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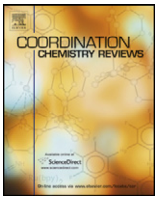

Review

Transition metal nanoparticle catalysis in green solvents

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ABSTRACT

Nanoparticle (NP) catalysis in liquid phase, which is usually called "soluble" NP catalysis, is an old topic but is now well advanced due to the great progress in nano-chemistry and nano-technology in green chemistry. After a short introduction of the history, this review describes the current status of NP catalysis in solvents and then discusses the main drawbacks hindering the particles from industrial practice. Efficiency, stability, sustainability, and recyclability (ESSR) criteria were suggested to evaluate NP catalytic systems. A state-of-the-art approach to satisfy ideal ESSR criteria is to produce cohesion over the individual contributions of metal center, stabilizer and solvent (MSS), i.e., a cohesive MSS approach. Based on reported examples, the roles that the metal core, the stabilizer and the solvent play in NP catalysis are discussed in detail. For clarity, a fairly complete list of NP catalytic systems in various green solvents reported in recent decade is provided.

1. Introduction

Nanocatalysis has undergone great prosperity in the past decade. A simple search through *Scifinder* with the key word "nanocatalysis" clearly indicates an exponential growth in scientific publications in the past 15 years (Fig. 1). In 2008 alone, for example, the number of publications was nearly 7000. One of the main branches of nanocatalysis is nanoparticle (NP) catalysis in liquid phase. NP catalysis in traditional solvents originated from colloidal chemistry that dated back to 19th century when Pt NPs were used to decompose hydrogen peroxide [1]. Since 1990, it became an independent field usually called colloidal catalysis or quasi-homogenous catalysis since it was believed, at that time, to be a bridge between classical homogenous catalysis and heterogeneous catalysis. "Soluble" NPs in solution phase enabled the direct usage of in situ techniques such as in situ IR and in situ NMR, which were successfully used in homogenous complex catalysis for mechanistic studies [2]. In some cases, NPs were the real active parts for the catalytic activity that molecular complexes generally showed [3]. The higher efficiency of these NP catalysts under mild conditions, in comparison with that of traditional solid state catalysts, was therefore thought to be due to their higher dispersion in solvent and three-dimensional rotational freedom.

There are quite a few excellent reviews on NP catalysis [4]. We would like to share our understanding of this field rather than simply presenting reported examples. The current review, which tries to give some clues to the improvement of NP catalysis for practical use, is divided into two main parts. The first part begins with introducing the efficiency, stability, sustainability, and recyclability (ESSR) criteria for the evaluation of a NP catalytic system which aims at satisfying industry demands and is followed by a detailed description of how to fulfill the ESSR criteria by designing the three basic elements, namely, the metal core, the stabilizer and the solvent (MSS), of a NP catalytic system (Sections 2–5). The second part is a collection of examples of NP catalysis in various green solvents after 1999, with particular attention paid to water, ionic liquids (ILs), supercritical carbon dioxide ($scCO_2$), fluorous solvents and high boiling point alcohols. Recent contributions from the authors' lab are also presented (Section 6).

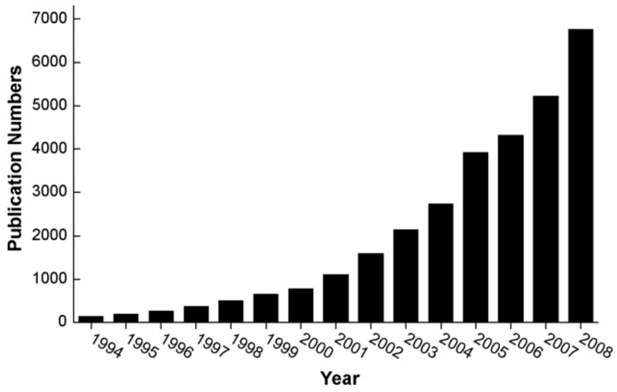


Fig. 1. Number of publications containing the key word "nanocatalysis" from 1994 to 2008.

2. Toward an ideal nanoparticle catalytic system in solution

2.1. Evaluation: the ESSR criteria

The NPs in solution phase are heterogeneous in nature. However, they "appear" incredibly homogenous since the catalyst is well dispersed in solvent so that the reactant reaches the catalytic site by diffusion. This feature endows the NP catalytic system with intrinsic advantages and limitations quite similar to those of the homogenous catalytic system. Homogeneous catalysts, usually transition metal complexes, present advantages of working at rather low temperature and giving very good selectivity. Moreover, homogeneous catalysts are usually structurally well-defined. Thus by implementing a structure–reactivity relationship, rational development of more efficient catalytic systems can be achieved for a given reaction [5]. Drawbacks include catalyst decomposition and complex separation of reactants/products from the homogeneous system; NP catalysis faces exactly the same situation.

The efficiency of a catalyst is normally estimated by TOF (turnover frequency per site per unit time). Homogeneous catalysts usually have very good TOF, higher than thousand (h^{-1}) at fairly low temperature, usually around 100 °C, while traditional solid state catalysts in heterogeneous catalysis generally have quite low TOF, less than hundred and even less than ten. Therefore, achieving a higher TOF close to a homogenous catalyst and retaining easy separation similar to that of the solid state catalyst, is the basis for the discussion of efficiency for a NP catalytic system. In fact, a higher TOF is not very difficult to obtain in a laboratory. We need, in a commercial sense, a higher TTO (total turnover number) based on a fair TOF, i.e. the stability of NP under reaction conditions is extremely important. NPs are usually lower in stability especially in comparison with the solid state catalysts. However, even for those solid state catalysts, good stability is obtained from a balance between efficiency and stability. This strategy may be adapted to the improvement of NP catalysts. Currently, an NP catalytic system is carried out in batch mode. TTO is realized via recycling the NPs. The recyclability of an NP system is normally a technical issue including the retreatment of the NP and recycling the stabilizer and the solvent. Easy separation, for example, by biphasic approach, and other smart approaches of the stabilizer and the solvent may significantly improve the recyclability of NP catalytic system, and may certainly enhance the possibility of an industrial application. We therefore suggest that efficiency (E), stability (S), sustainability (S) and recyclability (R) are the criteria, ESSR criteria, for the evaluation of an NP catalytic system.

2.1.1. *Efficiency*

High efficiency, i.e. high selectivity at high conversion rate under mild reaction conditions is the most prominent benefit that an NP catalyst can provide compared to typical heterogeneous catalysts. A homogenous catalyst can usually be much more active and selective, and in organic synthesis can be optimized for the system [6]. In principle, the NP catalyst, in a solvent, has the same opportunity. The high efficiency of an NP system relies mainly on the approach to the metal core, including the screening of the metal, the size of the particle, and the structure of the surface.

Moreover, the E criterion also requires NP catalytic systems, if possible, to be multifunctional to integrate catalytic steps into a one-pot, catalytic cascade process. The most significant merits of such a one-pot process are energy and time saving and waste reducing, in a word, improving reaction efficiency. Although there are very few examples of such efforts at present, as can be seen in Section 4, more attention should be paid to this aspect since it represents the future of green chemistry [7].

2.1.2. *Sustainability*

Sustainability is not only required by green chemistry, but also highly desirable for the long term development of NP catalysis. Sustainability involves many considerations. For NP catalysis, there are three factors that are of particular importance. One is the sustainability of the metal incorporated into the NP, since many metals are becoming scarce. Rare metals are, especially, becoming rarer. For example, platinum group elements are seen as future sources of alternative energy as fuel cell catalysts. However, the reserves of these elements will not fuel the world's cars to the middle of this century [8]. It is therefore imperative that we start on a path towards metals that are more abundant, including the field of NP catalysis. The first row of transition metals has been largely ignored in the study of NP catalysis.

Two other factors which concern sustainability in NP catalysis are consideration of PBT (persistence, bioaccumulation, and toxicity) [9] for both substrates (as well as products) and solvents. If any substrate is environmentally risky, a new process that involves safe starting materials and intermediates should be developed; this is beyond the scope of the current review. Nevertheless, the PBT consideration is one of the key issues to judge a “green” solvent and is discussed in Section 6.1.

2.1.3. *Stability*

NP is only kinetically stable and therefore stability is crucial for real processes in which the catalysts are required to be stable for months or years. In order to enhance the stability, stabilizers are often employed. However, absolute NP stability is not necessarily the aim, and what we want to do is to protect the particles against aggregation via weak interactions between the functional group(s) of the stabilizer and the surface sites of the particles. This protection is enhanced via multi-site interaction, i.e. most of the surface atoms of the particle may be involved in the weak interaction. The solvent chosen can have two effects. The first is interactions with the NP surface, which can compete with the stabilizer and the second is solubilizing the stabilizers, the regulation of which can sometimes be helpful.

Since NP is at the lowest end of the so-called “colloidal” range (1 nm to 1 μm) [10], Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [11] originally developed for the aqueous colloidal solution, is used to explain the NP stability. However, the DLVO model fails to describe the interactions of NPs in all applicable solvent systems. Nevertheless, some general guidelines for the stability issue of NP are available and will be discussed in Section 4.2.

2.1.4. *Recyclability*

It is highly probable that recyclability will be the bottleneck for the industrial application of NP catalysis in solution phase. Good dispersion of NP within a solvent is a double edged sword. It usually results in a catalytic system with high activity under mild reaction conditions. Meanwhile, it makes separation of the catalyst from the product more complicate. An additional concern for the pharmaceutical or polymer industry is metal contamination of the products. To solve this problem, a good strategy for easy and efficient recycling has to be applied.

Although it seems to be a general trend to transform a successful homogeneous catalyst into a heterogeneous one [12], we do not particularly recommend this strategy for NP catalyst. As they are three-dimensional freely particles and as such possess a high surface area and catalytic activity, which is negatively affected by heterogeneous immobilization. As traditional solid state catalysts have to be operated in fluid bed reactors to partly improve their two-dimensional limitation, such a strategy, i.e. changing a three-dimensional NP into a two-dimensional heterogeneous catalyst may result in a significant activity loss as is often the case with immobilized (heterogenalized) complex catalysts. Other approaches to solve the recycling problem without influencing the activity of the catalyst is still under consideration. For example, a hydroformylation process is industrialized based on a biphasic aqueous-organic solvent system [13]. Fortunately, the experiences gained from the recycling of homogenous catalysts during the past decades can be easily adapted to NP catalysts for the same purpose. Additionally, some features of certain NP, which a homogenous complex does not share, such as magnetism, can enable more diversified options for the recycling of NP catalysts.

2.2. *Cohesive relationship between metal–stabilizer–solvent*

An NP based catalytic system involves at least three components, i.e. metal core (M), stabilizer (S), and solvent (S). The metal core is the catalytic material with an activity and selectivity, with the latter with assistance from the stabilizers. The stabilizer protects the metal core against aggregation. However, this protection may negatively affect the activity of the system. The solvent is responsible for the dispersion of both metal core and stabilizer. However, the “solubility” of the metal core is controlled not by the solvent, but by the stabilizer. Thus, the solvent is the carrier transferring the reactant(s) to the metal core and product(s) away from the active site. The solubilities of both the stabilizer and the reactant(s) in the solvent are therefore related to the final activity of the system. This is the cohesive relationship among metal–stabilizer–solvent, the state-of-the-art approach to this relationship is fundamental in NP catalysis.

In classical heterogeneous catalysis, catalyst optimization is largely based on manipulating the active species, usually inorganic species loaded on the support. In a homogenous catalytic system, improvements are mostly achieved by ligand design and proper solvent selection. In solution phase NP catalyst's optimization can be achieved by both approaches. On one hand, the variation of the metal type, the control of the NP size and morphology are effective ways for the optimization of the metal core. Also, the magnetic properties of some NP can be used for separation purpose in catalysis. These approaches are discussed in detail in Section 3. On the other hand, the stabilizer provides another way to tune the performance of the NP catalysis. The solid supports applied in traditional heterogeneous catalysis are usually inorganic oxides or

Table 1
Relationship between the MSS and the ESSR criteria.

	Efficiency (E)			Sustainability (S)	Stability (S)		Recyclability (R)
	High activity	High selectivity	Multi-function		Long lifetime	Poison resistance	
Metal (M)	Type selection Alloy design Size control Shape control	Type selection Alloy design Size control Shape control	–	Use cheap and more abundant metals	Mono-disperse	–	Magnetic separation
Stabilizer (S)	Balance between activity and stability	Chiral approach for enantioselective reactions	Functionalized stabilizer	–	Strong stabilization ability	Effective protection	Polarity modulation
Solvent (S)	Dispersion issue	–	Functionalized solvent	Employment of green solvent	Stabilization effect	Solvation effects	Functionalized solvent

Table 2
Nanoparticles that have been used as catalysts in solution phase.

IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La–Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

carbon with much fewer variations compared to the ligand variety in homogenous catalysis. However, a wide range of organic compounds bearing various functionalities have been used as NP stabilizers, suggesting that stabilizers can be used to customize the catalytic system. Indeed, an appropriate stabilizer is the key for a stable and highly active NP catalyst. The developments, as well as other benefits, that a stabilizer may offer (such as multi-functionality) will be described in Section 4. Additionally, proper solvent design and/or selection could prove advantageous in NP catalysis. The most obvious benefit from the solvent is that it may simplify the separation process. For example, the biphasic approach based on ionic liquids or water, according to the principles of green chemistry, is desired for the separation of a catalyst from products. This, and other functions of the solvent in NP catalysis will be discussed in Section 5.

It has to be kept in mind that metal core, stabilizer and solvent are not isolated from each other but are acting together to make the system effective. However, to make the story clear, we have to discuss each of them separately as an independent section. To elucidate the detailed MSS relationship for satisfying the ESSR criteria, a comprehensive table is given (Table 1).

3. Roles of the transition metal

3.1. Metal type

The catalytic activity of transition metals is mainly decided by their *d* orbital properties and therefore metal type selection is the first choice for selectivity control. Mainly according to their catalytic behavior, we divided the frequently encountered metals in catalysis into five categories: (1) Ti, Zr, Nb, Mn, V, Cr, Mo and W; (2) Fe, Co and Ni; (3) Cu, Ag and Au; (4) Ru, Rh, Pt and Ir; (5) Pd (Table 2).

3.1.1. Ti, Zr, Nb, Mn, V, Cr, Mo and W

A major advantage of these early transition metals in catalysis is their cheap price. They exhibit weak hydrogenation ability and sometimes can be used in hydrogenation reactions. For example, Bönnemann et al. prepared Ti, Zr, Nb and Mn NP in THF by $K[BEt_3H]$ reduction from metal halide precursors [14]. They found colloidal Ti NPs are very efficient catalysts for the hydrogenation of titanium and zirconium sponges as well as for nickel hydride battery alloy [15].

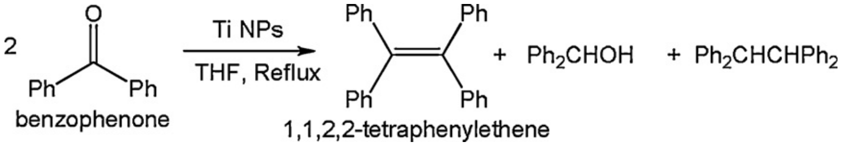
Ti NPs have also been successfully utilized in catalyzing McMurry coupling reaction (Scheme 1). 1,1,2,2-tetraphenylethene was obtained from benzophenone in refluxed THF with a yield of about 80%. The main byproducts were diphenylmethanol and 1,1,2,2-tetraphenylethane. For other substrates, such as benzaldehyde and acetophenone, similar activities and selectivities were observed [16].

Compared to the metallic state, the oxides of these early transition metals are generally paid more attention as they can effectively catalyze many useful reactions in traditional heterogeneous catalysis. For instance, the oxides of Mn, V, Cr and Mo are extensively used in the selective oxidation of alkanes. In the field of photo catalysis, TiO_2 is widely recognized as an excellent catalyst that is capable of producing H_2 from water and degrading some environmental pollutants in the presence of UV light [17]. However, there are few reports on developing their soluble oxide NP for these reactions. The major challenges are the lack of proper preparation strategies and the instability of these "soluble oxide NP" under reaction conditions. The synthesis and application of oxide NP of early transition metals is comparatively a virgin area worth great efforts in the future.

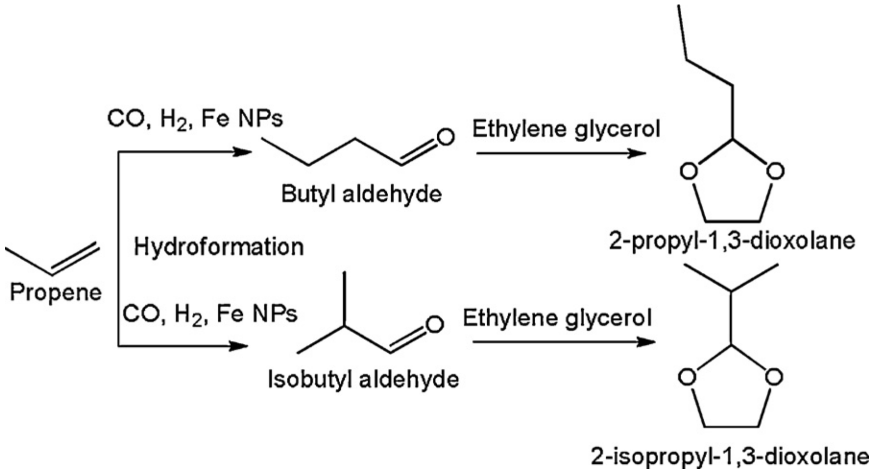
3.1.2. Fe, Co and Ni

Fe, Co and Ni are abundant and cheap elements, and are of great significance in catalysis. Recently, the potential of their metal NPs as catalysts in quasi-homogenous mode has attracted increased attention. The catalysts are currently applied in reactions including hydrogenation, hydrosilation, C–C coupling and oxidation reactions.

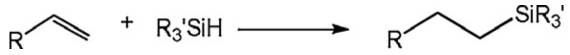
Hydrogenation reaction has been widely studied. Herein, just a few representative examples will be mentioned. Martino et al. prepared Fe NP by reducing iron ions with $LiBH_4$ in reverse micelle



Scheme 1. McMurry coupling reaction catalyzed by Ti nanoparticles [14].



Scheme 2. Plausible reaction pathways for the formation of dioxolanes from alkenes [23].



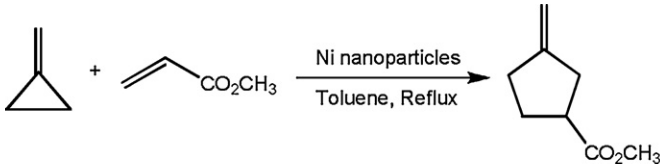
Scheme 3. Hydrosilation reaction.

solutions. These Fe NPs were active catalysts in the hydrogenolysis of naphthyl bibenzyl methane [18]. Ni NPs with a size of about 45 nm were prepared from $Ni(CH_3COO)_2$ via hydrazine reduction in solvothermal process, which exhibit excellent activity and selectivity in the hydrogenation of nitrobenzene [19]. The Ni NPs were also synthesized in IL phase through the decomposition of [bis(1,5-cyclooctadiene)nickel(0)] organometallic precursor. When applied in cyclohexene hydrogenation, the NPs exhibit two orders of magnitude higher activities than traditional heterogeneous Ni-based catalyst [20]. For Co NPs, Mertens et al. examined their catalytic property in the selective hydrogenation of α,β-unsaturated aldehydes, obtaining a selectivity ranging from 70% to 90% [21].

