ethylene-modification exhibited the best promoting effect on both the catalytic activity and the enantioselectivity in water-medium asymmetric transfer hydrogenation of various aromatic ketones, possibly owing to the strong hydrophobicity, the confined nature of the chiral organorhodium catalytic sites and the absent pore blockage by the small ethylene groups. This catalyst could be conveniently recovered and reused at least 12 times with almost the same catalytic activity and enantioselectivity. The enantioselectivity was slightly lower than the corresponding homogeneous catalyst due to the π-π interactions between ethenylene- or phenylene-bridged moieties and the Ph groups of 1,2-diphenylethylenediamine,[49] which might cause a certain configurational transformation of the active Rh species toward the chemical microenvironment that unfovouring the reaction.

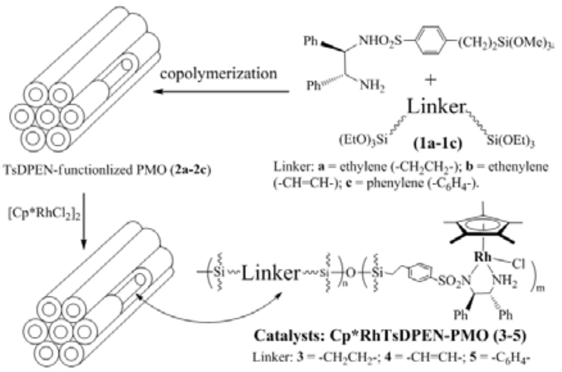


Figure 10 Schematic preparation of Cp*RhTsDPEN-PMO chiral catalysts by grafting method.

Functionalization of the organic moieties in the silica wall of PMO as chelated ligands provided a novel approach to obtain highly active solid organometal catalysts since it could guarantee the homogenous distribution of active sites and also prevent the damage of ordered mesoporous structure.[50] Recently, Li group reported a facile approach for synthesizing PMO supported rare earth triflate catalyst by chelating $Sc(OTf)_3$ with sodium benzenesulfonate ($NaPhSO_3$-) functionalized phenyl-bridged periodic mesoporous silica (Ph-PMO).[51] They firstly sulfonated the phenyl groups in the silica wall of Ph-PMO to generate HSO_3-Ph-PMO. Then, the $NaSO_3$-Ph-PMO support was achieved by ion-exchange approach, which was allowed to react with $Sc(OTf)_3$ to form $(OTf)_2Sc-SO_3$-Ph-PMO catalyst by replacing one OTf-group with the $PhSO_3$-ligand (Figure 11). It displayed much higher catalytic efficiencies than $(OTf)_2Sc-SO_3$-Ph-SBA-15 catalyst with Sc^{3+} active species terminally bonded to the pore surface, and was even more active than $Sc(OTf)_3$ homogeneous catalyst. Besides the high dispersion of active sites and the ordered mesoporous channels, it could be mainly attributed to the enhanced surface hydrophobicity resulted from the high content of phenyl-groups embedded in PMO silica walls, which promoted both the diffusion and the enrichment of reactant molecules on the catalyst pore surface. Moreover, it could be easily recycled and reused repetitively from at least 10 times since the Sc^{3+} complex incorporated into the PMO framework could effectively inhibit the leaching of active sites and also enhanced hydrothermal stability of ordered mesoporous structure.

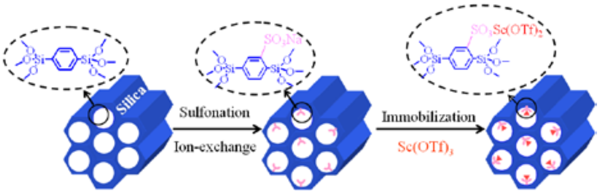


Figure 11 Schematic preparation of $(OTf)_2Sc-SO_3$-Ph-PMO catalyst

Polymer resins were also used as the supports instead of organo-functionalized silica supports, which showed stronger intrinsic hydrophobicity than the silica supports functionalized with organic groups. Moreover, they also display strong resistance againt alkaline corrosion, which allows them to be used in organic reactions with strong alkaline media, taking into account that silica could be easily dissolved in alkaline solution. Uozumi group designed a amphiphilic PS-PEG resin supported chiral imidazoindole phosphine ligand for chelating $Pd(OAc)_2$ catalyst (Figure 12),[52] which was tested in the asymmetric Suzuk-Miyaura coupling reactions for synthesizing a variety of axially chiral biaryl compounds. High yields with good enantioselectivities (88-99%) were achieved in aqueous solution at room temperature. However, their practical applications are limited by high Pd loading (10 mmol%) and excess boronic acid (5.0 equiv.). Recently, Li group reported a novel PPh_2-functionalized phenol-formaldehyde resin with ordered mesoporous structure synthesized by evaporation induced self-assembly (EISA) approach, which could coordinate various metallic ions (Pd^{2+}, Au^{+}, Ni^{2+}, Rh^{+}) (Figure 13).[53] All these catalysts exhibited comparable efficiencies with the corresponding homogeneous catalysts in various water-medium organic reactions including Barbier, Sonogashira, Heck, A^3-coupling reactions owing to the large surface area, ordered mesopore channels, uniform distribution of active sites and strong surface hydrophobicity and could be used repetitively. Superior over the silica-supported catalysts, they were stable in strong basic solution, which allowed the organic reactions to perform in alkaline media.

