Nanoparticles for Catalysis in Aqueous Media

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Abstract: This review highlights the recent development of nanocatalyst-enabled chemical transformations in water, leveraging the nanomicelle/surfactant chemistry and related technology. Various chemical reactions, including the most frequently used transformations in the pharmaceutical industry, are discussed herein. A potential implementation of such nano-technology in large-scale synthesis at an industry level is also briefly touched on.

Keywords: Surfactant, Micelle, Water, Nanoparticles, Catalysis, Sustainability

Introduction. For a little over a decade, chemistry with soft and dispersed matters has emerged as a prominent strategy in the quest for more sustainable practices [1-3]. The approach has offered the opportunity to move away from traditional fossil-based solvents. It has brought a generic solution to phasing out of the reprotoxic dipolar-aprotic solvents [4-9] and generated a real opportunity to conduct multi-step sequences in a common medium (water), rendering various types of chemistry compatible in an aqueous medium [10,11]. The rapid development of a chemistry toolbox in bulk water enabled a broader scope of impactful transformations, whether conducted stoichiometrically or catalytically [12]. The latter especially allows for the true power of the technology to be unleashed with profound advantages coming from the nano-reactors that the soft and dispersed matters constitute in virtue of the hydrophobic effects. The effect enables reactions under very mild reaction conditions, more often at room temperature or gentle warming, and leads to observed exquisite selectivities. These optimal selectivities reduce the number of operations, such as washings, extractions, and purifications, dramatically impacting productivity, environmental, and cost footprints. These advancements contribute significantly to the field of homogeneous catalysis [13-15]. However, the following account focuses on the emerging development and the use of nanoparticles (NPs) in heterogeneous catalysis.

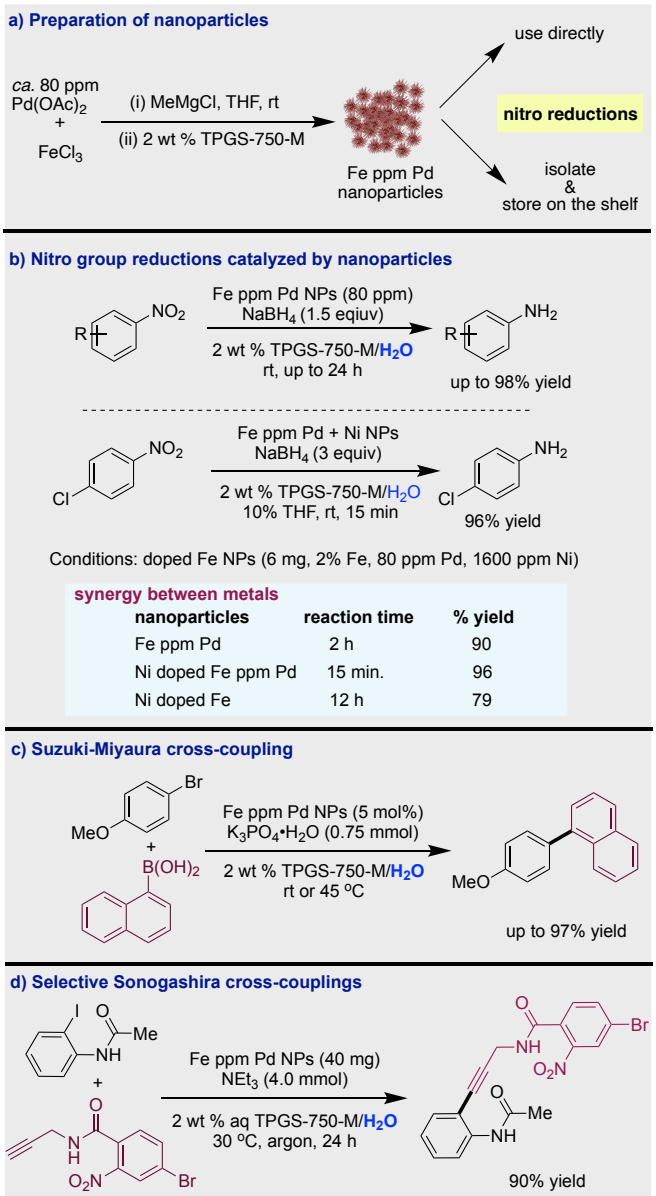
Heterogeneous Catalysis in Nanomicelles. The advent of chemistry in water by using benign surfactants has tremendously gained visibility, triggering interest from academia and industry. Its applications to catalysis provide environmental and economic benefits, including the worker's safety, reduced cost, and enhanced productivity due to high process yield and selectivity. Novartis became particularly interested in pushing the boundaries in both homogeneous and heterogeneous catalysis. A series of spectacular methodologies have been developed in homogeneous catalysis, and our collaborators and we have reported the related work [16-20]. Many associated examples can be found in the excellent recent reviews written by Lipshutz and co-workers [12-14]. In heterogeneous catalysis, the aqueous nanomicelles system enables the extraordinary catalytic performance of metallic NPs (the catalyst). Generally, the NPs aggregate in the hydrophilic regions of the supramolecular systems. Therefore, these NPs should be fine in size and morphology to readily interact and operate in the supramolecular arrangements. In collaboration with Lipshutz and Handa, suitable support for palladium NPs, displaying a superior catalytic activity, was rapidly identified [11,21]. In virtue of the very effective compartmentalization effect, it turned out to be active in very low palladium (Pd) loading, typically well below 0.1 mol%, and showed excellent yields in various cross-couplings or reduction events on a wide array of substrates [21]. The low Pd loading for high conversions is particularly remarkable, i.e., as little as 80 ppm for nitro reductions (Figure 1a) and 320 ppm for the more demanding Suzuki-Miyaura cross-couplings. We had interestingly arrived at these limits, starting our journey by using native iron chloride that was contaminated with this low amount of Pd. Later on, to gain robustness and reliability, systematic doping of the support with extraneous Pd was conducted using $Pd(OAc)_2$ as the Pd source. For cross-couplings, recycling the catalyst was also feasible due to the heterogeneous nature of the catalyst.