The hydrogenation reaction of carbon monoxide to produce alkanes, known as Fischer–Tropsch (F–T) reaction, is very attractive due to its great potential in the transport fuel production in the post-petroleum era. Co and Fe based catalysts are frequently used in industry. Recently, Co NP catalyzed F–T reaction has been demonstrated to be quite active in IL by Scariot et al. [22] and in squalane by our group. The observed activity is of the same order of magnitude as that of supported Co catalysts. In an attempt to use Fe NP for the F–T reactions in glycerol, we found that Fe NP catalyzed the formation of dioxolane derivatives as the main products. This novel reaction was thought to undergo the mechanism listed in Scheme 2 [23].

Hydrosilation is a reaction of significance for the synthesis of silica incorporated polymers. A representative reaction is formulated in Scheme 3. This reaction had long been regarded as catalyzed by homogenous complexes. However, recent advances lead to the conclusion that in some cases, Co and Ni NP formed in situ from their complex precursors in the presence of reductive silane in the induction period, may be responsible for the catalytic activity [24].

In addition, Ni NP can be used in C–C coupling reactions. Reetz et al. synthesized tetradodecylammonium bromide protected Ni NP via electrochemical method [25], which was further utilized in the [3+2] cyclo-addition reaction between methylenecyclopropane and methyl acrylate (Scheme 4). However, compared to the classical catalyst for this reaction, $Ni(COD)_2$, the activity of the Ni NP is much lower.



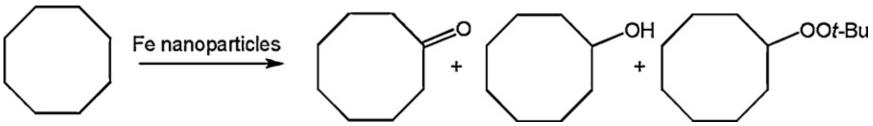
Scheme 4. The [3+2] cyclo-addition reaction catalyzed by Ni nanoparticles [25].

Fe, Co and Ni based catalysts are widely used in oxidation reactions in industry. A simple example is the production of adipic acid, an indispensible intermediate compound for the synthesis of nylon-6 and nylon-66 from the oxidation of cyclohexane via Co-based catalyst (Scheme 5). On the contrary, Fe, Co or Ni based soluble NPs under quasi-homogenous mode for oxidation reactions are seldom reported. The only available report came from Patin et al., who found that Fe NP prepared by reverse microemulsion can catalyze the oxidation of cyclooctane with acceptable activity under mild conditions [26].

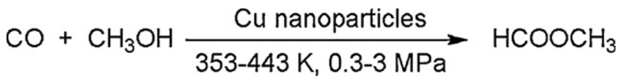
To conclude, Fe, Co and Ni NPs are widely investigated in many kinds of reactions. Being paid much attention, these NP promises a lot for the catalytic reactions in solution phase in the future.

3.1.3. Cu, Ag and Au

These metals are usually used for redox reactions. For example, Vukojevic et al. found that Cu NPs synthesized by the reduction of copper acetylacetonate with trialkylaluminum in THF were highly active in methanol synthesis [27]. The copper particle has a narrow size distribution, and the size can be tuned in the range of 3–5 nm. When applied to methanol synthesis, the Cu NP exhibited notable activity at temperatures above 130 °C. Under similar reaction conditions, their catalytic activity was comparable to that of commercialized Cu/ZnO catalyst. The author claimed that Cu NPs are remarkably active catalysts in the quasi-homogeneous phase for methanol synthesis, considering that traditional catalyst



Scheme 5. Oxidation of cyclooctane catalyzed by Fe nanoparticles in reverse microemulsions [26].



$$CO + CH_3OH \xrightarrow[353\text{-}443\ K,\ 0.3\text{-}3\ MPa]{Cu\ nanoparticles} HCOOCH_3$$

Scheme 6. Production of methyl formate from methanol carbonylation catalyzed by Cu nanoparticles [29].

requires a second component, generally zinc, to be active. However, this conclusion may not be convincing since it is highly possible that the Cu NP incorporated with Al during the reduction process, as suggested by other researchers [28].

In industry, methyl formate (MF) is produced from methanol by carbonylation reaction catalyzed by a strong base such as CH_3ONa which is highly efficient but obviously not green. It leads to inevitable problems such as corrosion, byproduct formation and the possible deactivation of catalyst by CO_2 and H_2O impurities. We recently discovered the Cu NP catalyzed synthesis of MF in the absence of any base [29]. Three nanometer Cu NP prepared from $NaBH_4$ reduction in methanol exhibited an activity of 1.0–16.8 mol MF mol Cu^{-1} h^{-1} and a selectivity of 100% towards MF formation (Scheme 6). Further advances in improving MF productivity will potentially lead to a green substitute for the current industrial process that requires environmental unfriendly alkaline metal alkoxides as catalysts.

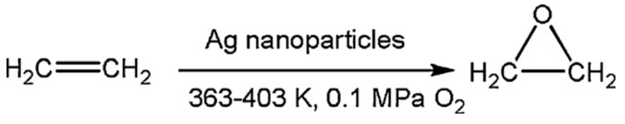
Ag NPs are mainly used in oxidation/dehydrogenation reactions. Ag catalyzed epoxidation reaction is well known and widely applied in ethylene oxide production. Soluble Ag NPs in ethanol/water mixture are superior catalysts relative to a conventional heterogeneous Ag catalyst (Scheme 7) [30]. The authors also found that the addition of Cs(I) and Re(VII) metal ions greatly enhanced the catalytic activities.

Research concerning the catalytic properties of Au NP is also focused on oxidation reactions. Current applications include oxidation of carbon monoxide into carbon dioxide and glucose into gluconic acid [31]. Au and Ag NP can also effectively decompose $NaBH_4$, a potential hydrogen storage material, into H_2 and $NaBO_2$ [32,33].

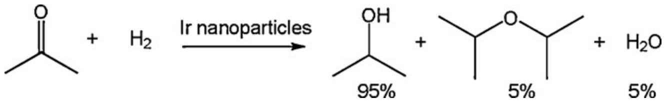
3.1.4. *Ru, Rh, Pt and Ir*

These noble metals are typical catalysts with excellent hydrogenation ability. For the hydrogenation of C=C bonds, the activity of their metal NPs usually follows the trend of Rh > Ru > Pt > Ir. This trend is similar to that observed in traditional heterogeneous catalysis. The hydrogenation of C=C bonds using these soluble NPs is comparatively easy and there are numerous studies on this topic. Detailed information can be found in pertinent reviews [34]. Hydrogenation of the benzene ring is a much more challenging task and this reaction received increased attention recently. Rh and Ru are the most active metals towards benzene hydrogenation. Rh is generally more active but Ru is much cheaper. The first example dates back to 1983 when Januszkiewicz et al. used Ru NP for the reaction [35]. Research focus is on the development of more stable and active NP. Until now, the record of the turn over numbers (TTO) on benzene hydrogenation is 20,000, which is attractive for practical applications [36].

For the hydrogenation of C=O bonds, Ir, Pt and Ru exhibit excellent activity. Özkar and Finke prepared Ir NPs and used them for the hydrogenation of acetones [37]. The reaction progresses effectively under ambient temperatures, with a selectivity of about 95% for 2-hydroxyl propanol and a TTO of 16,400 (Scheme 8). The authors pointed out that the typical temperature applied for this reaction under traditional supported catalyst is much higher, between 100 and 300 °C.



Scheme 7. Epoxidation reaction of ethylene catalyzed by Ag nanoparticles [30].



Scheme 8. Selective hydrogenation of acetone catalyzed by Ir nanoparticles [37].

When both C=C and C=O are present, a selectivity issue arises. It is easier for the C=C bond than the C=O bond to undergo hydrogenation. Unfortunately, in many applications selective reduction of only the C=O bond is desired, for example, cinnamaldehyde hydrogenation (Scheme 9). Pt and Ru NPs are frequently used for the selective hydrogenation of the C=O bond. Pt is more active and Ru generally exhibits better selectivity. Yu et al. found that for the reduction of cinnamaldehyde, the addition of some metal ions such as Fe^{3+}, Co^{2+} and Ni^{2+} can greatly enhance the selectivity of the aimed unsaturated alcohol product, which may be due to the induction effect of these ions that can activate C=O bonds [38]. Our group demonstrated that selectivity control of this reaction can also be manipulated by solvent design, which is discussed in details in Section 5.

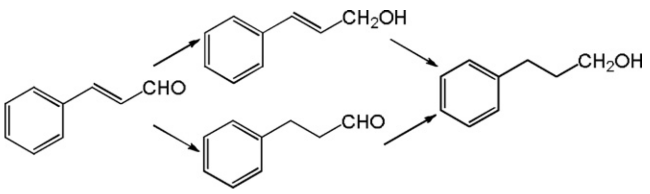
Ru NP can catalyze the hydrogenation of glucose to sorbitol. Notably, we discovered that they can catalyze direct hydrogenolysis of cellubiose into polyols, which opens up a new route for the utilization of cellulose. Ru/C catalyst did not exhibit such activity under the same conditions [39].

Furthermore, we found that unsupported Ru NP catalyst is more active than conventional catalysts for Fischer–Tropsch synthesis in water. A 35-fold increase in activity was observed for unsupported Ru NP at 150 °C. Note worthily, the hydrocarbon product is immiscible with water, so the fuel can be separated easily from the catalyst, which facilitates the working up process and is more energy efficient for the production of fuels [40].

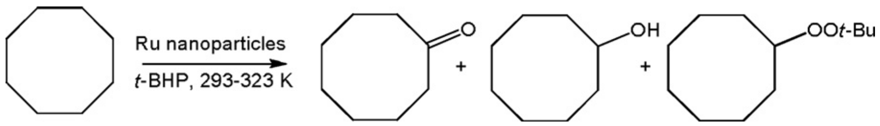
Reduction of N=O into NH_2 group is essential for producing some intermediates in dye manufacture. Similar to the reduction of C=O, the best catalysts for the N=O reduction are Ru and Pt NPs. Again, Pt exhibits higher activity whereas Ru is more selective [41]. As dye molecules generally contain halogen atoms, dehalogenation becomes the main side reaction. Adding metal ions can significantly improve the selectivity. The reason was proposed that the interaction between N=O and the metal ions can weaken the N=O bond strength [42].

Pt NPs are efficient catalyst for hydrosilylation reaction. Generally, Pt organometallic complexes were used for this reaction. However, through TEM analysis, Lewis et al. found the presence of Pt NPs which were the real catalysts for the reaction. These Pt NPs were formed in situ from the organometallic precursors by the reduction of silanes [43].

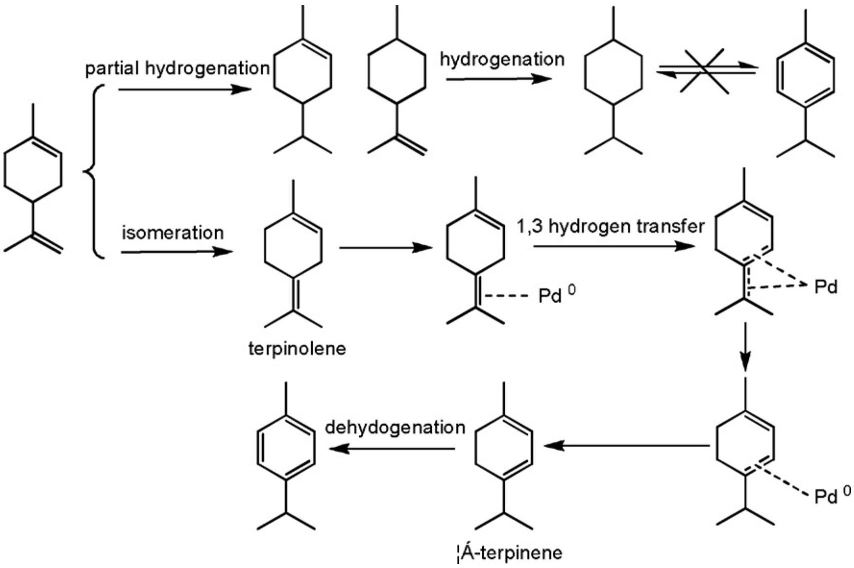
Oxidation reactions using these NPs as catalysts have also been reported. For example, our group prepared a soluble Pt NP in glycol, which displays good performance in the oxidation of both activated and non-activated alcohols including a wide range of



Scheme 9. Pathways of cinnamaldehyde hydrogenation [38].



Scheme 10. Oxidation of cyclohexane catalyzed by Ru nanoparticles under water/organic biphasic condition [45].



Scheme 11. Proposed mechanism of limonene conversion over soluble Pd nanoparticles [47].

aromatic alcohols, allylic alcohols, alicyclic alcohols, and primary and secondary aliphatic alcohols in water under aerobic conditions without using any bases [44]. Ru NP can also be utilized in oxidation reactions and under water/cyclooctene biphasic conditions, cyclohexane can be converted into cyclooctanone and cyclooctanol under mild conditions (Scheme 10) [45].

3.1.5. Pd

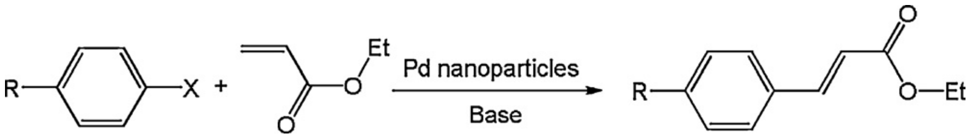
Pd has excellent catalytic activity toward hydrogenation/dehydrogenation. Furthermore, it is highly effective for many C–C coupling reactions. These features make the role of Pd in catalysis unique.

The most intriguing aspect of Pd in hydrogenation reactions is its unique selectivity. It is well known that Pd can selectively catalyze the hydrogenation of alkynes and diene compounds into alkenes. For example, Hirai et al. reported that PVP stabilized Pd NP can catalyze the production of cyclopentene and cyclooctene from cyclopenta-1,3-diene and cycloocta-1,5-diene, respectively [46]. Kinetic study of a series of cyclooctadiene revealed that the reaction rate follows the order of cycloocta-1,3-diene > cycloocta-1,4-diene > cycloocta-1,5-diene, indicating that the conjugated 1,3-diene is the intermediate for the hydrogenation of dienes into monoenes.

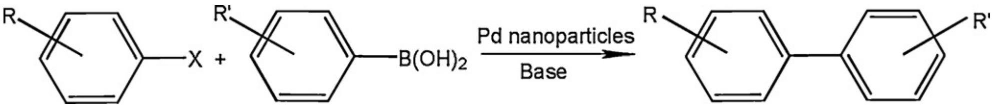
Pd NP can also be applied in dehydrogenation. The dehydroaromatization of limonene to *p*-cymene, a compound of great commercial interest, under hydrogen atmosphere (Scheme 11) comprises a relatively complex series of reactions. Our group established a biphasic dehydroaromatization of limonene, a renewable biomass material, into *p*-cymene using soluble Pd NP catalysts in aqueous solution in the presence of hydrogen under severe conditions (>150 °C), achieving a conversion of 93% and a selectivity of 82% [47]. A plausible reaction pathway involving initial isomerization followed by dehydrogenation was illustrated in Scheme 11.

The first Pd NP catalyzed Heck reaction was reported by Beller et al. [48]. They prepared tetraoctylammonium bromide protected Pd NP which can catalyze the Heck type cross coupling reaction between ethyl acrylate and benzyl halides, as demonstrated in Scheme 12. Pd NP catalyzed Heck reaction was also studied respectively by Reetz et al. [49], Antonietti et al. [50] and Bradley et al. [51] with different approaches. Generally, the Pd NP can effectively catalyze activated substrates.

Tetraalkylammonium bromide protected Pd NPs are also effective in catalyzing Suzuki cross-coupling reactions. Reetz et al. investigated the Suzuki cross-coupling reactions catalyzed by tetrabutylammonium bromide-Pd NP, which was prepared via electrochemical methods and dispersed in DMA (Scheme 13) [49]. Pd NP can convert bromide and iodide substrate much faster when electron withdrawing group is present in the benzene ring of the substrate. Dendrimer protected Pd NP for Suzuki reactions were studied by Narayanan and El-Sayed [52]. The Pd NP underwent aggregation under the reaction conditions. The authors believed the aggregation was due to the unreduced Pd precursor left in the preparation process.



Scheme 12. Heck reaction catalyzed by Pd nanoparticles [48].



Scheme 13. Suzuki reaction catalyzed by Pd nanoparticles [49].

There are also reports of Pd NP catalyzed Stille, Sonogashira and Hiyama reactions. It is interesting to note that a common drawback with these Pd NPs is that they are only active for reactive substrates like benzyl bromide and benzyl iodide. For the more economically attractive and more challenging benzyl chloride substrate, successful examples are extremely rare.

3.1.6. Bimetallic NP

Bimetallic NPs, composed of two different metal elements, are of greater interest in some aspects than monometallic ones for the improvement of catalytic properties. This is because bimetallization can improve catalytic properties of the original single-metal catalysts and create new properties. Bimetallic catalysis is in fact a very old concept in heterogeneous catalysis, as developed by Sinfelt in 1980s [53]. Bimetallic NP in solvent can be regarded as an extension of these efforts made with different synthesis approaches which was pioneered by Harada et al. who conducted a series of work on PVP stabilized bimetallic NP [54]. Current strategies for the preparation of bimetallic NP include co-reduction of mixed ions, successive reduction, reduction of double complexes and electrochemical approaches [55]. The effects of the added metal component can often be explained in terms of an ensemble and/or a ligand effect in catalysis [56,57] or in terms of more recent approaches such as electron transfer between the components [58]. At present various examples demonstrated the use of bimetallic NP with Pt–Fe [59], Au–Fe [60], Pd–Au [61], Cu–Au [62], Pd–Pt [63], and Pd–Ni [47] being the most representative. Recently an extreme example comes from Schroter et al. who found that Cu-ZnO NPs are highly active in methanol synthesis whereas Cu NPs alone are completely inactive (see Scheme 14) [64]. The current review will not go to more detailed discussion because of two reasons: (1) there is no fundamental difference between bimetallic NP in dispersion and classical heterogeneous catalysis and the latter has been extensively investigated; (2) there are several other recent reviews dealing with this subject [65].

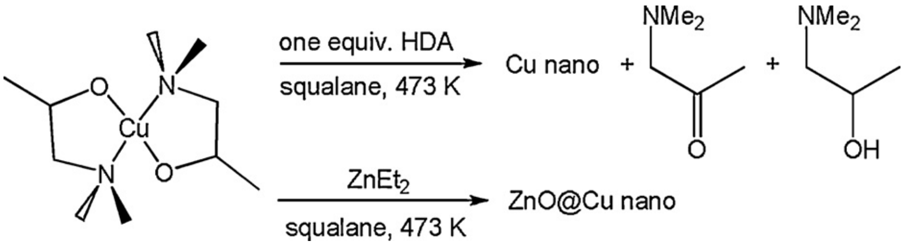
Finally, although this review focused on NP catalysis in solvents, the general trends discussed here are well suited for nanocatalysis of other branches since they illustrate intrinsic catalytic properties of the metals.

3.2. Nanoparticle size

Diameter is an important parameter which can be taken advantage of for the modification of the catalytic properties of the NP. The most obvious size-dependence relationship comes from the change in the percentage of surface atoms which are responsible for the catalytic properties when changing the diameter. However, the true story is not that simple as many variables influence the relationship between the diameter of NP and the catalytic performance. Because of limited space and the availability of previous more specific reviews [52,66], we will limit our discussion to the cases of NP catalysis in solvents by providing most representative examples.