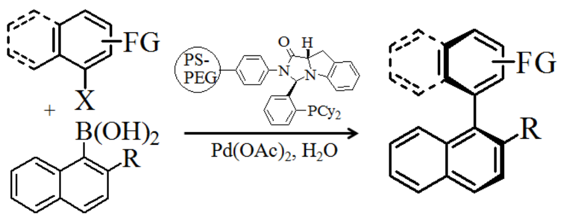


Figure 12 PS-PEG resin supported chiral palladium imidazoindole phosphine catalyzed asymmetric Suzuk-Miyaura reaction in water.

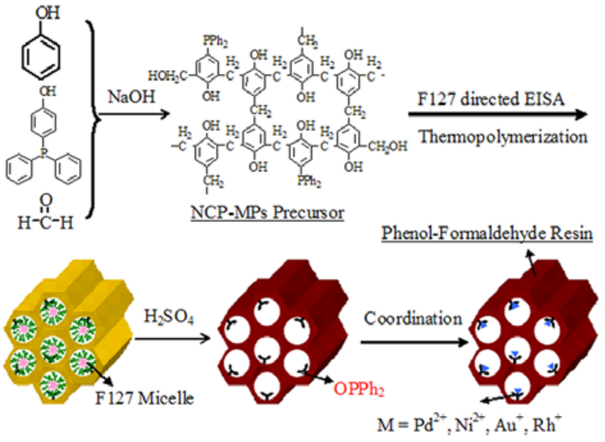


Figure 13 Illustration of the preparation of M-NCP-MPs catalysts.

Self-Assembled Organometal Catalysts

Although extensive efforts have been conducted on the fabrication of grafted organometallic catalysts, the inherent drawbacks such as inhomogeneous active sites distribution and the uncertain coordinated chemical microenvironment caused the unsatisfactory catalytic reactivity, selectivity and durability in water-medium organic reactions. Self-assembly approach appears as one of the most promising approaches towards the synthesis of highly active catalysts with desired structures and functions.[54] Self-assembly refers to a spontaneous organization of building blocks driven by noncovalent interactions such as hydrogen bonding and hydrophobic force.[55] To date, rapid advances in the self-assembled organometallic catalysts have been made by mimicking natural design, which resulted in the development of robust and reusable heterogeneous organometal catalyst in aqueous organic reactions.

Many fundamental molecular processes in living organism are governed by biological membrane, which plays a key role in cell signaling and transmitting the signal of external stimuli across cell membranes.[56] The concept of self-assembled membrane has recently expanded to catalyst preparation by Uozumi group.[57] They mimic lipid bilayer membrane system to synthesize an amphiphilic palladium catalyst *via* hydrophobic interaction (Figure 14). Specifically, they used the pincer palladium complex containing pairs of hydrophobic dodecyl chains and hydrophilic tri(ethylene glycol) chains located opposite to one another on the rigid planar backbone for the self-assembly process. After assembling in water at 60°C for 4.0 h, hard vesicles in spherical shape with membrane thickness around 6.0 nm were obtained. Their catalytic performances were tested in arylating oxirane ring-opening reaction of vinyl epoxide with phenylboronic acid, which showed 84% yield of product, much higher than the Pd precuror without assembly treatment (7.0% yield). It was suggested that the organic substrate should be concentrated within the hydrophobic region of the bilayer membrane under aqueous conditions, where the potentially catalytic palladium species was located in immediate proximity.[58]

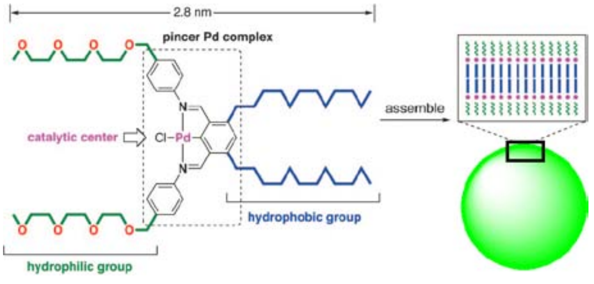


Figure 14 Schematic formation of catalytic vesicle by self-assembly of the pincer palladium complex.

Meijer group reported a novel compartmentalized polymeric Ru(II) nanoparticle catalysts through single-chain folding of linear polymers bearing different functional groups (Figure 15).[59] They were prepared by folding through hydrogen-bonding interactions and helical self-assembly of a water-soluble amphiphilic precursor terpolymer containing both chiral and ruthenium-bonded units. The formation of the Ru(II) organometal containing hydrophobic compartment inside the single-chain nanoparticles was observed. As a reseprentative sample, the Ru-PEGMA/BTAMA/SDP segmented terpolymer with molecular weight 105,000 displayed spherical nanoparticles with diameter around 3.0 to 4.0 nm. Such a catalyst displayed no intermolecular aggregation. The dots observed from HRTEM images probably indicated the hydrophobic cores of the core-shell-like structure, due to the low contrast of the swollen hydrophilic shell in water. During the reduction of cyclohexanone to cyclohexanol carried out in aqueous solution, this artificial enzyme-like catalyst exhibited both high turnover frequency (TOF = 11 h^{-1}).

Metalloenzymes are essential proteins that contain a metal ion cofactor, which can promote a variety of important chemical transformations in biological systems.[60] Learning from metalloenzymes, Uozumi and co-workers designed a highly active and reusable Pd organometal catalyst (MEPI-Pd) *via* self-assembly of poly(imidazole-acrylamide) and $(NH_4)_2PdCl_4$, which displayed a globular-aggregated structure.[61] Such a catalyst exhibited very high reactivity in water-medium allylic arylation and Suzuki-Miyaura reactions. As an example, the turnover number (TON) reached to 3570000 in Suzuki-Miyaura reaction with 1-iodo-4-methylbenzene and phenylboronic acid as reactants, which was the highest value among heterogeneous catalysts reported so far. Interestingly, it also exhibited much higher activity than the homogeneous catalyst system comprised of $(NH_4)_2PdCl_4$ and N-Me-imdazole (5.0% yield), indicating that the cooperative effect resulted from the imidazole unit and the amphiphilic polymer backbone greatly promoted the reactions. Moreover, such a catalyst could also be easily recycled and used repetitively for many times in water-medium allylic arylation reaction and Suzuk-Miyaura reactions.

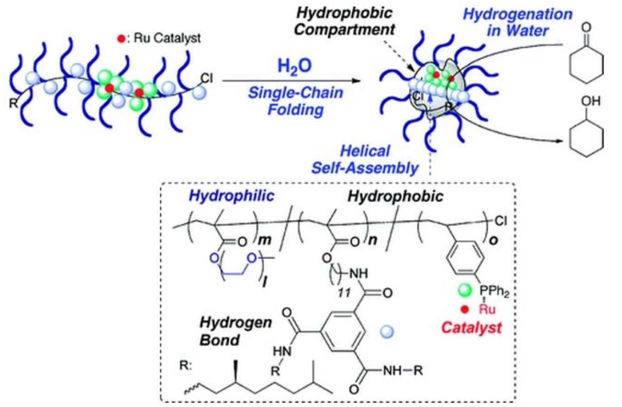


Figure 15 Illustration of preparing nanoparticle Ru(II) organometal catalyst for water-medium cyclohexanone reduction to cyclohexanol.

Self-assembled organometal-bridged PMOs represent a new class of heterogeneous organometal catalysts with ordered mesoporous structure and uniform dispersion of active sites in silica walls.[62, 63] Li and co-workers reported a general assembly route towards the synthesis of such catalysts.[64, 65] As illustrated in Figure 16, the organosilane monomer and organometalsiliane monomer co-condensed and self-assembled into periodic ordered mesoporous organometal-silica. Hydrophobic interactions between the surfactant and the organometallic building molecules preferably located the organometallic active species on their interface. Surfactant removal resulted in mesoporous channels with silica walls containing surface-anchored organometal catalysts (M-PPh_2-PMO). Such catalyst displayed several major advantages: 1) The mesoporous channles with tunable dimension provided effective mass transport pathways; 2) Incorporation of active organometal complexes into silica framework retained the chemical microenviroment of active sites and also resisted the leaching of active sites; 3) Homogenous immobilization of the active building molecules avoided the cross-interference, leading to uniform despersion of active sites. For example, Pd organometal-bridged silane could co-assemble with bis(triethoxysilyl)benzene and P123 surfactant. Removal of surfactant micelles *via* extraction in ethanol solution led to the Pd-PPh_2-PMO catalyst. As expected, it exhibited comparable catalytic efficiencies with homogeneous $Pd(PPh_3)_2Cl_2$ catalyst in water-medium Barbier and Sonogashira reactions. Similar results were also observed by using Au-PPh_2-PMO, Rh-PPh_2-PMO and Ru-PPh_2-PMO catalysts in water-medium hydration, Heck and isomerization reactions with various substrates. Generally, these catalysts exhibited much higher activity and longer lifetime than their corresponding ones prepared by grafting method owing to the retained chemical microenvironment of active sites, reduced spetial hindrance and enhanced stability against leaching of active sites.[66] For example, Pd-PPh_2-PMO catalyst could be reused for more than 10 times in the water-medium Barbier reaction without significant deactivation. On contrast, the Pd-PPh_2-PMO(G) showed a decrease of activity by 30% only after 5 repetitive cycles. It had been confirmed that the remarkable leaching of Pd(II) active sites and the slight damage of ordered mesopoeous structure responsed for the deactivation in the recycled Pd-PPh_2-PMO(G) catalyst.