Gold is probably the most frequently studied metal for its size dependent catalytic properties. Following Haruta's discovery of CO oxidation catalyzed by supported Au NP [67], the literature has been inundated with reports on gold-catalyzed oxidation reactions. Valden and co-workers described an inspiring result on size-selective catalysis by using a model Au/TiO_2 catalyst [68]. After that, numerous studies demonstrated the size dependence of the gold NP in carbon monoxide oxidation [69], alcohol oxidation [70], and propylene epoxidation reactions [71]. Besides, size dependences were also observed in various reduction reactions [72]. However, for supported heterogeneous catalysis, the particle size effect is not very well understood mainly due to the complexity of the interactions between the gold NP and the support. To avoid this, Tsukuda et al. studied the aerobic oxidation of benzylic alcohols catalyzed by monodisperse gold NP stabilized by PVP with a focus on the particle size effect on catalysis [73]. By using seeded growth method, Au NPs with diameters from 1.3 to 10 nm were obtained. The resulting Au NP exhibited significant difference in the oxidation of benzylic alcohols, with a sharp increase in activity when the diameter decreased to below 2.5 nm. Kinetic analysis rationalized such difference in catalytic activity to be the easier activation of oxygen by the smaller Au NP.

On many occasions, there seems to be a "threshold diameter" below which considerable catalytic activity is observed. Exhaustive experimental and theoretical studies were conducted to understand such phenomena and current explanations are mainly focused on quantum size effects and low-coordination numbers (support effects are excluded) [74]. For example, Valden et al. prepared gold clusters ranging in diameter from 1 to 6 nm on single crystalline surfaces of titania in ultrahigh vacuum. With scanning tunneling microscopy/spectroscopy (STM/STS) and kinetics measurements of elevated pressure reaction, they observed that a metal-to-insulator transition occurs as the particle size falls below 3.5 nm in diameter, coinciding with the specific activity of the model and high-area Au/TiO_2 catalysts [75]. Lopez and Nørskov carried out density-functional-theory (DFT) studies on the reactivity of both oxide-supported and isolated Au NP towards CO oxidation [76]. The results showed that the high concentration of Au atoms with low coordination number is the dominant factor in the catalytic activity of Au NP. If we take both electronic structural differences and geometrical configurations into account, we can make



Scheme 14. Preparation of Cu and Cu–ZnO nanoparticles in squalane [65].

a plausible explanation of the remarkable difference in catalytic activity observed between small Au clusters and large Au crystals [77].

The interplay of diameter and the catalytic activity of Pd NP has also been widely investigated. Pd NPs of different sizes (3–7 nm) were prepared by Boone and El-Sayed and used for Suzuki reactions. The general trend observed is that the catalytic activity of Pd NP increases as the particle size decreases, which also suggests that the low-coordination-number atoms (vertex and edge atoms) on the surface are responsible for the catalysis. However, the catalytic activity of the smallest Pd NP is the lowest. The authors attributed this irregularity to the strong adsorption of the intermediates on the Pd NP surface which act as a poison of the reaction [78]. Following this strategy, Trzeciak and co-workers prepared a series of Pd NPs with wider size distribution (1.9–19.8 nm). Not surprisingly, they found that in most cases higher yields of benzoic acid methyl ester were obtained when smaller Pd NPs were used in the methoxycarbonylation of iodobenzene. However, as these Pd NPs were obtained by using three different reductants including pyrogallol, chromium(II) acetate, and hydrazine, the observed difference in catalytic activity may not simply be caused by the size effect [79]. Heck reaction catalyzed by the Pd NPs with difference in size was also studied by Gniewek et al. Again, smaller NP displays higher activity [80].

Hirai et al. prepared Pd NPs with average diameters between 1.8 and 2.3 nm by reducing palladium(II) chloride with refluxing methanol in the presence of poly(N-vinyl-2-pyrrolidone), and studied their effect in the selective hydrogenation of cyclopentadiene or cyclooctadiene to form mononenes [81]. Pd NPs led to considerably higher yield (97.8%) than 5 wt% Pd/C catalyst (94.3%) in the hydrogenation of 1,5-cyclooctadiene. The selectivity of olefin increases with the decrease of the Pd NP size.

Semagina et al. prepared monodispersed Pd NPs of 6, 8, 11 and 13 nm in diameter by reverse microemulsion, and studied their performance in solvent-free hydrogenation of 2-methyl-3-butyn-2-ol to 2-methyl-3-buten-2-ol. A novel method, hydrocarbon evaporation and methanol-assisted particle purification, was developed to obtain pure monodispersed metal NP for size effect studies, avoiding other effects such as those of solvents and surfactants. The initial activity calculated per mole of surface palladium atoms was doubled when particle size increased from 6 to 13 nm, but it remained constant with the size change for a fixed number of specific Pd atoms on Pd (1 1 1) facets. The author claimed that the Pd size controlled the reaction rate as well as byproduct distribution in this model reaction. No dependence of selectivity for olefinic alcohol on particle size was observed [82].

Recently, Glöckler et al. prepared Rh NPs with very narrow size distribution (2–6 nm). The Rh NPs show high activity in the biphasic hydrogenation of olefins and are able to catalyze the hydrogenation of aromatic compounds. Again, the results show that under the same conditions small clusters exhibit significantly higher catalytic activity than large ones [83].

We synthesized Ru NPs with diameters ranging from 1.7 to 4.0 nm and found that the diameter of the Ru NPs had a significant effect on their catalytic activity in Fischer–Tropsch reaction in aqueous phase [84]. The surface-specific activity decreased gradually as the size of the NPs reduced from 4.0 to 2.5 nm. Then the activity increased dramatically resulting in an unprecedented maximum TOF value of 12.9 h^{-1} at 150 °C when the diameter of NP reached 2.0 nm, which is seven times higher than the activity obtained for previous heterogenous catalyst at 200 °C. Finally it decreased significantly with the NP diameter decreasing (Fig. 2). This phenomenon is very similar to that found in ammonia synthesis catalyzed by Ru NP, in which a smaller optimal ruthenium size was observed [85]. Based on single crystal studies and DFT calculations [86], Dahl suggested that B5 sites involving edge atoms are primarily responsible for the catalytic activity of Ru NP during ammonia synthesis. From the analysis of FCC cubo-octahedron model, B5 sites are only present on particles with a size larger than ca. 1.5 nm. The maximum probability of B5 sites was found for particles with diameters of 1.8–2.5 nm and for particles larger than that, the probability of B5 sites monotonically decreased. This explanation may also be suitable for the special catalytic activity observed in F–T synthesis.

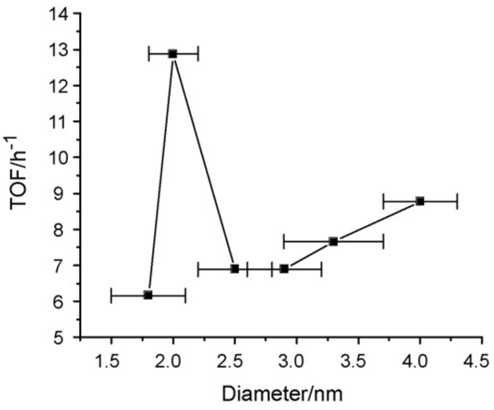


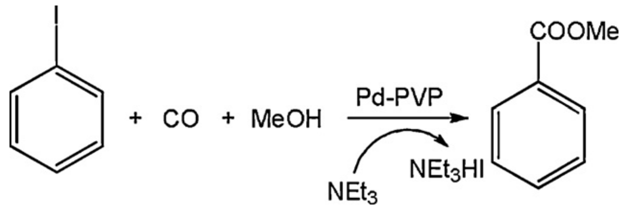
Fig. 2. The diameter–activity relationship of Ru NP in the F–T reaction [85].

It is noteworthy that in the study of the size effect of NP on its catalysis, other parameters have to be kept constant, which seems obvious but sometimes was ignored. For example when researchers are focused on the size effects of NP and a series of NPs with different sizes are obtained, particular attention has to be paid to the morphology consistency of these NPs, even if they are prepared in similar ways. José-Yacamán et al. reported the synthesis of Pd NP protected by $[CH_3(CH_2)_{11}SH]$ and reduced by $[LiB(C_2H_5)_3H]$ from $PdCl_2$. For a single batch of preparation, Pd NPs with FCC cubo-octahedra, icosahedra, truncated decahedra and single-twinned FCC configurations are all present as identified by HRTEM [87].

3.3. Nanoparticle morphology

Shape is another significant factor that influences the catalytic activity of NP. Different shapes bring surface sites with different coordination structures and electronic properties which are responsible for the catalytic process. Strategies for preparation and characterization of NPs with different shapes have been extensively investigated and detailed introduction can be found elsewhere [88].

The shape dependence of NP catalytic activity in solution phase, which is of interest here, was pioneered by Ahmadi et al. who synthesized Pt NPs with different morphologies [89]. Tetrahedral, cubic, and spherical Pt NPs were obtained by different combinations of stabilizers and reduction methods. These Pt NPs were applied for the electron transfer reaction between hexacyanoferrate (III) ions and thiosulfate ions. The activation energies and the average rate constants are determined at the early stage of the reaction to avoid any potential shape change of NP. The activation energy follows the order of cubic NP > spherically NP > tetrahedral NP and the rate constant follows the opponent trend of tetrahedral NP > spherically NP > cubic NP. A calculation based on simplified models indicated that these kinetic parameters are correlated with the fraction of surface atoms located on the corners and edges in each shape, which confirmed that for NPs of different shapes, the larger percentage of edge and corner atoms they have, the more active they are [90]. Different reactions give different responses according to the morphology change of catalyst [91]. For Suzuki reaction, tetrahedral Pt NPs are almost 1/3 as active as classical Pd NP catalysts in coupling boronic acid and iodobenzene, whereas spherical Pt NPs are completely inactive [92]. In this occasion, the difference in catalytic



Scheme 15. The methoxycarbonylation reaction catalyzed by Pd nanoparticles [94].

activity cannot be simply explained by the percentage of the edge and corner atoms, and the electronic difference of the surface atoms for each shape has to be taken into account.

Following this synthesis strategy, Gniewek and co-workers recently prepared PVP-stabilized Pd NPs with different shapes by selecting reducing reagents [93]. The morphology effects of Pd NP in methoxycarbonylation were evaluated in the reaction of iodobenzene, carbon monoxide and methanol (see Scheme 15). An increase in catalytic activity was observed when the fraction of surface atoms in the corners and edges increases.

Xiao et al. recently reported a strong dependence of the activity of Pd nanocatalyst on its morphology for the oxygen reduction reaction (ORR) [94]. Theoretical approaches for explaining the relationship between the shape and activity of NP have also been used. The surface-specific activity of Pd nanorods toward the ORR was 10-fold higher than that of Pd NP. By density functional theory calculations, they found the adsorption energy of O adsorption on Pd (1 1 0) facets (main exposed facets of Pd nanorods) is significantly lower than that on Pd(1 0 0) facets (main exposed facets of Pd NP). Based on the general strategy to improve the catalytic activity by decreasing the adsorption energy of O adsorption to an appropriate degree [95], it was concluded that the superior activity of Pd nanorods toward the ORR most likely arises from the morphology peculiarity of the exposed Pd(1 1 0) facets at the side surface.

Interestingly, the shape of NP in one reaction sometimes is not unchanged. The electron-transfer reaction between hexacyanoferrate (III) and thiosulfate ions catalyzed by Pt NPs with two shapes (tetrahedral and cubic) was studied by HRTEM [96]. During recycling, extensive dissolution of platinum atoms from the corners and edges for both types of NPs was observed. The rate for the disappearing (dissolution) of the surface Pt atoms is bigger for the tetrahedral NP than for the cubic NP, which suggests that NPs with sharp corners and edges, such as the tetrahedral NPs, are easier to undergo shape changes during catalytic process.

3.4. *Magnetic properties of some nanoparticles*

Magnetic NPs in general are of great interest today with a wide application potential in biochemistry, smart material and catalysis [97]. For catalysis, magnetic properties provide a unique way for catalyst separation and recycling and have been paid great attention to for a long time. One significant example is the magnetically stabilized bed reactor in which catalysts were loaded on magnetic materials and the reactor was handled under an intensive controllable magnetic field [98]. In the domain of NP catalysis, reports about the utilization of magnetic NP can be divided into two main categories: (a) magnetic NP as catalyst and (b) magnetic NP as the carrier for the real catalyst. Both approaches will be introduced in the following section.

Iron, cobalt and nickel are intrinsically catalytically active for some reactions. NPs of these metals and metal oxides are efficient and recyclable catalysts. For example, Ni NPs have been synthesized by the hydrazine reduction of nickel chloride in ethylene glycol at 60 °C with diameters ranging from 10 to 12 nm. The Ni NPs can be used to catalyze the decomposition of hydrazine into hydrogen and nitrogen gases at room temperature. Notably, the Ni NPs could be magnetically recovered and redispersed in ethylene glycol without agglomeration or size change [99]. Similarly, Fe NPs obtained through a simple reduction of $FeSO_4$ with $NaBH_4$ were applied for H_2 production from NH_3BH_3. These Fe NPs were very stable, even in the presence of air and water, and easy to recover [100].

Oxide NPs based on Fe and Co have also been reported. Beller et al. prepared Fe_2O_3 NPs which were highly stable, active, and highly selective for various oxidation reactions using hydrogen peroxide. The high recyclability of these Fe_2O_3 NPs has also been demonstrated, indicating they are well suited for continuous processes [101].

Unfortunately, magnetic properties belong to a few metals and their oxides that are only catalytically active in limited reactions. To take full advantages of the magnetic properties for separation purpose, there are continuous interests in integrating different functional nanocomponents into one single nanoentity to exhibit multifunctional properties [102]. Specifically, combining magnetic NP with other catalytically active moieties can obtain an easily recyclable catalyst that is active for certain reaction. Reported hybrid magnetic NPs usually have a core/shell structure, consisting of a magnetic iron oxide core surrounded by a layer of organic shell [103]. The organic shells prevent magnetic cores from aggregation and offer an interface for immobilization of catalysts. Various methods can be used for the preparation of hybrid magnetic NP as shown below.

3-Aminopropyl triethoxysilane (APTS) is one of the frequently used modification reagents for Fe_2O_3 to form multicomponent nanocomposites. It reacts with hydroxyl groups on the surface of Fe_2O_3 to form covalently bonded silane moiety that can be further functionalized. By such a protocol, Wang et al. reported the preparation of Pd–Fe_2O_3 NP. The catalytic behavior of Pd–Fe_3O_4 NP was measured toward the Heck cross-coupling reaction between acrylic acid and iodobenzene. Although the catalyst is recyclable under external magnetic field, the activity underwent a gradual and continued decrease upon recycling. The author attributed this to the aggregation of Pd NP in the recycling process [104].

In 2007, Hyeon and co-workers reported a new magnetically recyclable and efficient NP catalyst for the epoxidation of olefins, which was based on molybdenum oxide NP incorporated with magnetite NP. Despite of the fact that very large Fe_2O_3 NPs were applied (400 nm), the resulting hybrid NPs exhibited well dispersion in the solvents [105]. Following this strategy, Shylesh et al. developed similar Mo–Fe_2O_3 NP for epoxidation reaction, with similar activity and recyclability [106].

Very recently, Ru–Fe_2O_3 NPs were developed for catalyzing the coupling between sulfonamides and alcohols. The underlying C–N bond formation reaction takes place with high selectivity giving only water as side product. Again, the catalyst is easily isolated and reused because of its magnetic property [107].

Homogenous catalysts could also be attached to magnetic NP for recycling. Generally, a nanocomposite that bears a magnetic core with homogenous complex anchored to its surface was used. Stevens et al. reported the use of super paramagnetic NP as matrices for supporting catalysts for homogeneous Suzuki, Heck and Sonogashira cross-coupling reactions [108]. The complexes of Pd and N-heterocyclic carbenes (NHCs) were coated on Fe_2O_3 cores to form iron oxide-Pd. These nanocomposites, due to their very small dimensions (11 nm) and organic coatings could partially dissolve in organic solvents. The superparamagnetism of the Fe_2O_3 core allows the catalyst to be magnetically concentrated and re-dispersed without forming permanent magnetized clumps in the reaction media. No significant loss of the catalytic activity of the immobilized catalyst was observed after several reaction cycles. For better dispersion of the Fe_2O_3 NP, the same group reported later an “emulsion polymerization” method to form a highly branched polymer of styrene and 1,4-divinylbenzene, which leads to NPs with narrower size distribution and therefore higher stability [109]. Similarly, magnetically recoverable NPs bearing chiral catalysts were prepared and used for asymmetric hydrogenation of aromatic ketones [110].

Abu-Reziq et al. grafted PAMAM dendrimers onto the Fe_2O_3 NP. After modification of Fe_2O_3 NP with APTS, G2 dendrimers were prepared by the classical stepwise method. The resulting dendronized magnetic NPs were used to support $[Rh(COD)Cl]_2$ for the hydroformylation reactions. The reactivity and selectivity of the catalyst were very high, in addition to its facial and complete recover under magnetic field [111].

Other synthesis strategies, such as click chemistry [112], were also reported for the preparation of magnetic and multifunctional NP. Furthermore, magnetic NPs found their application in classical non-metal organic catalytic reactions. For example, an acylation catalyst, 4-N,N-dimethylaminopyridine (DMAP) was grafted on the silica modified Fe_2O_3 NP, which gave birth to the first DMAP–Fe_2O_3 NP as a robust heterogeneous nucleophilic catalyst [113]. Later on, chiral DMAP–Fe_2O_3 NPs for enantioselective acylation were reported by the same group [114].

4. Role of the stabilizer

4.1. Stabilizers in green solvents

4.1.1. Typical stabilizers that are used in water

Water is among the most polar solvents in the polarity scale of common solvents. A common feature of the stabilizers that are used in aqueous phase is their high polarity, as indicated by their molecular structure in Fig. 3. The oldest NP stabilizer in water is trisodium citrate (**3**), which is actually a multi-carboxyl acid with a hydroxyl group at C-2 position. The carboxyl group can provide coordination to the NPs and thereby the NPs are stabilized. Furthermore, the hydroxyl group in the molecular provides additional protection for the NP. In fact, carboxyl group or hydroxyl group alone can provide sufficient stabilization to the NP. Mono-carboxyl acids, (like acetate **4**), dicarboxyl acids (like succinate **11**), poly hydroxyl alcohols (like ethylene glycol **8**) and sugars (for example carboxymethyl cellulose **16**) all are efficient stabilizers for NP. Tetraalkyl ammonia salts represent another category of widely used stabilizers, with tetrabutyl amine bromide (**7**) and trimethylhexadecan aminium bromide (**6**) being the most representative. Their stabilization towards the NP is mainly due to the formation of electrostatic double layers. Surfactants that form micelles in water, such as sodium dodecyl sulfate **12** and some water soluble ligands containing N or P atoms (4-Dimethylaminopyridine **13**, phosphinophosphonic acids **20**), can also be used as stabilizers. Dendrimers can behave as molecular boxes that entrap and stabilize NP especially if there are heteroatoms (N, S) in the dendrimer's interiors [115]. Various dendrimers are applied in water as NP stabilizer, as can be seen in Fig. 3. Some stabilizers can provide combined effects to protect the NP, which are usually more effective. For example, poly(2-aminothiophenol) **2**, polyethylene glycol **9** and polyaniline **10** have combinations of steric and coordination properties, whereas poly(diallyldimethylammonium chloride) **27** provides a combination of steric and electrostatic protections.

4.1.2. Typical stabilizers that are used in ILs

The most widely applied stabilizers in ILs are in fact ILs themselves, especially for the case of imidazolium based ILs, since they provide both hydrophobic and hydrophilic regions [116]. Migowski and Dupont are the first to recognize the potential of these imidazolium based ILs in the preparation of NP. Until now, the utility of imidazolium ILs as a stabilizer and immobilizing agent for NP catalyst has been convincingly demonstrated [117]. However, in some cases agglomeration still happens, leading to a loss of activity during recycling. This suggests that ILs alone have limitations in stabilizing NP, especially under harsh reaction conditions.