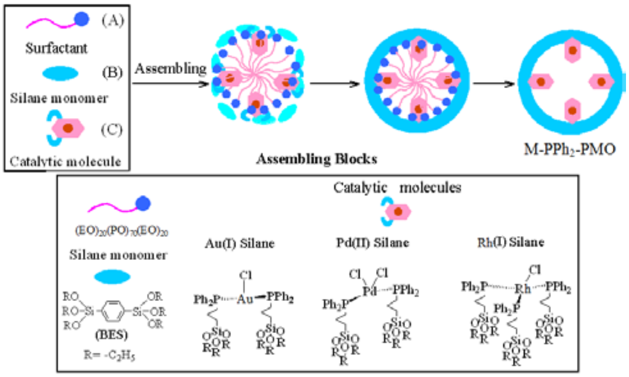


Figure 16 Illustration of preparing M-PPh_2-PMO catalysts *via* co-condensation self-assembly.

To furthemore investigate the intrinsic benefical effect of the self-assembled mesoporous organometallic catalyst (M-PPh_2-PMO), Li group employed ^{31}P CP MAS NMR method to analyze the coordination model in the representative control Pd-PPh_2-SBA-15 catalyst obtained by coordinating $PdCl_2(PPh_3)_3$ with the $PPh_2(CH_2)_2$-ligands originally grafted onto the SBA-15 support. They found that two kinds of coordination models co-existed in the Pd-PPh_2-SBA-15 catalyst.[67] At high PPh_2-content, the catalyst mainly contained Pd-2P model, i.e., each Pd(II) ion was coordinated with two PPh_2-ligands. While at low PPh_2-content, it contained mainly Pd-1P model, i.e., each Pd(II) ion was coordinated with one PPh_2-ligand (Figure 17).[68] During various C-C bond forming reactions including Suzuki, Heck, Barbier, and Sonogashira, the Pd-2P coordination model exhibited higher activity and better selectivity than the Pd-1P model. This further confirmed the superiority of the self-assembled organometal catalysts over their corresponding grafted ones, since the former usually contained only one coordination model with the highest coordination number presented in the organometal silane (see Figure 15), while the latter usually conatined multiple coordination models with low coordination number depending on the content of ligands originally grafted on the supports.

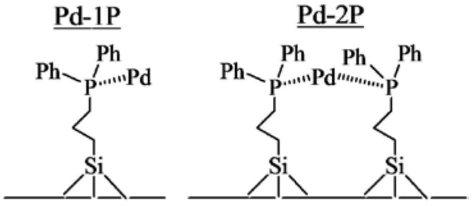


Figure 17 Two typical coordination models presented in the Pd-PPh_2-PMO(G) catalyst prepared by grafting method.

An important merit of immobilized organometal catalysts was their convenient recycle and reuse. Li et al examined the lifetime of immobilized Ru(II) organometal on the mesoporous silica prepared by either grafting protocol (Ru-PPh_2-PMO(G)) or co-condensation approach ((Ru-PPh_2-PMO).[65b] As shown in Figure 18, during water-medium isomerization of 1-(4-methylphenyl)-3-buten-1-ol, the Ru-PPh_2-PMO catalyst could be used repetitively for at least 7 times, but the Ru-PPh_2-PMO(G) catalyst could be reused for only 4 times. ICP analysis revealed that the deactivation of Ru-MOC was mainly due to the decrease of Ru(II) loading. Obviously, each Ru(II) ion in the Ru-MOC prepared by co-condensation was coordinated with three PPh_2-ligands covalently bonded with the silica support while in the grafted Ru-MOC each Ru(II) was coordinated with only one PPh_2-ligand. Thus, the former displayed stronger durability because of the stronger stability against leaching of Ru(II) active sites.

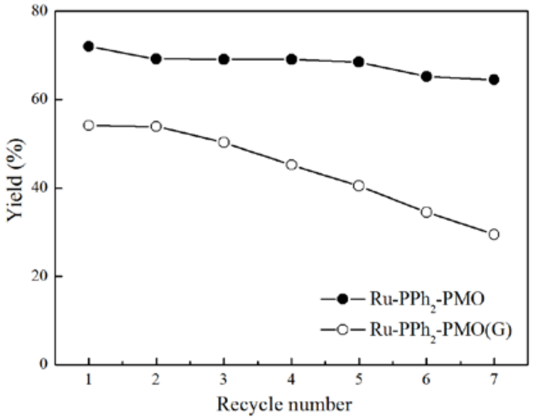


Figure 18 Recycling tests of Ru-PPh_2-PMO and Ru-PPh_2-PMO(G) catalysts in the water-medium homoallylic alcohol isomerization reaction.