Combination of ILs with another stabilizer or functionalization of ILs could provide additional benefit, making NP more stable. In our group, we first tested the combination of PVP and ILs, but obtained limited success. PVP and $[Bmim]PF_6$ co-protected metal NPs, including Ag, Rh, Pd and Pt were synthesized and used as catalyst in olefin hydrogenation reaction. However, due to the poor solubility of PVP in ILs, the NPs only exhibit moderate activity and stability in the reaction. This promoted our further studies to overcome the problem. Two strategies were developed. One is to synthesize ionic copolymers that contain both PVP and imidazolium ion units, which can act as soluble bifunctional co-stabilizers when applied in ILs [118]. The copolymer was synthesized through the free radical polymerization of N-vinyl-2-pyrrolidone and 1-vinyl-3-alkyl imidazolium halide, with the later prepared by the reaction between 1-vinyl imidazolium and alkyl halide. Then Rh NPs with a narrow unimodal size distribution centered at 3 nm were prepared by the reduction of $RhCl_3$ and stabilized by the co-polymer in IL phase, which were highly active and stable in hydrogenation of benzene under comparatively forcing conditions, with a TOF about 250 h^{-1}. TEM analysis and mercury test verified the heterogeneous nature of the reaction. During recycling, no visible agglomeration of the NP was observed, and the catalyst could be reused without loss of activity, leading to an unprecedented lifetime (TTO > 20,000). The other strategy is to design new ILs that can dissolve PVP, which has recently been realized under collaboration with Prof. Dyson in EPFL [119]. Since PVP is highly soluble in water and alcohol, it is not surprising that PVP is readily soluble in $[HOC_2MIm]BF_4$ (>5%) and completely insoluble in $[Emim]BF_4$. The direct combination of hydroxyl-functionalized ILs (OH-ILs) and PVP formed a media for the stabilization of highly active and stable NP. Rh again was selected and Rh–OH-IL–PVP was prepared through classical ethanol reduction of Rh salts in the presence of PVP followed by immobilization of Rh–PVP into OH–ILs. In the hydrogenation reaction of styrene, these Rh NPs exhibited excellent catalytic performance under mild conditions, and the products can be easily isolated from the catalytic system by decantation without contamination from either the IL or the metal nanocatalyst. One of the most appealing features of this system is that it enables the direct use of PVP, which is a cheap, commercially available and powerful stabilizer for NP in IL phase. Other stabilizers, such as various pyridine based ligands, are also used in combination with ILs to protect the NP.

On the other hand, ILs can be tuned with enhanced stabilization ability. Zhao et al. developed a series of functionalized ILs bearing nitrile, ether and hydroxyl groups that provided weak coordination to the NP when used as stabilizers resulting in better catalytic performance in C–C coupling reactions such as Suzuki, Stille and Heck reactions [120]. Reported stabilizers that are effective in ILs are provided in Fig. 4.

4.1.3. Typical stabilizers that are used in fluorous solvents and carbon dioxide

The stabilizers used in fluorous solvents and carbon dioxide are very special. For both solvents, in order to increase the compatibility of catalyst to the solvents, it is necessary to modify the stabilizer by introducing a fluorous moiety. For fluorous solvents the application of fluorous containing stabilizer makes a "like-dissolve-like" effect to the NP, leading to soluble NP in the fluorous solvents. In the case of $scCO_2$, conventional surfactants themselves could not form reverse micelles or microemulsions in it because the van der Waals interdroplet attractions are too high. To overcome this problem, surfactants or cosurfactants with fluorinated tails were applied as NP stabilizer, which provides a layer of weak attractive compound covering the highly attractive droplet cores and thus prevents the short-range interactions that are detrimental to the stability of the system. Therefore, ligands and surfactants containing fluorous atoms (see Fig. 5) are used as the stabilizer. Among them, the dendrimer type stabilizers are used very frequently. This is partly because the terminal groups of the dendrimers can be easily tuned to provide the desired solubility in $scCO_2$ or fluorous medium.

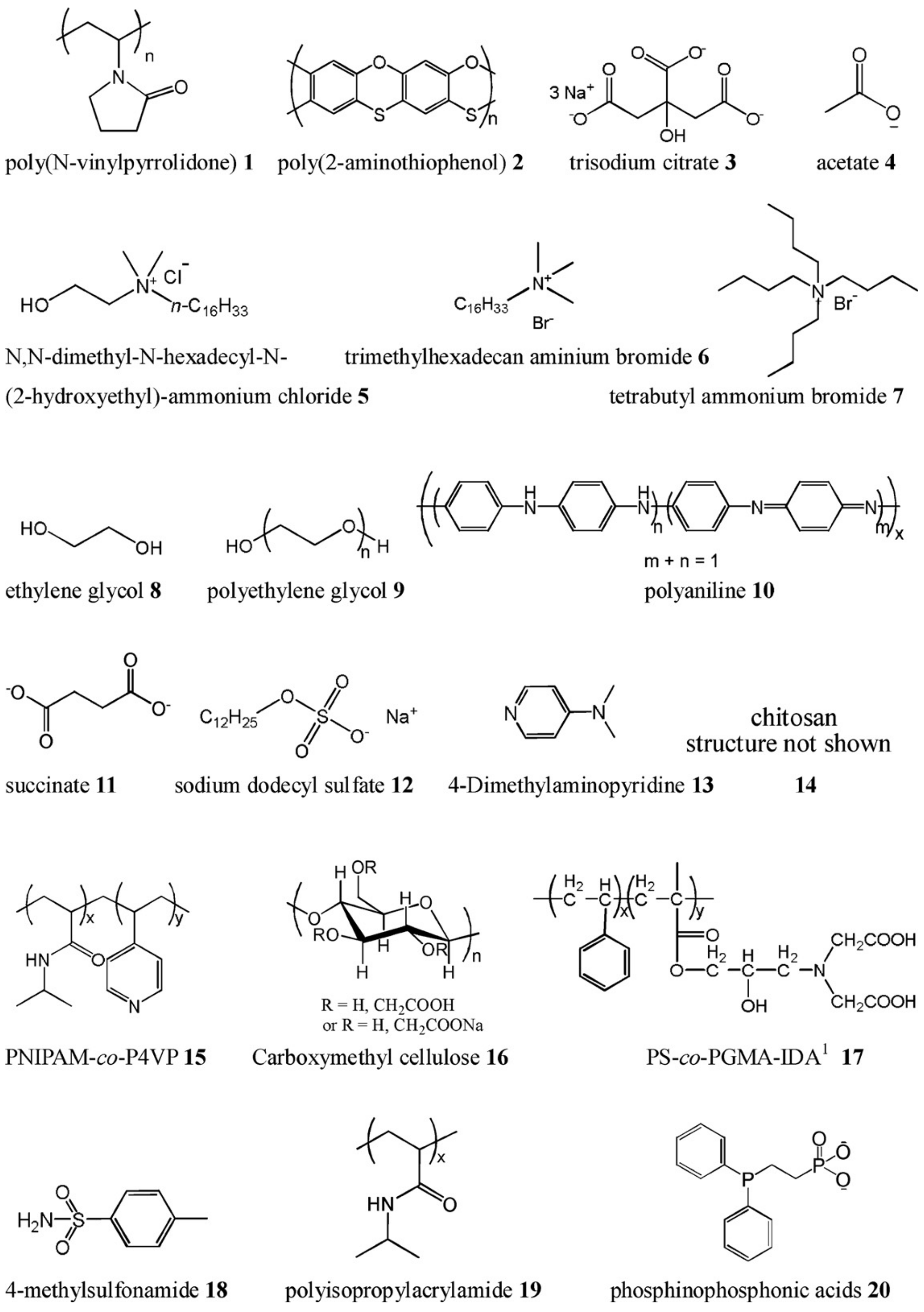
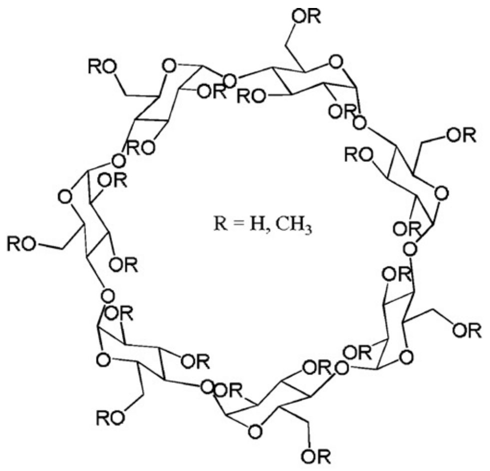
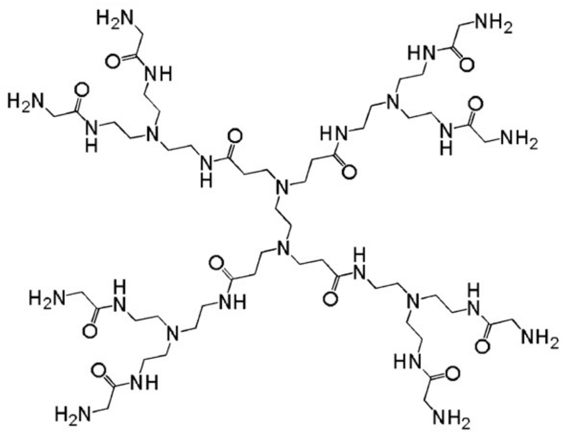


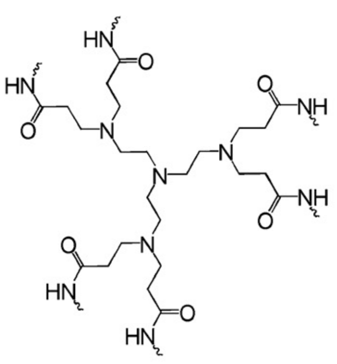
Fig. 3. Typical stabilizers that are used in water. ([1]Short for polystyrene-co-poly[2-methacrylic acid 3-bis-(carboxymethylamino)-2-hydroxypropyl ester]; [2]Only G0 version was shown; [3]Short for poly[styrene-*co*-2-(acetoacetoxy)ethyl methacrylate-*co*-methyl acrylic acid])



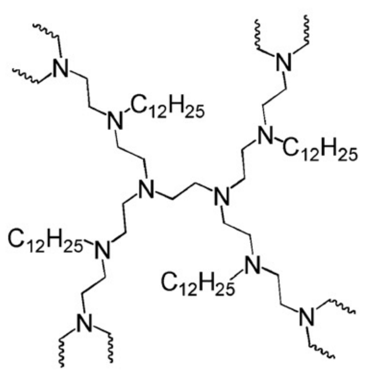
randomly methylated cyclodextrins **21**



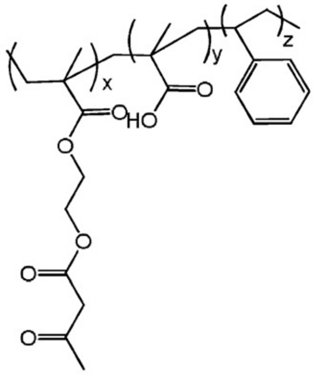
polyamidoamine (PAMAM)^2 **22**



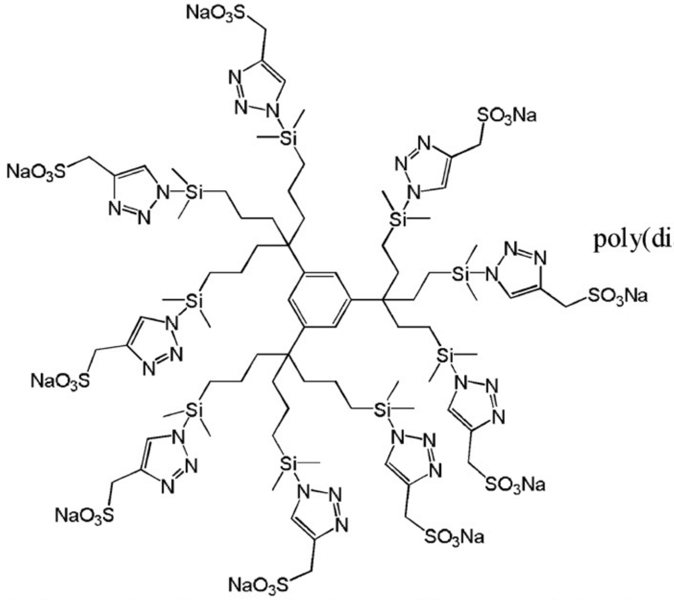
polyamidoamine **23**



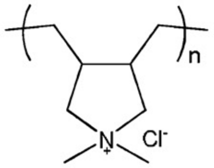
alkylated polyethylenimine **24**



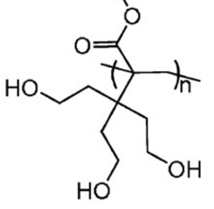
PS-*co*-PAEMA-*co*-PMAA^3 **25**



1,2,3-triazolylsulphonate dendrimers **26**

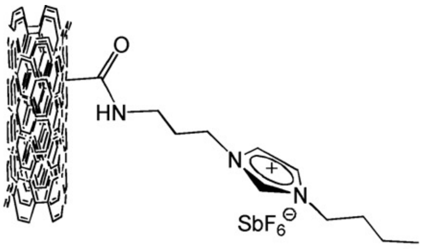


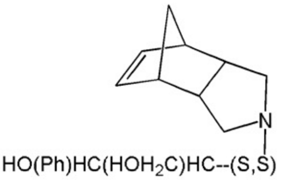
poly(diallyldimethylammonium chloride) **27**



poly(methoxytri(ethylene glycol) methacrylate) **28**

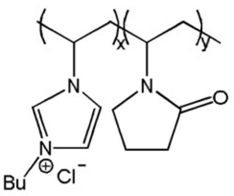
Fig. 3. (*Continued*).



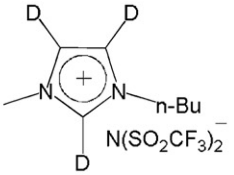


endo-carbic anhydride derived amine ligand **30**

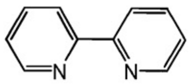
imidazolium -functionalized multi-walled carbon nanotubes **29**



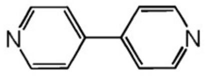
poly[(N-vinyl-2-pyrrolidone)-*co*-(1-vinyl-3-butylimidazolium chloride)] **31**



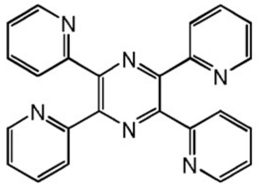
[BMI]-d_3.NTf$_2$ **32**



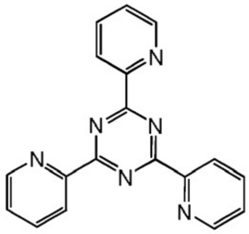
2,2'-bipyridine **33**



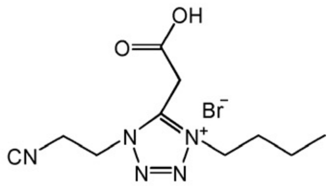
4,4'-bipyridine **34**



2,4,6-tris(2-pyridyl)-*s*-triazine **35**



tetra-2-pyridinylpyrazine **36**



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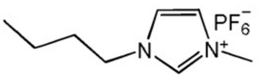
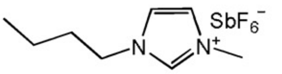
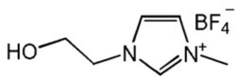


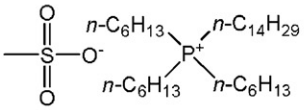
[BMI][PF$_6$] **38**



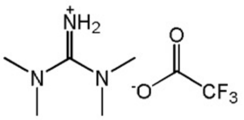
[BMI][SbF$_6$] **39**



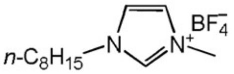
[C$_2$OHMIM][BF$_4$] **40**



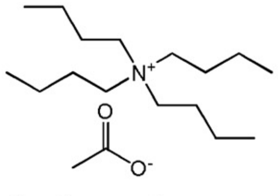
trihexyltetradecylphosphonium methylsulfonate **41**



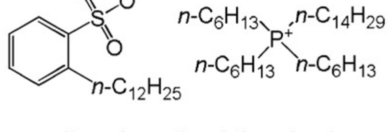
1,1,3,3-tetramethylguanidine trifluoroacetic acid **42**



[*o*mim][BF$_4$] **43**



tetrabutyl ammonium acetate **44**

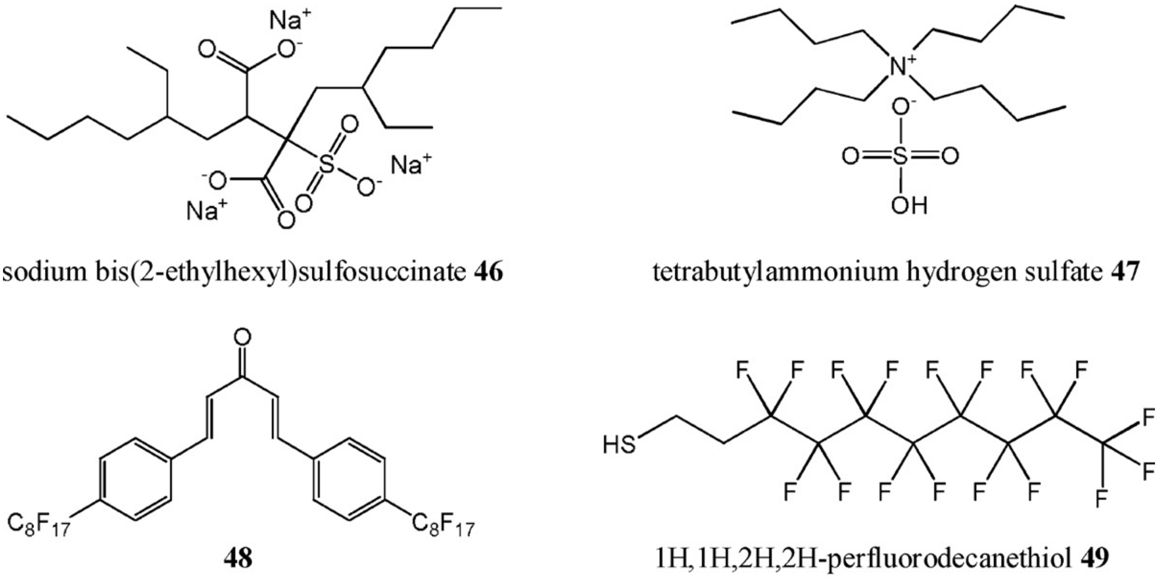


trihexyltetradecylphosphonium dodecylbenzenesulfonate **45**

Fig. 4. Typical stabilizers that are used in ILs.

4.1.4. Typical stabilizers that are used in high boiling point alcohols

These solvents are very polar due to the hydroxyl groups. In principle, all stabilizers that work in water could be transferred into these solvents. Current examples show the high boiling point alcohols (most examples use PEG as reaction media), just like imidazolium based ILs, are sufficient in protecting the NP. All reported systems avoided the use of any additional stabilizer, though the involvement of a second stabilizer may further enhance the NP stability without exerting detrimental effects on the activity.



sodium bis(2-ethylhexyl)sulfosuccinate **46**

tetrabutylammonium hydrogen sulfate **47**

48

1H,1H,2H,2H-perfluorodecanethiol **49**

$$(HO)_2PO\text{-}O\text{-}(CH_2CH_2O)_n\text{-}CH_2\text{-}CF_2\text{-}O\text{-}Rf\text{-}CF_2\text{-}CH_2\text{-}(OCH_2CH_2)_n\text{-}O\text{-}PO(OH)_2$$

perfluoropolyether phosphate [PFPE-PO_4] **50**

Fig. 5. Typical stabilizers that are used in $scCO_2$ and fluorous solvents.