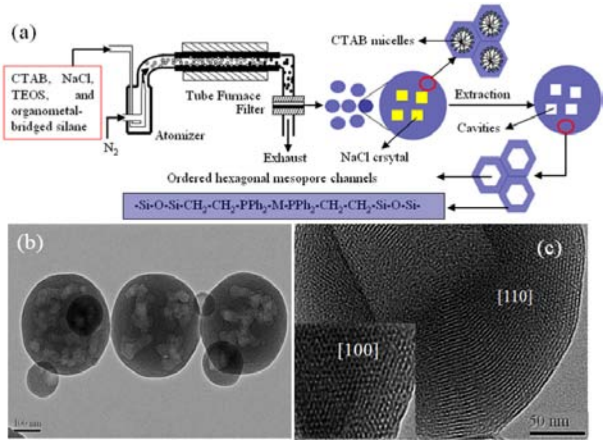
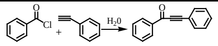
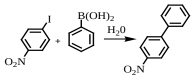
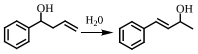
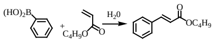


Figure 19 (a) Illustration of preparing M-PPh_2-PMO(H) catalysts by aerosol-spray assisted co-condensation, and (b-c) the TEM images of representative Pd-PPh_2-PMO(H) catalyst.

Most of these protocols for the reported self-assembled organometallic catalysts were conducted in the tedious and time-consuming preparation technique, resulting in the limited physical structure and/or chemical functionality. Meanwhile, the major difficult in the implementation of these laboratory-designed catalysts is the scale-up into technically demanding process. Aerosol process has attracted significant interest since it is comprised of a limited number of preparation steps and produces materials continuously with very low waste.[69] Recenetly, the coupling of template-directed assembly with aerosol process showed the great potential in the synthesis of ordered mesoporous materials with tunable pore strucure, size and surface chemistry owing to its simplity and economy.[70] Li group developed an elegant method for the synthesis of organometal catalysts by rapid aerosol-spray assisted co-condensation between different organometal-bridged silane and TEOS in the presence of cetyltrimethyl ammonium bromide (CTAB) and NaCl as double templates (Figure 19a).[71] These catalysts were present in uniform microspheres contained two-dimential ordered mesoporous channels in silica walls and nanocubic cavities inside the sphere chamber (Figure 19b-c).[72] The size of microspheres could be controlled by adjsuting the flow speed of carrier gas N_2. Meanwhile, the number of chamber cavities was parallel to the content of NaCl in mother solution. The as-prepared M-PPh_2-PMO(H) catalysts (M = Pd^{2+}, Rh^+ and Ru^{2+}) exhibited high catalytic activities and selectivities during water-meidum Barbier, Suzuki, Sonogashira, acylation and isomerization reactions (Table 1) owing to the high surface area, the uniform distribution of active sites, the ordered mesoporous channels and especially, the cavities as microreactors favoring the diffusion and adsorption of organic reactants, which had been confirmed by controlled adsorption tests for various organic molecules with different sizes. Meanwhile, they could be easily recovered and showed strong durablity owing to the organometals incorporated into silica walls and short mesoprous channels as mentioned above. More interestingly, they displayed longer lifetime than the corresponding catalysts without chamber cavities, since these cavities could effectively retard the damage of ordered mesoporous structure and the leaching of active sites owing to the dimished structural corrosion from reactants by enhancing their diffusion rate.

Table 1 Catalytic performances of different M-PPh$_2$-PMO(H) catalysts in corresponding water-medium organic reactions

Reactions	Catalyst	Conv. (%)	Select. (%)	Yield (%)
	Pd(PPh$_3$)$_2$Cl$_2$	97	97	94
	Pd-PPh$_2$-PMO(H)	97	92	89
	Pd(PPh$_3$)$_2$Cl$_2$	100	91	91
	Pd-PPh$_2$-PMO(H)	99	87	86
	Ru(PPh$_3$)$_2$Cl$_2$	90	99	89
	Ru-PPh$_2$-PMO(H)	90	99	89
	Rh(PPh$_3$)$_2$Cl	99	99	98
	Rh-PPh$_2$-PMO(H)	99	95	94

Bifunctional Catalysts for “One-Pot” Cascade Reactions

In living systems, enzymes can easily realize the complicated but efficient metabolic processes through “one-pot” synergic catalytic performance, which could be attributed to their complex polypeptide architecture with different multiple active species.[73] Organic synthesis process is usually comprised of iterative reactions.[74] Generally, the iterative reaction is conducted individually and step-by-step with the corresponding catalyst. After each step of reaction, the product and catalyst should be isolated and purified, followed by adding new catalyst and other reactants as well as solvent media for the subsequent step of the cascade reaction. Obviously, it is the most time- and cost-demanding and waste-producing manual operations. “One-pot” cascade reactions could proceed all steps of reactions to the final products without isolation steps in each intermediate step, which have received increasing interest in modern organic chemicals owing to the simplified process with the reduced time, cost and waste.[75] Learning from enzymes, most studies are focused on homogeneous organometal catalysts with multiple kinds of active sites for synergetically driving “one-pot” cascade reactions. Recently, heterogeneous organometal catalysts with multiple kinds of active sites and/or hierarchical structures have also been developed by controlled self-assembly.[76] However, it has remained largely unexploited in the highly efficient and water-compatible solid organometallic catalysts with two or more different active sites since the general interference existed between different organometallic complexes.[77] Herein, we briefly introduce heterogeneous bifunctional organometal catalysts comprised of two active sites for “one-pot” cascade reactions.

“One-pot” cascade reactions can be easily carried out with the mixture of different homogeneous catalysts. However, catalysts can not be conveniently recycled and reused. Sometimes, homogeneous catalysts can not be mixed in the same system due to their own reactions and interference. For example, the combination of acid and base catalysts for cascade process is recognized as a more attractive approach since the acidic and basic functions can activate electrophiles and nucleophiles, respectively.[78] Obviously, the use of both strong acidic and basic species in the homogeneous system is impossible due to the neutralization that forms inactive salts. Interestingly, heterogeneous catalyst could address this challenge by the spatially isolated acidic and basic sites, avoiding their destructive interaction in the so-called “wolf-and-lamb” reactions.[79] To date, acid-base bifunctional catalysts hosted into the solid matrix such as silica, clay, polymer and graphene have been reported.[80] As a result, these catalysts sucessfully realized several cascade reactions including deacetalization-aldol and deacetalization-Baylis-Hillman reactions. Inspired by this site-isolation strategy, Li and co-workers reported an “one-pot” cascade reaction comprised of sequential Fe(III)-catalyzed phenylacetylene hydrolysis and Cp*Rh-catalyzed asymmetrical hydrogenation by using the mixture of homogeneous FeCl$_3$ catalyst and solid Cp*RhTsDPEN-PMO(Et) chiral catalyst, where Cp* refers to pentamethylcyclopentadiene.[81] The Cp*RhTsDPEN-PMO(Et) was prepared by grafting method (see Figure 20), where PMO(Et) refers to the ethylene-brdidged periodic mesoporous organosilica. This bifunctional catalyst system exhibited equivalent activity, selectivity and ee value with the corresponding homogeneous catalytic system comprised of FeCl$_3$ and (Cp*RhCl$_2$)$_2$. The Cp*RhTsDPEN-PMO(Et) catalyst showed superiority since it could be recycled and used repetitively for more than 5 times.

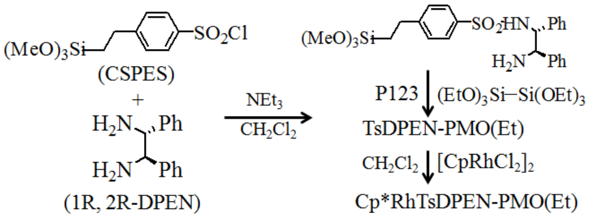


Figure 20 Illustration of preparing Cp*RhTsDPEN-PMO(Et) chiral catalyst.

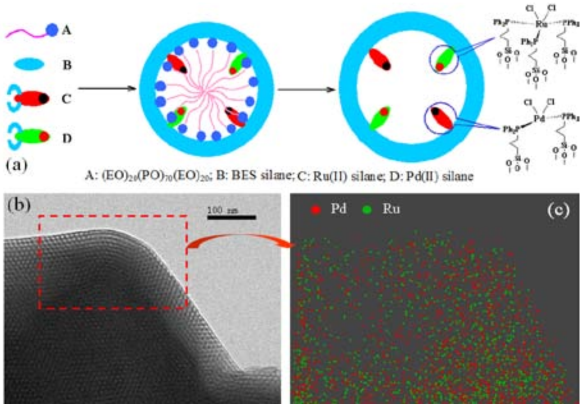
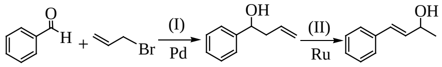


Figure 21 Schematic prepartion (a), HRTEM image (b) and chemical mapping (c) of Pd-Ru-PMO bifucntional catalyst.