4.2. Strategies: balance between activity and stability

Stabilization strategies, according to their mechanism, are generally divided into four kinds including electrostatic, steric, electrosteric and coordinative stabilizations, which was first suggested by Roucoux and Patin in their excellent review [121]. There are ongoing interests in the discovery of more efficient stabilizers that can produce robust NP [122]. For catalytic purpose, however, the central issue is to find a suitable stabilizer that provides a balance between the catalytic activity and the stability of the NP, no matter what stabilizing strategy is used.

There are numerous examples supporting the idea that robust NPs are not necessarily good catalysts. An elegant case was provided by Korgel and co-workers in 2005 in which Ir NP was prepared by the reduction of (methylcyclopentadienyl)(1,5-cyclooctadiene)Ir with hexadecanediol in the presence of four different stabilizers, namely oleic acid/oleylamine, trioctylphosphine, tetraoctylammonium bromide, and tetraoctylphosphonium bromide. Among them, the oleic acid/oleylamine stabilized NPs were of the highest quality, with the narrowest size and shape distribution. However, in the hydrogenation of 1-decene, oleic acid/oleylamine protected Ir NPs were completely inactive. Ir NPs stabilized by trioctylphosphine, which is also a strong ligand, were also inactive. Less robust Ir NPs which were protected by the other two stabilizers were highly active in the catalytic reactions. From these the authors concluded that "Good capping ligands (i.e. those that stabilize robust nanocrystals with very narrow size distributions) appear to be poor choices for catalytic applications" [123]. Similar trend was also observed for Rh NP [124]. For Pd NP, Li and El-Sayed compared the effect of different stabilizers such as PVP, polystyrene-b-poly(sodium acrylate) block copolymer, and G2–G4 PAMAM-OH dendrimers on its catalytic activity toward Suzuki reaction. PVP stabilized Pd NP exhibited high catalytic activity whereas block copolymers were found to provide better protection for the NP surface compared to PVP. When the stability and catalytic activity of Pd NP using different generations of PAMAM-OH dendrimers as stabilizers were compared, it was observed that G2 and G3 dendrimers stabilized Pd NPs are efficient catalysts for Suzuki reaction. G4 dendrimers which can reasonably produce more stable Pd NPs, however, led to a decrease in catalyst activity. The authors proposed that G4 dendrimers encapsulate the NP so strong that they cause a catalytic activity loss [125].

Therefore, it has been quite widely accepted that the stability and catalytic activity are anti-correlated, which means the most stable NPs are the least catalytically active. It is quite frustrating for investigators in NP catalysis since it means E and S criteria cannot be simultaneously met. However we believe that achieving a satisfying stability does not necessarily cost an activity loss. To elucidate this, we have to look into the stabilization mechanism and the way the NP catalysts work. In our view, stabilizers, according to the strength of their interactions with the NP surface, can be divided into three main categories:

(a) "Strong" stabilizers. These stabilizers, including many nitrogen (III) and phosphine containing agents such as oleylamine and trioctylphosphine discussed previously, can interact with NP surface strongly. In fact, these stabilizers are also widely used ligands with excellent electron donating properties in homogenous catalysis. They form covalent bonds with the surface and therefore prevent particles from aggregation.
(b) "Medium" stabilizers. This kind of stabilizers is generally composed of ionic surfactants and some simple ions, which form a protective double layer to prevent the NP from aggregation. They have interactions with the NP surface, but to a less extent compared to "Strong" stabilizers.
(c) "Weak" stabilizers. This kind of stabilizers is usually non-coordinating polymers which can afford physical steric hindrance to protect the NP. These polymers are generally physically absorbed on the NP surface and their interaction with NP is the weakest.

If we consider a reaction catalyzed by NP, the first elemental step is always the adsorption of the reagents onto the NP surface. As a result, the availability of the NP surface atoms is crucial for obtaining a high catalytic activity. Therefore it is not surprising to see that NP stabilized by "Strong" stabilizer has an anti-correlated relationship between its activity and stability. As stabilizer with stronger coordination property is used, more surface atoms are occupied by the irreversible adsorption of the stabilizers, leading to a decrease in activity. In this occasion, the more stable the NPs are, the less catalytically active they are. For the other types of stabilizers, increasing the protection ability (for example increasing the amount of the stabilizer), which produces more stable NP, will not change the catalytic activity to a considerable extent since the active surface atoms of the NP are still available for the substrates. As a result, it is possible to find a stabilizer that can produce robust and highly catalytic active NP at the same time. The way to achieve this is (1) avoiding the participating of "Strong" stabilizers and (2) designing stabilizers that combine steric/electrostatic stabilization or steric/weak coordinating stabilization.

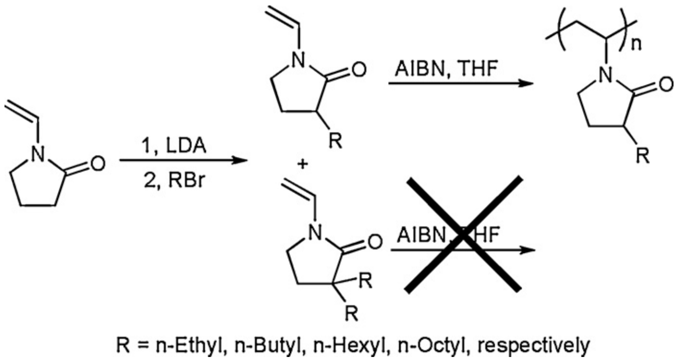
This point has not been clearly stated in previous literatures. However, some clues can be gained from publications which are in accordance with our hypothesis. For example, one of the most successful stabilizer, PVP, can provide both steric hindrance and weak coordination properties through its N–C═O structure. Another piece of evidence, coming from one of our own reports, is that PVP with higher molecular weight gave much more stable Pd NPs whereas their catalytic activity toward the transformation of *p*-cymene to limonene was intrinsically the same as those stabilized with low molecular weight PVP [126].

4.3. Potentials in nanoparticle catalysis

As illustrated in Section 4.2, the stabilizer plays a dominant role in the stability and activity of NP catalysts. In fact, the potentials of stabilizer in NP catalysis are far beyond that. At least, as already demonstrated by researchers including us, there are two other functions that the stabilizer can provide. One is recyclability and the other is multi-functionality.

The control of the NP catalysts becomes possible when stimuli-responsive polymers are used as stabilizers. The structures and properties of the stimuli-responsive polymers can change with environmental parameters. Among them thermal sensitive polymer which undergoes a low critical solution temperature (LCST) phase transition [127] (also known as an inverse temperature transition [128]) has attracted particular attention due to its great potential in many fields such as catalysis [33,129], functional material synthesis [130], and nanoreactor manipulation [32]. Current investigations of thermal-responsive polymers are largely based on poly(N-isopropylacrylamide) (PNIPAAm). The PNIPAAm exhibits a LCST of 32 °C, which was discovered by Heskins and Gillet, some 40 years ago [131], and has been extensively explored ever since [132].

In this group, a series of alkyl-functionalized PVP were synthesized, all of which are excellent NP stabilizers (Scheme 16) [133]. Interestingly, the LCST of these polymers has a dependence on the alkyl chain length. For example, C_2-PVP had a LCST of 26 °C whereas C_4-PVP had a LCST of 34 °C (Fig. 6). The properties can be used for the control of the reaction and the separation of catalysts. When the temperature was below the LCST, the NP dispersed well in water and the reactions progressed effectively. By contrast, once the temperature was raised up to LCST, the NP precipitated and thereby the reaction was shut down. It also leads to the separation of the NP from the solution. It was observed that in the decomposition reaction of $NaBH_4$ catalyzed by Au NP stabilized by C_2-PVP, the reaction rate increased as temperature increased from 15 to 20 °C, and then the reaction completely ceased when the temperature was 30 °C [134].



Scheme 16. Synthesis strategy for the preparation of alkyl group modified PVP [135].

Furthermore, stabilizer has the potential to provide multi-functionality to NP catalytic systems. Some stabilizers can be regarded as the solid support that is used in classical heterogeneous catalysis. And multifunctional solid supports are also widely used. For example, the Pt/zeolite catalysts, used in the cracking process in petroleum industry, are bifunctional. Pt centers provide the dehydrogenation capacity and the zeolite provides acid center for the activation of alkane rearrangements [135]. In contrast, multifunctional catalytic systems for NP catalysis have not been well-examined. We believe that such system, for example that composed of tailored stabilizer that bears acidic/basic moieties and the NP center, will be one of the future research interests.

5. Role of the solvent

5.1. Key issue: reaching green

NP catalytic systems are greener than many stoichiometric reactions if judged by the twelve principles of green chemistry in which a catalytic process is preferred. However, solvent is an even more important parameter that determines the green nature of the NP catalysis, regarding the fact that the solvent accounts for 50% of the green house gas emissions during post-treatment and 60% of the energy used in pharmaceutical processes [136]. Over the last 20 years, conventional solvent alternatives have attracted much

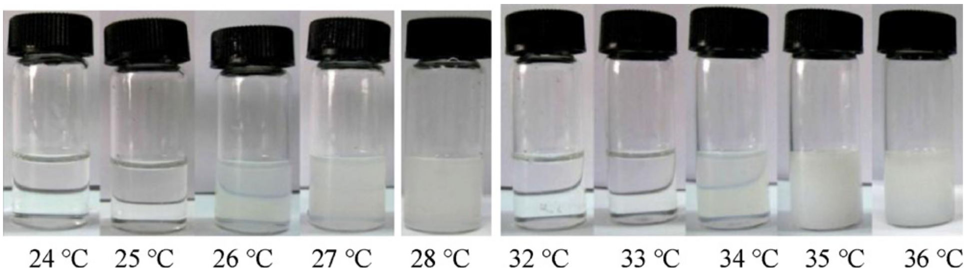


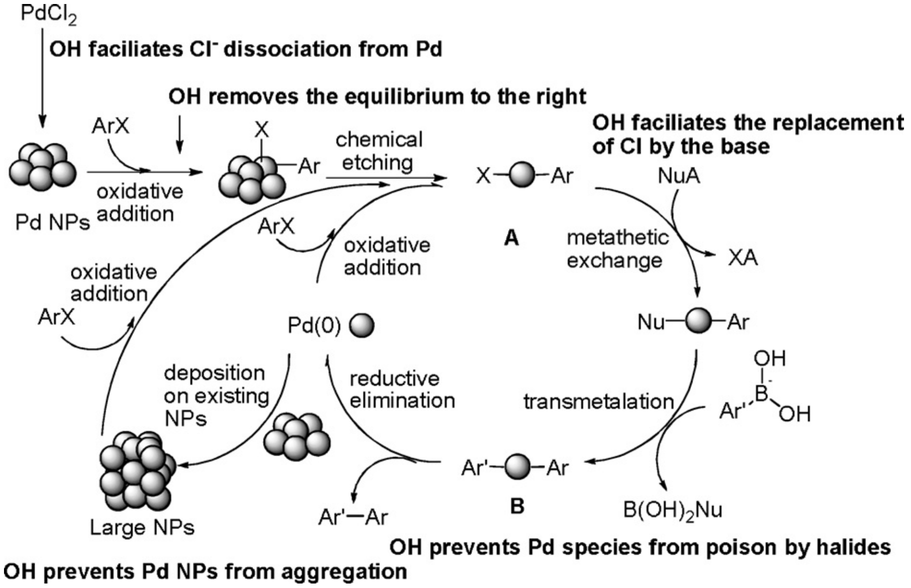
Fig. 6. Temperature dependent behavior of Cn-PVP (5 bottles in the left are C_2-PVP, 5 bottles in the right are C_4-PVP in water) [136].

attention from both academia and industry. In the domain of NP catalysis, water, ILs, fluorous solvents and carbon dioxide all draw considerable attention. However, as predicted by DeSimone, environmental advantage alone probably will not enable alternative solvents to achieve widespread applicability [137]. The full potential of alternative solvents will only be reached if researchers exploit their benefits beyond their intrinsic environmental advantages. Indeed, efficiency and cost-effectiveness are also the demands of green chemistry itself [138]. In the context of NP catalysis, we believe that such “advantageous properties” including accelerated reaction rates, improved selectivities, enhanced NP stabilities, and diminished catalyst leaching, will enable NP catalysis in green solvent to be a fully green and sustainable process.

It is well known that solvents play a critical role in many organic and inorganic reactions as they modify both reaction equilibrium and kinetics [139]. In NP catalysis, it has been demonstrated that solvents can bear other functions such as acting as reductants, (co)-stabilizers, promoters and even co-catalysts beyond their role as green reaction media. For example, polyethylene glycol (PEG) can be used as a reductant, stabilizer and reaction solvent in the same system (see Section 6.5 for details). In the NP catalyzed aqueous reaction, the pH value of the solvent is an important factor that can influence the catalytic behaviors. Some stabilizers are pH-sensitive [140]. And in water the acidity/basicity may strongly influence the micellar characteristics which are correlated with catalytic properties, and may be used as an important tool to tailor the catalytic activity and selectivity. For instance, the selective hydrogenation of dehydrolinalool (3,7-dimethyloct-6-ene-1-yne-3-ol) to linalool (3,7-dimethyloct-1,6-dene-3-ol) catalyzed by Pd NPs, which were stabilized by poly(ethylene oxide)-block-2-vinylpyridine (PEO-b-P2VP) micelles, was studied by varying the pH value of the reaction medium. The highest selectivity (99.4%) was obtained at pH 9.4 and 95 vol% of *i*-PrOH, and the highest TOF was 24.4 h^{-1} at pH 13.0. The authors attributed this pH dependence to the local concentration variation of the pyridine unit according to the pH change, i.e. higher pH value causes less dense micelles, which increases reaction rate by increasing diffusions of the substrate within the micelles and meanwhile decreases the selectivity since it causes higher pyridine unit density [141].

The potential of utilizing solvents to benefit NP catalytic process was largely achieved by ILs. ILs, also called tailoring solvents because of their great flexibility in properties by modifying the structures of catalysts, provide an ideal platform for studying the “additional benefits” of solvents in NP catalyzed reactions. Similar to PEG, ILs can be used as stabilizers for NP, as first demonstrated by Dupont et al. in 2002 [142]. Indeed, the driving forces for NP aggregation are much low in ILs, and therefore, the metal NP could be better stabilized [143]. ILs can be functionalized and attached with weak coordination groups to further enhance the stability as well as catalytic activity in the reaction. For example, Zhao et al. used nitrile-functionalized IL to protect Pd NP with an average diameter of 5 nm. The resulting Pd NPs were excellent recyclable catalysts for Suzuki, Heck and Stille coupling reactions, achieving an optimum balance between stability and reactivity. Besides, the Pd NPs were very stable and could be kept for more than several months without obvious aggregation [121]. The weak coordinative ability of the CN group was believed to eliminate the aggregation of the Pd NP during the reaction. Using functionalized ILs can broaden the synthesis methodologies. For example, the most widely used stabilizer, PVP, is only soluble in very polar solvents such as water and alcohol, which limits its utilization considerably. Recently, it was reported that the OH group functionalized ILs enable the direct use of PVP for the protection of NP. The Rh NPs were prepared and used for the hydrogenation of styrene with easy catalyst recovery and excellent stability [120]. OH group functionalized ILs were also used as the media of Pd NP catalyzed Suzuki reactions [144]. Compared to non-functionalized ILs, the OH-IL system leads to much better NP activity and resistance to poison. Furthermore, the OH-IL system is capable of converting challenging substrates such as hindered and chloro substituted substrates. The IL plays a critical role in catalyst/substrate activation by directly facilitating a ligand-free catalytic system. First, it facilitates the generation/stabilization of the catalyst. Second, its OH group bonding with the halogen atom helps activate the C–X bond. Third, it aids the dissolution of salts generated during the catalytic cycle facilitating reaction and preventing catalyst poisoning (see Scheme 17).

Based on the study of NP catalysis in ILs, it is demonstrated that solvents may also be critical parameters for the selectivity in the reaction. For example, partial hydrogenation of arenes is a big challenge as much more active catalysts are required compared with that of alkenes, because of the need to break the aromaticity. ILs present a potential solution for this. Partial hydrogenation of arene [145] or diene [146] compounds into monoenes over NP in ILs has been reported by several groups, including us. In



Scheme 17. Role of the solvents in the nanoparticle catalyzed Suzuki reaction.

our group, an IL-like polymer stabilized Rh NP in $[BMIM]BF_4$ was applied to the hydrogenation of *n*-alkyl-benzene, phenylmethanol and xylenes [147]. For all the cases, partially hydrogenated products were observed, with the yield ranging from 1 to 32%. The unique selectivity towards the partially hydrogenated products may be due to the solubility difference between the substrate and the products, i.e. the monoene product is insoluble in IL phase and therefore separated from the catalytic system upon formation, suppressing the full hydrogenation reactions. Water exhibited similar selectivity trends in the partial hydrogenation of arene and diene compounds for the same reasons, as demonstrated by Widegren and Finke [148].

Solvent may have selected interactions with moieties of a substrate, which can influence the selectivity of a reaction. We found that in the hydrogenation of *o*-chloronitrobenzene (*o*-CNB) catalyzed by Pt NP, the selectivity for *o*-chloroaniline (*o*-CAN) was nearly 100% when the reaction was performed in $[BMIM]BF_4$ whereas a selectivity of less than 50% was observed in methanol with similar Pt NP catalyst [149]. It was reported that the addition of metal ions as additives can significantly improve the reaction selectivity since these metal ions may interact weakly with the nitro groups [150]. To understand if ILs have similar effects as these metal ion additives, IR absorption spectroscopy and DFT study were applied. A red shift of the asymmetric stretch vibration of the nitro group (from 1537 to 1533 cm^{-1}) was observed when the solvent was switched from diethyl ether to $[BMIM]BF_4$. However, the vibration frequency did not alter when the solvent changed from diethyl ether to methanol. These results indicated that there were strong molecular interactions between the nitro group on *o*-CNB and ILs. Further evidence was obtained from DFT calculations, showing that the intermolecular interactions of $[BMIM]BF_4$ and *o*-CNB did not weaken the C–Cl bonds but only N=O bonds. ILs can also enhance the selectivity of the hydrogenation of C=O bonds in the presence of C=C. An example reported by us is the hydrogenation of cinnamaldehyde into cinnamyl alcohol over Ru NP in ILs [151].

Compared to the extensive study of NP catalysis by modifying the metal center and the stabilizer, the potential effects of the solvent on the reaction are still a relatively unexplored area though a few successful examples have already been achieved. More attention should be paid to this aspect since solvent is one of the three key factors for NP catalysis in liquid phase.

5.2. *Key issue: reaching biphase*

Solvent also plays an important role in the recovery and reuse of catalyst. As described in Section 2, the recyclability issue is a big obstacle for the practice of NP catalysis in solutions. Although there are many attempts to heterogenise homogeneous catalysts by attaching them to organic or inorganic supports, only quite limited successes were achieved and no commercially viable process was developed. The need for efficient separation of product and catalyst, while maintaining the advantages of a homogeneous catalyst, has led to the concept of liquid–liquid biphasic catalysis [152].

Biphasic catalysis was first developed for the utilization of homogenous catalyst. Due to the similarity of homogenous catalysis and NP catalysis in solutions, this technique makes it possible to fully utilize the inherent advantages of NP catalysis in solution phase as well. Since most conventional organic solvents are miscible with each other, the biphasic catalysis usually involves at least one nonconventional solvent. Almost all kinds of green solvents have been intensively studied under biphasic conditions with different combinations with conventional solvents.