Liu et al developed that a mesoporous silica-supported bifunctional Ti-Ru-SBA-15 catalyst with ordered two-dimensional hexagonal mesostructure by post-grafting organometallic complexes RuCl$_2$(PPh$_3$)$_3$ and Ti(OiPr)$_4$ onto PPh$_2$-functionalized SBA-15 support.[82] During the tandem addition-isomerization reaction of benzaldehyde under microwave irradiation in aqueous media, this Ti-Ru-SBA-15 catalyst exhibited high catalytic activity (more than 97%) and selectivity (up to 96%). These authors also tested the controlled experiments using Ti-SBA-15 catalyst under the same reaction conditions and showed no activity, suggesting the isomerization reaction was triggered from the Ru(II) complexes. Such a catalyst could be recovered easily and used repetitively for five times without significantly deactivation. However, these authors did not comapare the catalytic performance of the Ti-Ru-SBA-15 with either the mixture of corresponding Ti(IV) and Ru(II) homogenoeus organometal catalysts or the physical mixture of Ru-SBA-15 and Ti-SBA-15 catalysts in "one-pot" cascade reactions. In addition, they did not compare the reaction efficiencies with those by using individual reactions catalyzed by Ru-SBA-15 and Ti-SBA-15 catalysts, respectively. Therefore, the advantages of such a bifunctional organometal catalyst was not clearly displayed.

An excellent self-assembled bifunctional organometal catalyst (Pd-Ru-PMO) containing Pd(II) and Ru(II) active sites was demonstrated by Li group. This catalyst was synthesized using the surfactant directed assembly approach in an acidic aqueus solution by using $PdCl_2[PPh_2(CH_2)_2Si(EtO)_3]_2$, $RuCl_2[PPh_2(CH_2)_2Si(EtO)_3]_3$, and 1, 4-bis(triethoxysilyl)benzene (BES) as starting materials.[83] Hydrolysis and condensation reaction of these functional molecules in the presence of and surfactant P123 as a soft template generated mesoporous nanocomposite containing both Pd(II) and Ru(II) organometals. Subsequent surfactant extraction resulted in a Pd(II)-Ru(II) bifunctional organometal catalyst with Pd(II) and Ru(II) organometal complexes incorporated into silica walls (Figure 21a), which had been confirmed by tesing the change of pore size through N_2 adsorption-desorption isotherms. The HRTEM imgae in Figure 21b demonstrated the ordered two-dimentional mesoporous channels, which also further confirmed by low-angle XRD pattern. Meanwhile, the chemical mapping in Figure 20c clearly showed the uniform distribution of Pd(II) and Ru(II) active sites. For comparison, the grafted Pd(II)-Ru(II) bifunctional organometal catalyst with Pd(II) and Ru(II) organometal complexes terminally bonded to the silica surface of ordered mesoporous channels was also prepared by the afore-mentioned grafting protocol (denoted as Pd-Ru-PMO-G). A water-medium two-step cascade reaction composed of (I) Pd(II)-catalyzed Bariber reaction and (II) Ru(II)-catalyzed homoallylic alcohol isomerization was chosen as a probe reaction. As shown in Table 2, the Pd-Ru-PMO bifunctional catalyst exhibited comparable activity and selectivity as well as yield with their corresponding homogenous catalysts. Meanwhile, its catalytic performance was much better than that of the Pd-Ru-PMO-G, possibly owing to both the suitable chemical microenvironment of active sites as confirmed by ^{31}P solid NMR spectra and the diminished mesopore blockage corresponding to the low diffusion limit of reactant molecules. Furthermore, the Pd-Ru-PMO catalyst also exhibited much higher efficiency than the physical mixture comprised of Pd-PMO and Ru-PMO. It displayed even much higher efficiencies than the mixture of either the Pd-PMO or the Ru-PMO with the $RuCl_2(PPh_3)_3$ or the $PdCl_2(PPh_3)_3$ homogeneous catalyst. These results demonstrated that the suitable distance between two kinds of active sites in bifunctional catalysts was beneficial for their cooperative effect in "one-pot" cascade reactions.[84] More importantly, the Pd-Ru-PMO catalyst could be easily recycled while still retaining their activity and selectivity even after seven repetitons.

Table 2 Comparisons of the catalytic behaviors of bifunctional system.[a]



Catalyst	Pd/Ru content (mmol)	Conv. (%)	Select. (%)	Yield (%)
$PdCl_2(PPh_3)_3$ + $RuCl_2(PPh_3)_3$	0.040/0.040	97.2	75.0	72.9
Pd-Ru-PMO	0.040/0.040	94.3	71.5	67.2
Pd-Ru-PMO-G	0.040/0.051	76.1	69.4	52.8
Pd-PMO + Ru-PMO	0.040/0.040	82.5	58.3	42.3
Pd-PMO + $RuCl_2(PPh_3)_3$	0.040/0.040	90.0	66.0	59.4
Ru-PMO + $PdCl_2(PPh_3)_3$	0.040/0.040	97.1	61.5	59.7

[a] Reaction conditions: benzaldehyde (0.5 mmol), tribromhydrin (1.5 mmol), $SnCl_2$ (0.45 g), 5 mL H_2O, t=12 h, T=100°C.