The idea of aqueous/organic biphasic systems is first expressed by Manassen in 1973 [153], which finally led to the first industrialized hydroformylation process in the early 1980s [154]. Aqueous/organic biphasic systems for NP catalysis came in late 1980s [155] and were intensively investigated ever since [156]. One disadvantage of the aqueous/organic biphasic systems is the low distribution efficiency of the organic substrate in water, which resulted in low reaction rates. To overcome this problem, phase transfer reagents are sometimes required. In some occasions, NP stabilizers themselves were surfactants which can help phase transfer during the reaction [157].

Traditional aqueous/organic biphasic systems are now being augmented by other biphasic combinations such as IL/organic [158] and fluorous/organic systems [159]. The benefit of both ILs and fluorous solvents is their tunability. They can be designed to reach desired phase properties. For fluorous solvents, it is even possible that the reaction is homogenous at elevated temperatures whereas became biphasic after cooling down due to the thermal sensitive solubilities of some fluorous solvents in organic phase [160].

6. Current examples of nanoparticle catalysis in green solvents

Solvents are playing critical roles in establishing an efficient and sustainable process given the fact that the use of solvents accounts for 50% of the post-treatment of green house gas emissions and 60% of the energy used in pharmaceutical processes [161]. There are many investigations on NP catalysis in green solvents. In order to give the readers more complete information, we decided to describe briefly the history and/or advantages as well as environmental considerations of the solvent followed by exhibiting fairly complete lists of the reported reactions in tables. The selection rule for the examples in the tables is that if a paper described only one type of reactions, the optimized conditions for the most challenging substrates are selected. If the paper involves more than one type of reactions, representative example from each type is provided.

6.1. *The greenness of green solvents*

As solvent for organic reactions, water bears a number of attractive physicochemical properties over traditional organic solvents. It is non-flammable, non-toxic and non-carcinogenic, and in addition, water is probably the least expensive and most easily accessible solvents [162]. $scCO_2$ bears most of these benefits that water has. Besides, $scCO_2$ is characterized by gas like viscosities and solvating properties of a wide range of various organic solvents. Furthermore, the rapid mass transfer properties associated with the low viscosity of supercritical fluid (SCF) carbon dioxide can bring about efficient production capabilities for various types of important industrial processes [163]. Therefore, the use of water and $scCO_2$ as reaction media is consistent with the current trend towards the use of renewable, biomass-based raw materials, which are ultimately derived from carbon dioxide and water. Due to these environmental benign natures, few will challenge water and $scCO_2$ as green solvents. The concern of using water as reaction medium is that its heat capacity is one of the biggest in all materials, which means a lot more external energy input compared to organic solvents in the heating process. The issue with $scCO_2$ is the inherent high pressure involved in all $scCO_2$ related process, which is against the basic principle of green chemistry.

ILs have widely been promoted as “green solvents”. The reason for calling them green generally includes their nonvolatility, nonflammability and nontoxicity. The perceived environmentally friendly nature of ILs is however under scrutiny now since they may not as green as we thought, especially when we consider their toxicity [164]. Recent research results clearly indicate that most ILs in fact exhibit detrimental effects on aquatic ecosystems, microorganisms and animals [165]. Therefore they are not fully environmentally benign [166].

Although ILs are still "greener" than most common organic solvents, the concern for their potential environmental risk makes ILs that were thought fully green and ideally bio-derived, highly derisible. The adjustable nature of ILs once again embodies the importance of designing solvents, i.e. ILs can be designed to be nontoxic. With this conception, a new generation of ILs, where the cations were derived directly from natural α-amino acids and α-amino acid ester salts were used [167]. Consequently, the greenness level of this new generation of ILs has been enhanced to full-greenness using nontoxic inorganic or organic anions [168]. ILs with anions derived from natural amino acids have also been developed [169]. We believe that the combination of metal NPs and these novel bio-derived ILs represents a direction for future research and will better fulfill the ESSR criteria.

Fluorous solvents, with perfluorinated alkanes being the most representative, possess unusual physicochemical properties, such as low dielectric constants, high chemical and thermal stability, and low toxicity. There are, however, some concerns on fluorous solvents regarding bio-safety and environmental issues. For example, they are bioaccumulative. Also, they are greenhouse gases [170]. Although perfluoroethers are less problematic, they cannot be treated as fully green solvents. The reason that in this review the fluorous solvents are still included is mainly that they obey some of the basic principles in green chemistry. They form many biphasic systems which make separation extremely facial and they can easily be reused for many times due to their stability.

High boiling alcohols, including glycerol and PEG, have recently attracted much attention as reaction media [171]. They are cheap, easily functionalized and more importantly, nontoxic. Glycerol is a natural product and is widely used as cosmetic and food additive. PEG is also nontoxic [172] and in fact it is so benign that they are approved for use in pharmaceutical [173] and food industry [174]. The low-toxicity, low volatility, and biodegradability of high boiling point alcohols represent important environmentally benign characteristics, which are particularly attractive when combined with their relatively low cost as a bulk commodity chemical [175].

6.2. Water

"The best solvent is no solvent and if a solvent is needed then water is preferred", statement from Sheldon in his recent review [176], in which the methods to assess environmental impact of chemical process were described, reflects the current perception in chemical industry. Indeed, water is cheap, readily available, nontoxic, non-flammable and safe to environment. In particular, for the catalysis purpose, there are several other advantages that water can provide:

(a) *The inertness against oxidation and reduction*. Water can be neither oxidized, nor reduced easily. In fact, both the oxidation and reduction of water are among the most challenging reactions for chemists. This feature is of great value when water acts as the reaction medium, especially for oxidation reactions, which are much less practiced in other green solvents, such as ILs.
(b) *High polarity*. Since most reactions of interest are the transformation of organic compounds that usually have quite lower polarity compared to water. As a result, biphasic catalysis becomes available, which thereby dramatically decreases the working up process.
(c) *High solvation ability*. Water has very high solvation ability towards many cations and anions. Some ions that are usually poisons for the catalyst, such as Cl^-, can be solvated by water and their affinity to metals are greatly reduced.

With so many benefits, it is not surprising that there are numerous studies on NP in water. The investigated reactions almost covered all catalytic reaction types except a few that are sensitive to water. Investigations focused on the use of noble metal NP, partly due to the general instability of 3-d zero valent metal NP. Recently, however, some investigations suggested that 3-d metal NPs are far more stable than people had anticipated if they are prepared in water. The first example of water-dispersible nickel(0) NP was reported by Özkar and co-workers. The Ni NPs were prepared from the reduction of nickel(II) acetylacetonate by sodium borohydride in aqueous solution and stabilized by hydrogen phosphate anion. The authors tested the catalytic behavior of the Ni catalyst toward the hydrolysis of sodium borohydride. A TON of 1450 was found before the catalyst underwent deactivation. Interestingly, it was observed through kinetic analysis that the apparent activation energy of the Ni NP catalyzed hydrolysis of sodium borohydride was substantially lower than that of the Ni bulk metal catalyzed reaction [177]. Fe NPs have also been prepared and were used for catalyzing the decomposition of ammonia borane recently [178]. For detailed information of current status of metal NP catalysis including that of both noble and 3-d metals in water, please refer to the examples in Table 3.

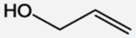
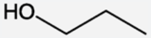
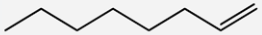
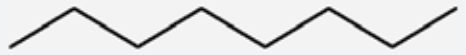
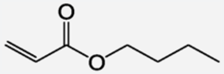
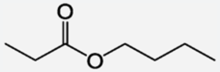
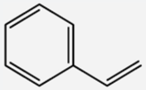
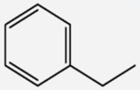
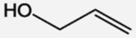
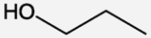
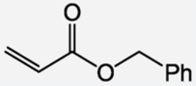
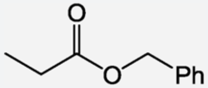
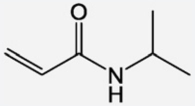
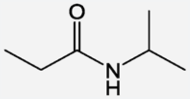
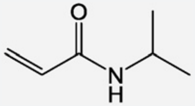
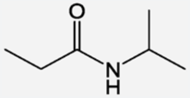
6.3. Ionic liquid

In 2001–2002 when we prepared a review paper for *Catalysis Today* entitled "Ionic liquids: applications in catalysis", there was few studies on NP catalysis in ILs up to the end of 2001. However, we realized that ILs should be of great potential for the development of highly efficient NP catalytic systems. In the conclusion, we proposed that "Ionic liquids offer the opportunity of combining the advantages of both homogeneous and heterogeneous catalysis in one system. That is to say, immobilization of a catalyst (metal/oxide/complex) by supporting it in an ionic liquid rather than on a surface may create highly free, three-dimensional centers as in a homogeneous catalyst but the catalytic reaction occurs at the interface between the ionic liquid (rather than a solid) and the reactants in either the gas or immiscible liquid phase. Development of application of three-dimensional heterogeneous catalysis using ionic liquids as supports should present challenges for us over the next decade and beyond [179]." More than 7 years have passed since we prepared this review, it is indeed a pleasure to find that NP catalysis in ILs has already grown from a little seed into a giant tree. The first example of NP catalysis in ILs comes from Dupont's group, in which Ir NPs were obtained by the reduction of organometallic precursor and stabilized by $[BMIM]PF_6$ [180]. Following that, extensive studies on NP preparation and application in catalysis were reported, covering a wide range of reaction types including hydrogenation, C–C coupling, and occasionally oxidation [181]. The benefit that ILs can provide first comes from the fact that the tendency of the aggregation of NP is much lower in ionic environment. Therefore, the NP can be stabilized to some extent without any additional stabilizers. Second, the tunable miscibility of ILs enables facial recycling of the solvents as well as the immobilized NP. Furthermore, some reactions catalyzed by NP exhibit unusual but desired selectivity patterns when performed in ILs, as demonstrated by selective hydrogenation reaction in Section 5.1. These advantages, coupled with the intrinsic "green" nature of ILs, made NP in ILs an appealing field to explore. Since there are recently several excellent reviews, even one textbook [182] on this topic, we only provide in Table 4 a collection of research reported on NP catalysis in ILs from 2002 to mid-2009, which to our knowledge has not been done so far.

6.4. Supercritical solvents

$scCO_2$ was widely used in extraction as a replacement of the toxic conventional organic solvent. In the recent 15 years, the focus

Table 3
Nanoparticle catalytic reactions in water.

Type	Substrate	Product	Catalyst (metal)	Stabilizer	Solvent	TOF/h^{-1}	Yield	Reaction condition	Recycling	Ref.
Hydrogenation (C=C bond)			Pt (1.4 ± 0.2 nm)	**22**	H_2O	25	-	20 ± 2 °C	No	[218]
Hydrogenation (C=C bond)			Pd (2–4 nm)	**24**	H_2O	–	>99%	80 °C, 5 h	5	[219]
Hydrogenation (C=C bond)			Pd (3.9 nm)	**25**	Organic/H_2O	2150	100%	35 °C, 1 atm, 1 h	8	[220]
Hydrogenation (C=C bond)			Pd (8.6 ± 3.0 nm)	**28**	H_2O/octane	98	>80%	25 °C, 111 min	5	[221]
Hydrogenation (C=C bond)			Pd (2.3 ± 0.2 nm)	**26**	H_2O	8088	–	25 °C, 1 atm	No	[222]
Hydrogenation (C=C bond)			Pd (not mentioned)	**4, 7**	H_2O	25	98%	H_2 (gas bag), r.t., 4 h	10	[223]
Hydrogenation (C=C bond)			Pt (1.4 ± 0.2 nm)	**22**	H_2O	57	–	20 ± 2 °C	No	[220]
Hydrogenation (C=C bond)			Pd (1.3 ± 0.3 nm)	**22**	H_2O	372	–	20 ± 2 °C	No	[220]
Hydrogenation (C=C bond)			Rh (2.0 nm)	**20**	H_2O	5700	–	20 °C, 20 atm	No	[84]

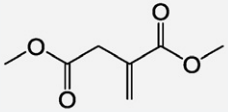
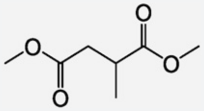
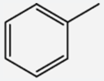
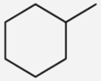
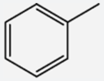
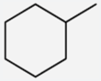
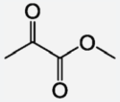
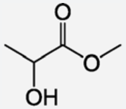
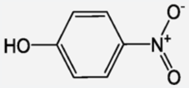
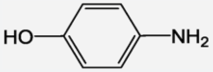
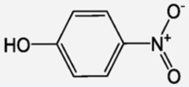
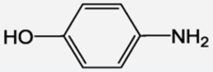
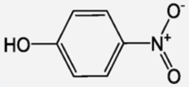
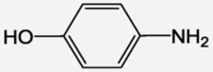
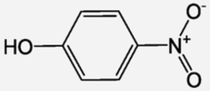
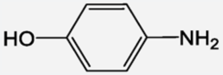
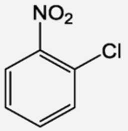
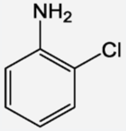
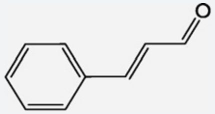
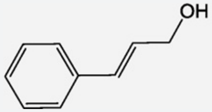
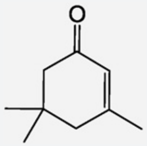
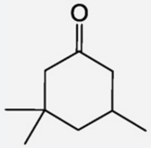
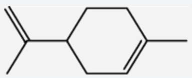
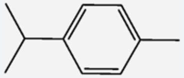
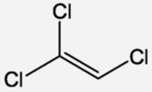
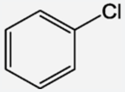
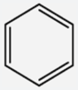
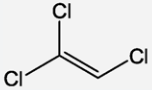
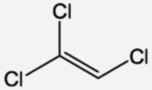
Hydrogenation (C=C bond)			Rh–Fe_2O_3 (∼10 nm)	TPPTS	H_2O	6	100%	50 °C, 3.5 atm, 4 h	10	[224]
Hydrogenation (arene)			Ru (∼4 nm)	**6, 21**	H_2O	10.1	81%	20 °C, 1 atm, 24 h	–	[225]
Hydrogenation (arene)			Ru (2–3 nm)	**21**	H_2O	17	100%	20 °C, 1 atm, 6 h	–	[226]
Hydrogenation (C=O bond)			Pd (2–8 nm)	**27**	H_2O	160	–	27 °C, 12 h, 50 atm	–	[227]
Hydrogenation (nitro group)			Au (2 nm)	**15**	H_2O	7.9	–	25 °C, air, 6 h	1	[228]
Hydrogenation (nitro group)			Au (6.7 ± 0.9 nm)	**1**	H_2O	–	100%	20 min	–	[229]
Hydrogenation (nitro group)			Ag (2–4 nm)	**14**	H_2O	5.4	100%	23–24 °C, air, 0.1 h	10	[230]
Hydrogenation (nitro group)			Ag (2–4 nm)	**19** on PS	H_2O	–	–	–	–	[231]
Hydrogenation (nitro group)			Pd (2–8 nm)	**27**	H_2O	779	–	27 °C, 2 h, 50 atm	–	[229]

Table 3 (*Continued*)

Type	Substrate	Product	Catalyst (metal)	Stabilizer	Solvent	TOF/h^{-1}	Yield	Reaction condition	Recycling	Ref.
Selective hydrogenation			Co–B (6–20 nm)	**9**	EtOH	1	82%	100 °C, 10 atm, 3.5 h		[232]
Selective hydrogenation			Pt (1.8 ± 0.6 nm)	**23**	H_2O	25	–	r.t., 2 atm, 8 h	–	[233]
Other reduction	$NaNO_3$	N_2	Pd–Cu (60:40 Pd:Cu, 3.3 ± 0.6 nm)	**1**	H_2O	–	–	r.t., 1 atm	–	[234]
Dehydrogeantion			Pd (2.4 ± 0.3 nm)	**1**	H_2O	≥30	76%	180 °C, 2 atm	4	[127]
Dehalogenation		Ethane	Fe–Pd (2.4 ± 0.5 nm)	**16**	H_2O	–	–	r.t.	–	[235]
Dehalogenation			Pd (2.7 nm)	**6**	H_2O	31	100%	20 °C, 1 atm, 3.2 h	–	[236]
Dehalogenation		Ethane	Pd/Au (4 nm Au, Pd surface coverage 71.2%)	**3**	H_2O	88	–	r.t., 1 atm H_2	–	[237]
Dehalogenation		Ethane	Pd (2.4 nm)	**16**	H_2O	–	–	–	–	[238]

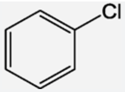
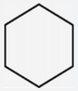
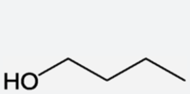
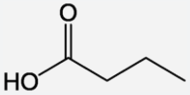
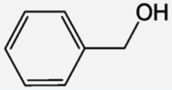
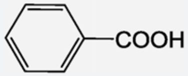
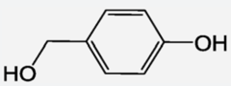
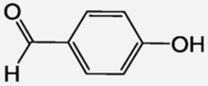
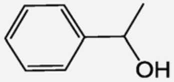
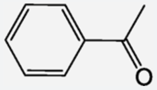
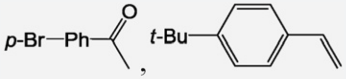
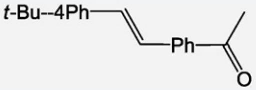
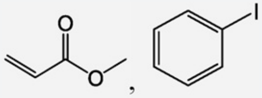
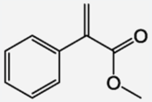
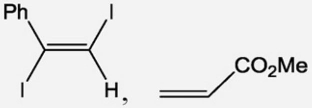
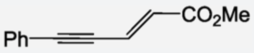
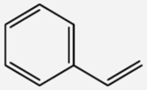
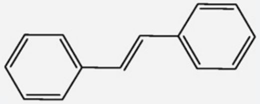
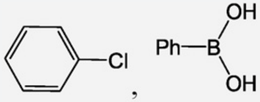
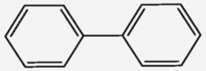
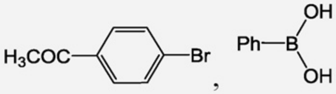
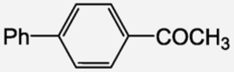
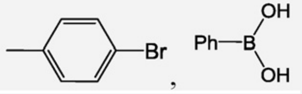
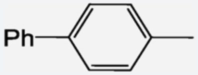
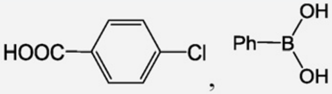
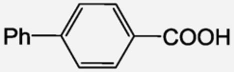
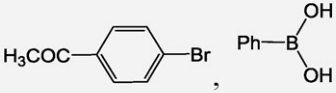
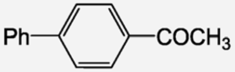
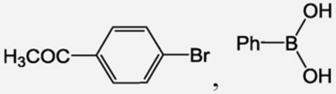
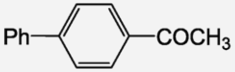
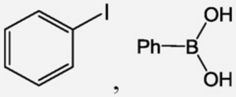
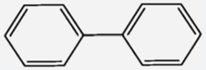
Dehalogenation/hydrogenation			Rh (2.7 nm)	**6**	H_2O	59	100%	20 °C, 10 atm, 1.7 h	–	[238]
Oxidation			Pt (1.5 ± 0.2 nm)	**1**	H_2O	46.4	99.7%	80 °C, 1.0 atm O_2, 24 h	–	[239]
Oxidation			Pt (2–8 nm)	**27**	H_2O	37.5	98%	80 °C, O_2 as oxidant, 8 h	6	[240]
Oxidation			Au (1.1 ± 0.2 nm)	**1**	H_2O	33	>95%	27 °C, air, 6 h	–	[74]
Oxidation	H_2O		IrO_2 (2 nm)	**11**	H_2O	1	–	pH = 5.8	–	[241]
Oxidation			Pd (2.3 ± 0.7 nm)	**19**	H_2O	52	49%	pH = 7, 100 °C, 1 atm O_2, 2 h	3	[242]
Heck C–C coupling			Pd (7–10 nm)	**9**	H_2O	5	90%	100 °C, 10 h	–	[243]
Heck C–C coupling			Pd (200 nm)	**25**	H_2O	40	89%	90 °C, 12 h	–	[244]
Heck C–C coupling			Pd (2–6 nm)	**7**	H_2O	–	82%	80 °C, 6 h	2	[245]

Table 3 (*Continued*)

Type	Substrate	Product	Catalyst (metal)	Stabilizer	Solvent	TOF/h^{-1}	Yield	Reaction condition	Recycling	Ref.
Heck cross-coupling	$Ph_3Bi(O_2CCF_3)_2$, 		Pd (2.6 ± 0.6 nm)	**19**	H_2O	21	20%	50 °C, air, 24 h	–	[246]
Suzuki C–C coupling			Au (1.0 nm)	**2**	H_2O	420	84%	80 °C, air, 4 h	6	[247]
Suzuki C–C coupling			Pd (200 nm)	**25**	H_2O	80	100–79%	80 °C, 6 h	4	[248]
Suzuki C–C coupling			Pd (2–6 nm)	**18**	H_2O	29,333	88%	25 °C, 3 h	5	[249]
Suzuki C–C coupling			Pd (50–100 nm and 2 nm)	**10**	H_2O	500	97%	80 °C, air, 4 h	2	[250]
Suzuki C–C coupling			Pd (7–10 nm)	**9**	H_2O	50	98%	25 °C, 2 h	–	[251]
Suzuki C–C coupling			Pd (6–8 nm)	**12**	H_2O	480	96%	100 °C, 5 min	3	[252]
Suzuki C–C coupling			Pd (2.3 ± 0.2 nm)	**26**	H_2O/EtOH	1533	92%	25 °C, 6 h	–	[224]

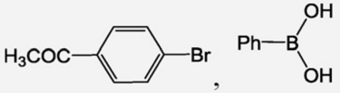
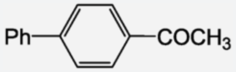
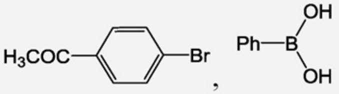
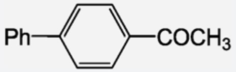
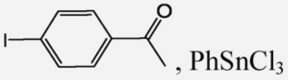
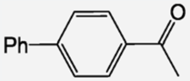
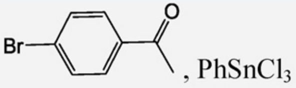
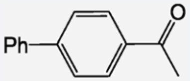
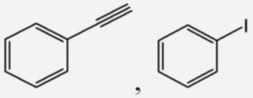
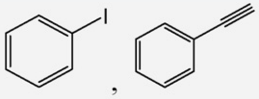
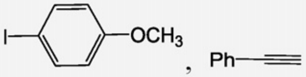
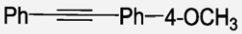
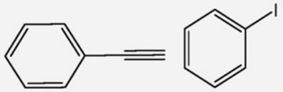
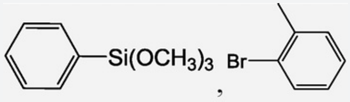
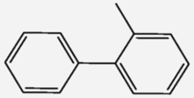
Suzuki C–C coupling			Pd (6 nm)	**17**	H_2O	500	97%	90 °C, 2 h	4	[253]
Suzuki C–C coupling			Pd (4.4 ± 1.5 nm)	**15**	H_2O	100	99%	90 °C, 4 h	6	[254]
Stille C–C coupling	 , $PhSnCl_3$		Pd (1.6 ± 0.3 nm)	**22**	H_2O	9	66%	80 °C, 24 h	4	[255]
Stille C–C coupling	 , $PhSnCl_3$		Pd (7–10 nm)	**9**	H_2O	25	95%	80 °C, 2 h	–	[256]
Sonogashira cross-coupling			Pd (3.2 ± 0.8 nm)	**21**	H_2O	0.5	90%	25 °C, N_2, 20 h	–	[257]
Sonogashira cross-coupling			Pd (10–15 nm)	**6**	Micro-emulsion	2400	>99.9%	80 °C, 5 min	–	[258]
Sonogashira C–C coupling			Pd (7–10 nm)	**9**	H_2O	20	94%	65 °C, 5 h	–	[245]
Sonogashira C–C coupling			Pd (15–20 nm)	**6**	Micro-emulsion	6000	100%	80 °C, 2 h	–	[259]
Hiyama C–C coupling			Pd (9.7 nm)	**9**	H_2O	33	95%	90 °C, 3 h	–	[260]

Table 3 (*Continued*)

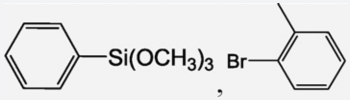
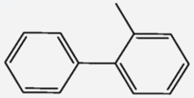
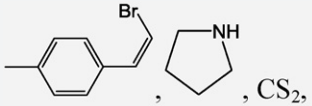
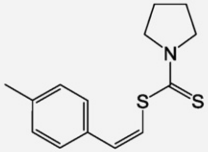
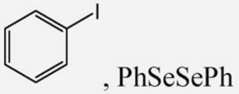
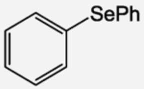
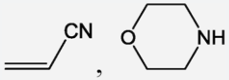
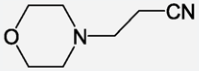
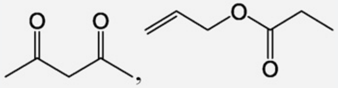
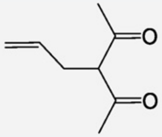
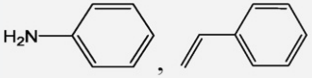
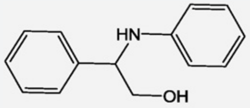
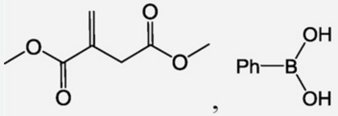
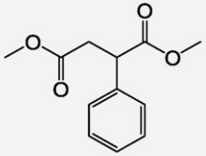
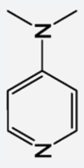
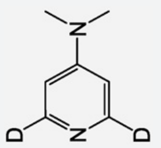
Type	Substrate	Product	Catalyst (metal)	Stabilizer	Solvent	TOF/h^{-1}	Yield	Reaction condition	Recycling	Ref.
Hiyama C–C coupling			Pd (3–6 nm)	**12**	H_2O	–	92%	100 °C, 5 min	–	[261]
Other couplings	 , CS_2		Cu (4–6 nm)	**8**	H_2O	4	91%	100 °C, reflux, 7 h	4	[262]
Phenyl-selenylation	 , PhSeSePh		Cu (4.3 ± 0.6 nm)	**8**	H_2O	0.4	88%	100 °C, 10 h	–	[263]
Aza-Michael reaction			SiO_2@Cu (~57 nm)	No	H_2O	1389	98%	r.t., 4 min	5	[264]
Monoallylation			Pt (5–8 nm)	–	H_2O	–	86%	1 atm, 9 h	–	[265]
Nucleophilic ring opening of epoxides			SiO_2 (60–70 nm)	No additional	H_2O	6	90%	r.t., 15 min	5	[266]
1,4-Addition of boronic acids			Rh–Fe_2O_3 (~10 nm)	TPPTS	H_2O	0.6	Conversion 100%	100 °C, 24 h	Continuous, 5 runs	[267]

Table 3 (*Continued*)

Type	Substrate	Product	Catalyst (metal)	Stabilizer	Solvent	TOF/h^{-1}	Yield	Reaction condition	Recycling	Ref.
Polymerization	$C_{18}H_{37}SiH_3$, H_2O	Polymer microspheres	Ag (10–20 nm)	**1**	H_2O/butanone	–	–	90 min, 1 atm	–	[268]
Selective H–D exchange			Pd (3.4 ± 0.5 nm)	**13**	H_2O	–	90%	50 °C, 3 h	–	[269]

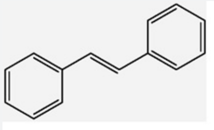
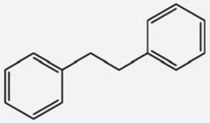
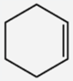
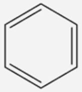
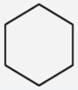
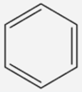
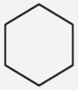
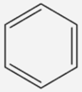
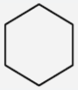
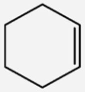
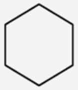
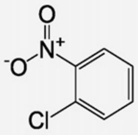
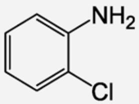
of its research has been shifted from separation techniques to catalytic reactions and synthesis. For general applications of $scCO_2$ in creating green process and products, please refer to some excellent more specific reviews [183]. In the domain of NP catalysis, the applicability of colloid catalysts in SCFs was first tested by Zemaian et al. and only very low conversion rates were obtained [184]. They reported the hydrogenation of naphthalene to tetralin using a colloidal $CoMoO_3$ catalyst in reverse micelles in supercritical butane at about 150 °C. However, the reaction was sluggish, with a conversion rate of less than 1%. This example indicates that catalyst solubility is a big issue for NP catalysis in SCF. Ji et al. in 1999 reported a stable suspension of Ag NP in $scCO_2$ by employing a mixture of sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and a perfluoropolyether-phosphate ether (PFPE-PO_4) as the stabilizer [185]. The formation of optically clear microemulsions containing Ag NP was confirmed by in situ UV–vis spectroscopy as well as off-line TEM analysis. The main drawback of this work is that the resulting Ag NP exhibited a rather large size distribution ranging from 5 to about 25 nm as observed from TEM pictures, which is not favorable for subsequent catalytic applications. This problem was soon addressed by selecting another stabilizer. In 2000, Johnston and Korgel found that by using a thiolated fluorocarbon molecule, 1H, 1H, 2H, 2H-perfluorodecanethiol, as capping agent, Ag NPs were formed from Ag^+ by $NaBH_4$ reduction [186]. The size distribution of the Ag NPs were 5.5 ± 2.2 nm, which is much narrower than previous results. An issue that was not considered by the authors is that as they used $(C_8H_{17})_4NBr$ as the phase transfer catalyst, their Ag NPs might be co-stabilized by thiolated fluorocarbon and $(C_8H_{17})_4NBr$. These results represent significant advance in $scCO_2$ solvent-based catalysis systems since they paved the way to the coming soluble NP catalysis in $scCO_2$.

The first example of catalysis in pure liquid or $scCO_2$ using soluble metal NP was done by Yeung et al. [187]. They used dendrimer-encapsulated NPs as catalysts, specifically, Pd(0) NP sequestered within fifth-generation poly(propylene imine) (PPI) dendrimers that have perfluoro-2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecanoyl perfluoropolyether chains covalently attached to their periphery. The perfluoropolyether chains in the dendrimer endowed Pd NP with miscibility in $scCO_2$. However, the catalytic performance is far from satisfying. In the hydrogenation of styrene into ethyl benzene, the TOF is between 10 and 25 h^{-1}, whereas in the Heck type reaction between methylacrylate and iodobenzene the TOF is even lower (ca. 1 h^{-1}).

Neither traditional organic (sodium triacetoxyborohydride, sodium cyanoborohydride, etc.) nor inorganic ($NaBH_4$) reducing agents are ideal for metal reduction in $scCO_2$ because they generally have limited solubility in $scCO_2$ and may form byproducts that could complicate further utilization. Ohde et al. used H_2 instead as the reducing agent [188]. By using AOT and PFPE-PO_4 as the stabilizer, they successfully synthesized Pd NP with a size range of 5-10 nm which is an active C=C double bond hydrogenation catalyst. The authors also demonstrated that this catalytic system is active toward hydrogenation reactions with both $scCO_2$ soluble and water soluble substrates.

Catalytic hydrogenation of arenes with soluble NP in a water-in-$scCO_2$ microemulsion has also been realized [189]. Again by using AOT and PFPE-PO_4 as the stabilizer, Rh NP with a diameter range of 3–5 nm formed in water core from Rh^{3+} by H_2 reduction,. Then naphthalene was selected for hydrogenation because it absorbs in the UV region that could be monitored by in situ cell. The TOF was ca. 15 h^{-1} at 50 °C. The Rh NPs are also active in phenol hydrogenation, with similar TOF values. Unfortunately, the Rh NPs were not stable under reactive conditions. After only 20–30 min, they began to lose activity. The authors attributed this to the aggregation of the Rh NPs.

Table 4
Nanoparticle catalytic reactions in ILs.

Type	Substrate	Product	Catalyst (metal)	Stabilizer	Solvent	TOF/h^{-1}	Yield	Reaction condition	Recycling test	Ref.
Hydrogenation			Pd (10 ± 0.5 nm)	**29**	[BMI][SbF_6]	600	100%	20 °C, 1 atm, 10 min	51	[270]
Hydrogenation			Rh (3.3 ± 1.5 nm)	**7**	neat	2000	100%	40 °C, 40 atm H_2, 0.5 h	5	[271]
Hydrogenation			Ir (~2.5 nm)	**38**	[BMI][PF_6]	6000	100%	75 °C, 4 atm, 2 h	6	[272]
Hydrogenation			Ir (2.1 ± 0.3 nm)	**38**	[BMI][PF_6]	85	100%	75 °C, 4 atm, 14 h	–	[273]
Hydrogenation			Rh (2.3 ± 0.6 nm)	**38**	[BMI][PF_6]	11	100%	75 °C, 4 atm, 22 h	–	[275]
Hydrogenation			Rh (2.9 ± 0.6 nm)	**31**	[BMI][BF_4]	250	100%	75 °C, 40 atm, 16 h	5	[119]
Hydrogenation			Ir (4.2 ± 0.8 nm)	**32**	[BMI]-*d3*.NTf	96	100%	75 °C, 5 atm, 2.6 h	–	[274]
Hydrogenation			Pd (~1.7 nm)	**31**	[BMI][BF_4]	6639	99%	60 °C, 40 atm, 1 h	4	[275]

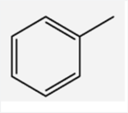
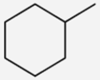
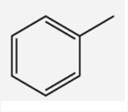
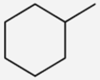
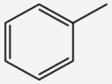
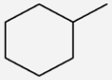
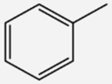
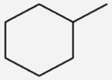
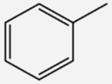
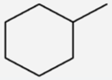
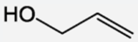
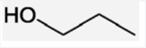
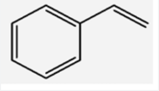
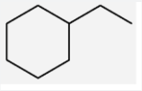
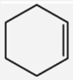
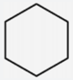
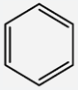
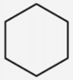
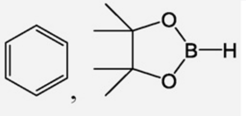
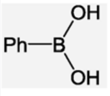
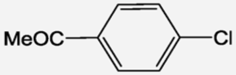
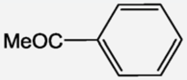
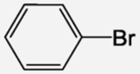
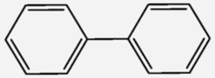
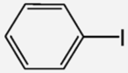
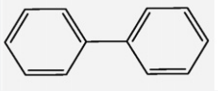
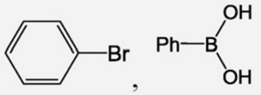
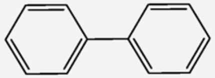
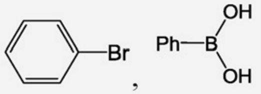
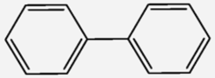
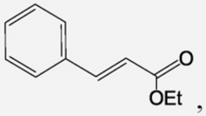
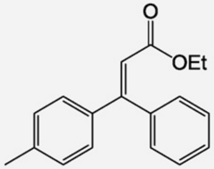
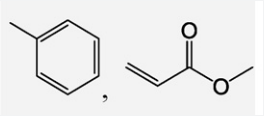
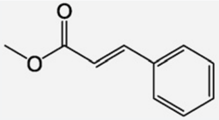
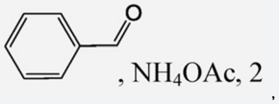
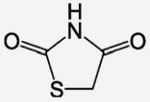
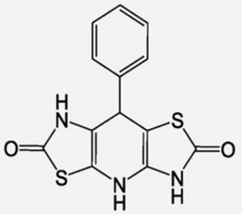
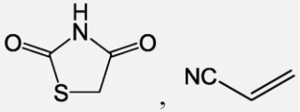
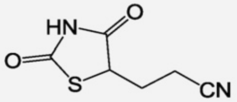
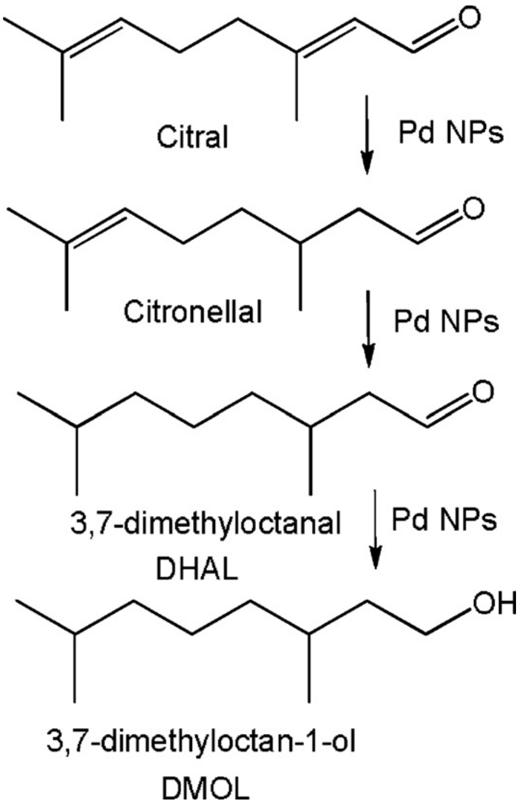
Hydrogenation			Rh (3.0 ± 0.8 nm)	**31**	[BMI][BF_4]	158	95%	75 °C, 40 atm, 12 h	–	[149]
Hydrogenation			Ru (2.1 ± 0.5 nm)	**32**	[BMI][NTf_2]	11	85%	75 °C, 4 atm, 18 h	Several times	[276]
Hydrogenation			Rh (∼2.0 nm)	**33**	[BMI][PF_6]	33	100%	20 °C, 1 atm, 3 h	2	[277]
Hydrogenation			Pd (2.2 ± 0.2 nm)	**22** with COO^- as terminal	[C_2OHMIM][BF_4]	167	100%	50 °C, 5 atm, 3 h	12	[278]
Hydrogenation			Rh (3.5–4.5 nm)	**36**	[BMI][PF_6]	7	96%	80 °C, 40 atm, 15 h	–	[279]
Hydrogenation			Pd:Au = 3:1 (3.2 ± 0.6 nm)	**1**	[BMI][PF_6]	∼380	–	40 °C	2	[280]
Hydrogenation			Rh (∼2 nm)	**34**	[BMI][PF_6]	7	100%	80 °C, 40 atm, 15 h	–	[281]
Hydrogenation			Pd (<5 nm)	**42**	–	10000	>99%	60 °C, 20 atm, 0.5 h	5	[282]
Hydrogenation			Ru (2.6 ± 0.4 nm)	**38**	[BMI][PF_6]	49	96%	75 °C, 4 atm, 13 h	2	[283]

Table 4 (*Continued*)

Type	Substrate	Product	Catalyst (metal)	Stabilizer	Solvent	TOF/h^{-1}	Yield	Reaction condition	Recycling test	Ref.
Phenylborylation			Ir (~3.5 nm)	**41, 36**	[THTdP][MS]	152	91%	130 °C, 1 h	6	[284]
Hydrodehalogenation			Pd (~3.3 nm)	**7**	TBAB	13	96%	90 °C, 1 atm H_2, 2.5 h	20	[285]
Ullmann C–C coupling			Pd	**44**	TBAA	17	90%	90 °C, N_2, 2 h	–	[286]
Ullmann C–C coupling			Pd (2.5 ± 0.5 nm)	**43**	[omim] [BF_4]	100	80%	25 °C, 8 h	6	[287]
Suzuki C–C coupling			Pd (~8 nm)	**30**	[BMI][PF_6]–H_2O	40	98%	60 °C, 1 h	–	[288]
Suzuki C–C coupling			Pd (6–8 nm)	**30**	[BMI][PF_6]	400	92%	100 °C, 1 h	10	[289]
C–C coupling			Pd (3.3 ± 1.2 nm)	**7**	TBAB	18	95%	130 °C, 3.8 h	–	[290]

Heck C–C coupling			Pd (<5 nm)	**42**	–	9234	100%	140 °C, 65 min	5	[284]
Other coupling	  NH_4OAc, 2		Cu (50–60 nm)	**37**	**37**	1413	92%	r.t., 5 min	4	[291,292]
Carba–Michael addition reaction			Cu (50–60 nm)	**37**	**37**	1536	90%	r.t., 5 min	5	[293]
Isotope exchange	$^{10}B_2H_6$, $B_{10}H_{14}$	$^{10}B_{10}H_{14}$	Ru (2.5 nm)	**41**	**41**	0.5	90%	50 °C, 1.08 atm, 6 h, recover $B_{10}H_{14}$ and repeat for 6 times	–	[294]



Scheme 18. Hydrogenation pathways of citral [193].