Encouraged by this excellent result, Li group extend this strategy to synthesize Rh-Pd-PMO bifunctional catalyst by using $RhCl[PPh_2(CH_2)_2Si(EtO)_3]_3$ instead of $RuCl_2[PPh_2(CH_2)_2Si(EtO)_3]_3$.[81] This catalyst was used in "one-pot" cascade reaction consisting Rh(I)-catalyzed cinnamaldehyde methylenation and Pd(II)-catalyzed Heck reaction. the Rh-Pd-PMO bifunctional catalyst exhibited much higher catalytic efficiency than either the Rh-Pd-PMO-G prepared by grafting method or the mechanical mixture of Rh-PMO and Pd-PMO. It displayed matchable efficiency with the mixed $RhCl(PPh_3)_3$ and $PdCl_2(PPh_3)_2$ homogeneous catalysts and could be easily recycled and reused, showing good potential in industrial applications.

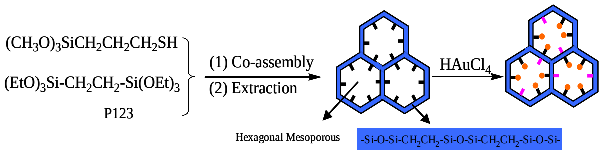


Figure 22 Illustration of preparing Au-SH/SO_3H-PMO(Et) catalyst (▬ = SO_3H, ▬ = SH, ● = Au).

Besides the bifunctional catalysts comprised of two kinds of organometal active sites, the organmetal catalyst could also cooperate with other kinds of catalysts to construct bifunctional and even multiple-functional catalysts. Li and his coworkers developed a novel approach to prepare Au organometal catalyst termibnally bonded to ordered mesoporous silica *via* forming Au-SH coordination bond.[85] The synthesis route could be simply illustrated in Figure 22. The P123 template directed the self-assemby between (3-mercaptopropyl) trimethoxysilane and bis-(triethoxysilyl)ethane to form SH-functionalized ethylene-bridgred PMO. Then, $HAuCl_4$ aqueous solution was added during which Au(IV) was reduced into Au(0) while HS was oxidized into SO_3H. The unrected HS-ligands could coordinate with Au(0) to form Au(0)-SH organometal. The Au-SH/SO_3H-PMO(Et) could be used as a bifunctional catalyst in water-medium phenylacetylene hydration. It was comprised of both the Au(0) organometal and SO_3H acid as two kinds of active sites. The catalytic results showed that it was much higher activity than either the SO_3H-PMO(Et), or the Au/SO_3H-PMO(Et), or the Au/HS-PMO(Et), or even the $Au(PPh_3)Cl$. This could be attributed to the cooperative catalytic effects between Au(0)-SH organometal catalyst and SO_3H acid catalyst since the absence of either Au(0)-SH organometal catalyst or SO_3H acid catalyst resulted in remarkable decrease in activity. Meanwhile, addition of H_2SO_4 into the reaction system containing Au/HS-PMO(Et) monofunctioanal catalyst could also greatly promote the reaction efficiency, which further confirmed the cooperative effect between Au(0)-SH organometal catalyst and SO_3H acid catalyst. Moreover, the Au-SH/SO_3H-PMO(Et) catalyst could be used repetitively for more than 10 times.

Summary

Heterogeneous organometal catalyst for water-medium organic synthesis is a fascinating field that has been rapidly developing during the recent years. An impressive growth in the potential applications of water as a green solvent clearly revealed that it provides new opportunity for environmental friendly chemical transformations. This Minireview has showed that a series of grafted organometallic catalysts with mesopore structure, nanoscale particle size and hydrophobic surface could effectively overcome the decreased accessibility and mass transfer limitations in water-medium organic synthesis. Furthermore, the reported examples of self-assembled organometallic catalysts demonstrated the benefits of the well-defined active sites and suitable geometric and coordination models on the enhancement of catalytic efficiency and recyclability. Moreover, the capability of self-assembly approach enabled the synthesis of bifunctioanl synergic catalysts by using mutliple active building molecules, resuling in the enhanced process economy and efficiency. However, many challenges remain unexplored, such as unsatisfactory catalytic reactivity, limited reaction types and inadequate understanding of heterogeneous organometal catalytic mechanism at the molecular level. Advances in nanocatalyst design and the development of ever-more-direct self-assembly synthetic protocols will continue to provide improvements in this regard. Owing to the increasing fossil fuel consumption and environmental concern, organic synthesis in water provides a powerful approach for the eco-compatible biomass refining. We anticipate that such a strategy will be of significant positive effect to develop economical and sustainable synthetic methods for the synthesis of valuable chemicals in the near future.

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Notes and references

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