Although it is not unreasonable to conclude that in all the above cases the NP stayed in the microemulsion, the direct evidence did not come until 2004 when Meric et al. reported the first direct visualization that the majority of metal NPs are in the microemulsion state, which is observed through a sapphire window reactor [190]. The NPs were prepared by using $CF_3(CF_2)_{12}COO^-NH_4^+$ fluorosurfactant as stabilizer, $Pd(NO_3)_2$ as the metal precursor and H_2 as the reducing agent. Interestingly, in the hydrogenation of citral, that has three reducible functionalities (see Scheme 18), the major product was citronellal, which is indicative of a kinetic reluctance of the double bond hydrogenation at the hydrophobic end of the citral by the micelle-hosted Pd particles. Such phenomena could lead to better control of catalytic selectivity by using designed micelle as a "soft" scaffold [191]. Later, the same group reported the CO_2 pressure dependent selectivity of the hydrogenation of citral by Ru and Pd NP protected by $CF_3(CF_2)_{12}COO^-NH_4^+$ in the water-$scCO_2$ microemulsion [192]. They found that selective formation of a particular hydrogenated product from citral became possible by careful tuning the pressure of the fluid. For example, in the case of Pd catalyzed hydrogenation of citral, DMOL, DHAL and citronellal were the main products at the pressure of 80, 95, and 150 bar, respectively. The effect of CO_2 pressure on the reaction selectivity was attributed to the change in metal surface accessibility towards substrates.

As aforementioned, to solve the solubility issues, stabilizers with fluorous tails are generally used. There is only one exception. Niessen et al. found that polystyrene-block-poly-4-vinylpyridine, a polymer that is generally thought to be only soluble in non-polar organic solvents, stabilized Pd/Cu bimetallic NPs which are extremely efficient hydrogenation catalysts in $scCO_2$ medium [193]. They selected five substrates containing C-C triple bond, including sterically hindered substrate, 3,3-dimethyl-1-butyne for catalyst test. In all the cases, TOF values were higher than 100,000 h^{-1}. For 1-hexyne, the TOF is as high as 4,000,000 h^{-1} under optimized conditions, a value of at least one order of magnitude higher than previous reports. Unfortunately, the author did not have any explanation on the extraordinary catalytic performance. And the claim that Pd/Cu NP suited in polystyrene-block-poly-4-vinylpyridine were homogenously dispersed in $scCO_2$ is against chemical intuition. There is no subsequent report on this work.

Recently, a combined extraction and hydrodechlorination of chlorinated biphenyls in $scCO_2$ was reported by Wai and co-workers. Polychlorinated biphenyls spiked in soil can be extracted by a continuous flow SCF carbon dioxide system and converted on-line to bicyclohexyl using a polymer-stabilized Pd NP catalyst [194]. $scCO_2$/aqueous [195], $scCO_2$/ILs [196] biphasic media are also applied for NP catalysis.

Besides, $scCO_2$ is widely used to facilitate nano-material preparation [197], but these investigations are beyond the scope of the current review. For a collection of NP catalysis in scCO2, see Table 5.

6.5. Fluorous solvents

Fluorous solvents, with perfluorinated alkanes being most representative, possess unusual physicochemical properties, such as low dielectric constants, high chemical and thermal stability, and low toxicity [198]. They are commonly immiscible with organic solvents at low temperatures but miscible at elevated temperature. This feature affords a homogeneous phase for the reaction at high temperature and easy catalyst/product separation at ambient conditions, which is of particular interests to biphasic catalysis [199]. In 2000, Crooks and co-workers reported their work on the application of dendrimer-encapsulated Pd NP in fluorous solvent for the first time [200]. In this work, poly(amidoamine) (PAMAM) dendrimers were non-covalently modified with perfluoropolyethers to increase the solubility in fluorous phase, which was achieved by complexing the terminal dendrimer amine groups with the carboxylic end groups of the perfluoropolyethers. The Pd NPs were an active and stable catalyst for alkene hydrogenation in a mixture of THF/perfluoro-2-butyltetrahydrofuran (FC-75). Recycling test showed that after 12 runs, neither appreciable loss of catalytic activity nor detectable leaking of the catalyst into the organic phase was observed. The hydrogenation reaction is the first successful applications of NP in fluorous solvents, and very few other examples are known. A recent investigation done by West et al. introduced CO_2 into the fluorous-organic mixture [201]. By using the same Pd NP as described above, they found that the hydrogenation reaction of allylic alcohol to *n*-propanol was accelerated, probably because CO_2 induced miscibility of the fluorous-organic mixtures.

The pioneer work of NP catalyzed C–C coupling reactions in fluorous solvents was also done by Yeung and Crook. [202]. Since PAMAM is only stable at temperatures lower than 100 °C, they use poly(propylene imine) (PPI) derivative instead as the stabilizer. The thermal decomposition temperature of PPI is higher than 400 °C, therefore it is much better suited for applications in which long periods of refluxing at high temperatures are necessary such as most C–C coupling reactions. The NPs were prepared by introducing Pd^{2+} into the interiors of amine-terminated PPI dendrimers, which were previously end-group derivatized (>90%) with perfluorinated polyether chains, followed by the reduction of Pd ions. The Pd NP exhibited excellent performance in catalyzing the Heck coupling of inactivated aryl halides with butylacrylate under comparatively mild conditions. Interestingly, selectivity for the production of the trans isomer of n-butyl-formylcinnamate, which had previously been reported to be in the range of 74–98% in homogenous catalysis in fluorous phase [203], reached 100% in the case of Pd-dendrimer systems. The authors believed the region-selectivity is a result of the sterically confined environment within the dendrimer.

Table 5
Nanoparticle catalytic reactions in super critical solvents.

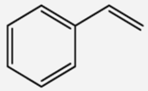
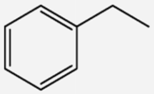
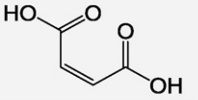
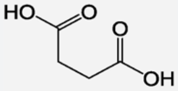
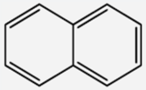
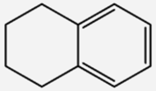
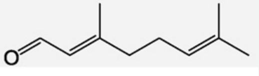
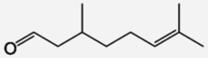
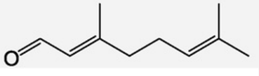
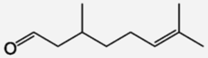
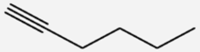
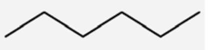
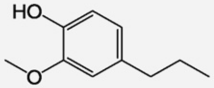
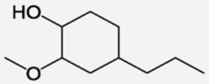
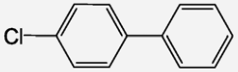
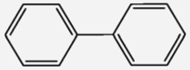
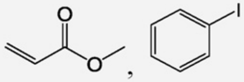
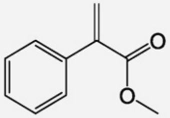
Type	Substrate	Product	Catalyst (metal)	Stabilizer	Solvent	TOF/h^{-1}	Yield	Reaction condition	Recycling test	Ref.
Hydrogenation			Pd (1–2 nm)	PPI terminated with perfluoro-2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecanoyl perfluoropolyether chains	$scCO_2$	10–25	100%	4 h	–	[295]
Hydrogenation			Pd (5–10 nm)	**46, 50**	$scCO_2$	130	95%	20 °C, 200 atm, 10 atm H_2, 2 min	–	[296]
Hydrogenation			Rh (3–5 nm)	**46, 50**	$scCO_2$	10	~90%	50 °C, 240 atm, 10 atm H_2, 20 min	–	[297]
Hydrogenation			Pd (3.65 ± 0.85 nm)	$CF_3(CF_2)_{12}COO^-NH_4^+$	$scCO_2$	13	68%	40 °C, 150 atm, 10 atm H_2, 4 h	–	[298]
Hydrogenation			Ru (3–4 nm)	$CF_3(CF_2)_{12}COO^-NH_4^+$	$scCO_2$	13	68%	40 °C, 105–150 atm, 10 atm H_2, 4 h	–	[299]
Hydrogenation			Pd/Cu (~2 nm)	Polystyrene-block-poly-4-vinylpyridine	$scCO_2$	4,000,000	50%	50 °C, 150 atm, 15 atm H_2	–	[300]
Hydrogenation			Rh	**49**	scC_2H_6	0.1	100% conversion	36 °C, 240 atm, 10 atm H_2, 72 h	–	[301]
Hydrodechlorination			Pd (2–10 nm)	Polyethylene beads	$scCO_2$		100%	100 °C, 200 atm, 1 h	–	[302]
Heck reaction			Pd (1–2 nm)	PPI terminated with perfluoro-2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecanoyl perfluoropolyether chains	$scCO_2$	1	57%	75 °C, 340 atm, 24 h	–	[273]

Table 6
Nanoparticle catalytic reactions in fluorous solvents.

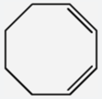
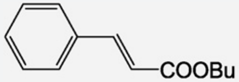
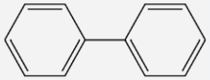
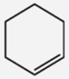
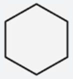
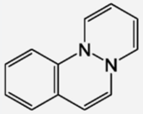
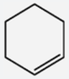
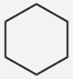
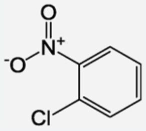
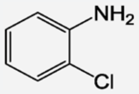
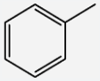
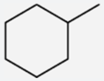
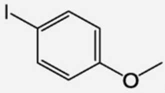
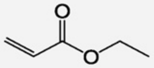
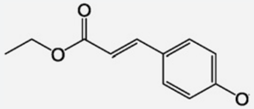
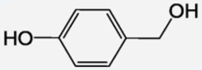
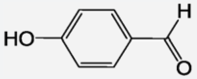
Type	Substrate	Product	Catalyst (metal)	Stabilizer	Solvent	TOF/h^{-1}	Yield	Reaction condition	Recycling test	Ref.
Hydrogenation			Pd	**22** with poly(hexafluoropropylene oxide-co-difluoromethylene oxide) monocarboxylic acid	Perfluoro-2-butyl-tetrahydrofuran (FC-75)	40	99%	25 °C, 1 atm	12	[202]
Hydrogenation	Allylic alcohol	*n*-Propanol	Pd	**22** with poly(hexafluoropropylene oxide-co-difluoromethylene oxide) monocarboxylic acid	C_6F_{14} and $scCO_2$ mixture	1858	99%	25 °C, 20–50 atm	Conducted, no detail	[203]
Heck C–C coupling	*n*-Butylacrylate and bromobenzene		Pd	PPI with end-group derivatized with perfluorinated polyether chains	Perfluoro-2-butyl-tetrahydrofuran (FC-75)	1–3	20–60%	90 °C	–	[204]
Suzuki Reaction	PhBr and $PhB(OH)_2$		Pd	**49**	C_6H_6–$C_8F_{17}Br$	2–5	60–90%	80 °C	–	[206]

Table 7
Nanoparticle catalytic reactions in high boiling point alcohols.

Type	Substrate	Product	Catalyst (metal)	Stabilizer	Solvent	TOF/h^{-1}	Yield	Reaction condition	Recycling test	Ref.
Hydrogenation			Pd (2–6 nm)		PEG400	83	74%	30 °C, 1 atm, 4 h	6	[303]
Hydrogenation			Pd (7–9 nm)	PEG2000	PEG2000	4231	100%	70 °C, 10 atm, 1.3 h	10	[304]
Hydrogenation			Pt (4–6 nm)	PEG2000	PEG/MeOH=1/3	1000	>99%	40 °C, 10 atm, 0.5 h	6	[305]
Hydrogenation			Ru (2–4 nm)	PEG/carbon nanofiber	PEG	14,200	>99%	100 °C, 30 atm, 2.5 h	5	[306]
Heck C–C coupling	 , 		Pd (∼5 nm)	PEG2000	toluene/ethanol =9:1	3	95%	100 °C, 8 h	9	[216]
Aerobic oxidation			Pd (5–7 nm)	2,2'-dipyridylamine modified PEG2000	PEG2000	5	>86%	80 °C, O_2, 4 h	4	[307]

Pleixats and Moreno-Mañas reported the first Pd NP catalyzed Suzuki reaction in fluorous phase [204]. Their first attempt was to synthesize complex Pd(dba-Rf)$_2$ following a similar procedure for the preparation of Pd(dba)$_2$. However, instead of obtaining Pd(dba-Rf)$_2$, they generated Pd NP stabilized by the fluorinated ligand. The ligand rendered the NP soluble in fluorous media. The chosen reaction was the production of 1,3-diphenylpropene from cinnamyl bromide and phenylboronic acid. After five batches, the catalytic system remained active, with a slightly decrease in yield of 1,3-diphenylpropene from 90 to 78%. The Pd NPs were also active in Heck reactions under similar conditions. A considerable drawback of the work is the high loading of the catalyst (from 4 to 64%).

The exploration of NP catalysis in fluorous solvent tended to cease after 2004. Applications of fluorous solvents in NP catalysis are practiced to a much smaller extent compared to other green solvents such as water and ILs. The potential of the catalysis of soluble NP in fluorous fluid has not been fully explored. Some literature reported the preparation of soluble metal NPs in fluorous solvents, including those of Ag [205] and Au [206], without considering their catalytic properties. Others synthesized NP protected by stabilizers bearing fluorous moiety. But their catalytic reactions were performed in conventional molecular solvents like DMF [207].

All reported examples of NP catalysts in fluorous solvents are compiled in Table 6.

6.6. *High boiling point alcohols*

The utilization of PEGs as reaction media has attracted much attention recently [208]. PEGs are cheap, nontoxic, and their properties can be tuned by changing their molecular weight [209]. There are numerous studies on the synthesis of metal NP in PEG (polyol method) where PEG acts as a reducing agent [210]. The first attempt of using PEGs as both reducing agent and reactive media appeared in 2004. Pillai and Sahle-Demessie carried out selective hydrogenation of olefins using phenanthroline stabilized Pd NP as the catalyst in PEG400 (PEG400 stands for PEG with an average molecular weight of 400 g/mol) [211]. The catalyst can effectively and selectively catalyze the hydrogenation of C=C groups without effecting C=O group. Neither decreased activity nor leaching of Pd was observed in the recycling test. Similar results were obtained by other groups. For example, Cheng et al. reported that Pd NP, synthesized in PEGs without additional stabilizer, is a reusable and selective catalyst for the hydrogenation of C=C functionalities. Other metal NPs rather than Pd were also investigated. PEG-stabilized Pt NP [212] and PEG/carbon nanofiber co-stabilized Ru NP [213] were applied for the selective hydrogenation of *o*-CNB to *o*-CAN and the hydrogenation of arenes, respectively.

Pd NP/PEG systems for C–C coupling reactions have been investigated by several groups. Luo et al. explored Heck reaction catalyzed by Pd NP in PEGs with different molecular weights [214]. Interestingly, the reactivity of PEG in the reduction of Pd^{2+} into Pd NP is very sensitive to its average molecular weight. The larger the PEGs were, the easier the reduction of Pd^{2+} was. The activity of Pd NP toward Heck reaction, on the other hand, did not exhibit such monotonic trend, with PEG2000 being the best system. Under optimized conditions, Pd NP/PEGs are able to catalyze coupling of challenging substrate such as chlorobenzene. Corma and co-workers also reported C–C coupling reactions in PEGs [215]. Their strategy was to covalently anchor oxime carbapalladacycle on PEG6000 scaffold, and use the resulting polymer as soluble catalyst for Suzuki, Sonogashira and Heck reactions in PEG media. During the reaction (recycling) the catalysts decompose and form catalytically less active Pd NP with an average particle size of 6 nm. As a result, for less demanding Pd catalyzed reactions, such as the Sonogashira coupling of aryl bromides, the catalytic system can be reused for many cycles. On the contrary, for highly demanding reactions, such as aryl chloride coupling reactions, reusability is low.

Very recently, the aerobic oxidation of various alcohols was studied with the stabilized Pd NP as catalyst in PEG media [216]. In previous studies, soluble Pd NPs are active and selective for alcohol oxidation [217]. But conventional organic solvents were used and the formation of Pd-black was observed in some cases. To solve both problems, a stabilizer derived from PEGs, which contains bidentate nitrogen ligands was synthesized and used for the preparation of Pd NP in PEGs. The obtained Pd NP exhibited excellent activities in the oxidation of a number of alcohols with excellent recyclability. The authors suggested that the functionalized-PEG played a very crucial role in stabilizing Pd NP. Available examples for NP catalysis in high boiling point alcohols are provided in Table 7.

To summarize, reported NP catalysis in PEGs shows that PEGs have many advantages. They can act as reducing reagents, co-stabilizer and reaction media. The activities are usually high and some systems exhibit intriguing selectivities. And in most cases, the catalytic systems are recyclable. Nevertheless, NP catalysis in PEGs is still an open arena for researchers, since only a few metal NPs have been tested in this green media.

7. Conclusion and perspective

Catalysis is a central field of nanoscience and nanotechnology [308]. NP catalysis in the solution phase is an old topic but is now well advanced due to the great progress in nanochemistry. Despite the fact that this field is in its gold rush era as reflected by the ever increasing publications, for future implementation of NP catalysis in industry, there are some requirements to meet. ESSR criteria are therefore a timely standard to evaluate the current examples and a guideline for designing new systems from a practical point of view. Furthermore, we built up the links between ESSR criteria and the three key parameters in NP catalysis, which have been thoroughly discussed in Section 2. The systematic guidelines for the improvement of a NP catalytic system are therefore available for the first time. For the ease of making stories we divided a NP catalysis system separately into metal cores, stabilizers and solvents. In a real system one must consider the delicate interplay of the three factors. We hope our efforts would be helpful for rational design of novel NP catalytic system, which could finally be applied in industry process in the future.

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