A variety of transformations were achieved using this strategy, including Suzuki-Miyaura and Sonogashira cross-couplings [21], click chemistry [22], selective nitro reductions [23,24], or halides embedded dihalocyclopropantions [25], all under very mild reaction conditions (Figure 1b-d). The activity and selectivity were associated with the careful choice of the metal, such as Pd or nickel (Ni) ligated with the suitable ligand. SPhos was used with Pd for the Suzuki-Miyaura cross-couplings, while X-Phos [26] or HandaPhos [27] with Pd was used for the Sonogashira cross-couplings. In contrast, Pd or Ni only was required for nitro and halide reductions. Likewise, copper (Cu) salt was used for click chemistry.

We also discovered the synergistic effect of iron (Fe) doping resulting in the formation of bimetallic NPs, presumably minimizing the extent of aggregation and enabling faster catalysis [28]. Such NPs can be readily formed by reducing (with a Grignard reagent) the transition-metal pre-catalyst deposited in situ onto iron chloride. The resulting solid particles

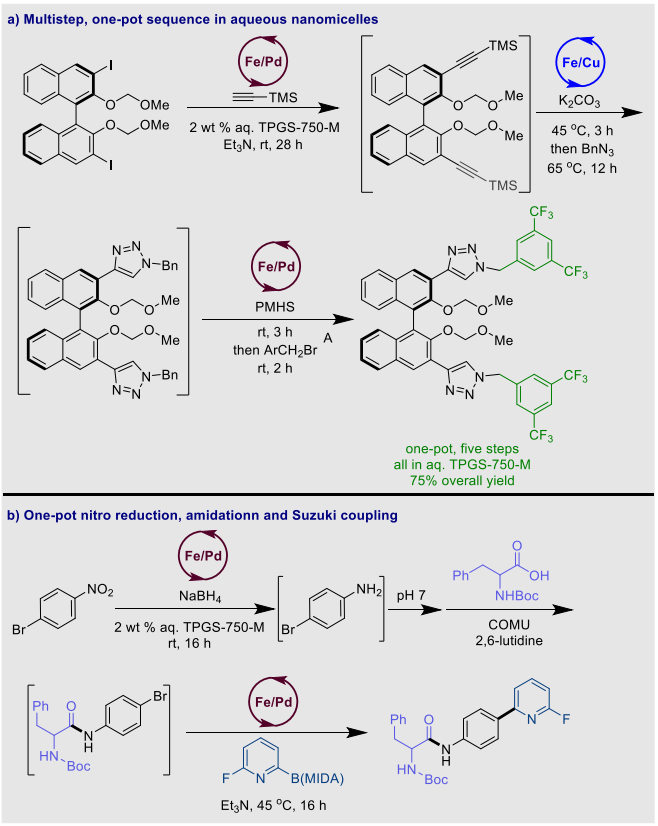
can be used as such or isolated and stored for future use. One of the additional benefits of such systems is using them in flow [29,30]. This standard protocol for the synthesis of NPs was general to a variety of ligand-free or ligated metals. These NPs are applied to broad arrays of catalytic transformations on a production scale. However, we cannot build the necessarily sustainable supply chain that would allow us to procure and use these NPs reliably. The main reason has been our relative inability to define proper specifications that ensure the adequate performance of the catalyst. Nonetheless, such NPs used for micellar catalysis can provide tremendous opportunities to conduct smooth, complex sequences in operationally straightforward and effective processes (Figure 2).

Figure 1



Fe-based nanoparticles-mediated transformations in water. (a) Preparation of nanoparticles. (b) Nitro group reductions. (c) Suzki-Miyaura couplings catalyzed by Fe ppm Pd nanoparticles. (d) Cu-free selective Sonogashira couplings.

Figure 2

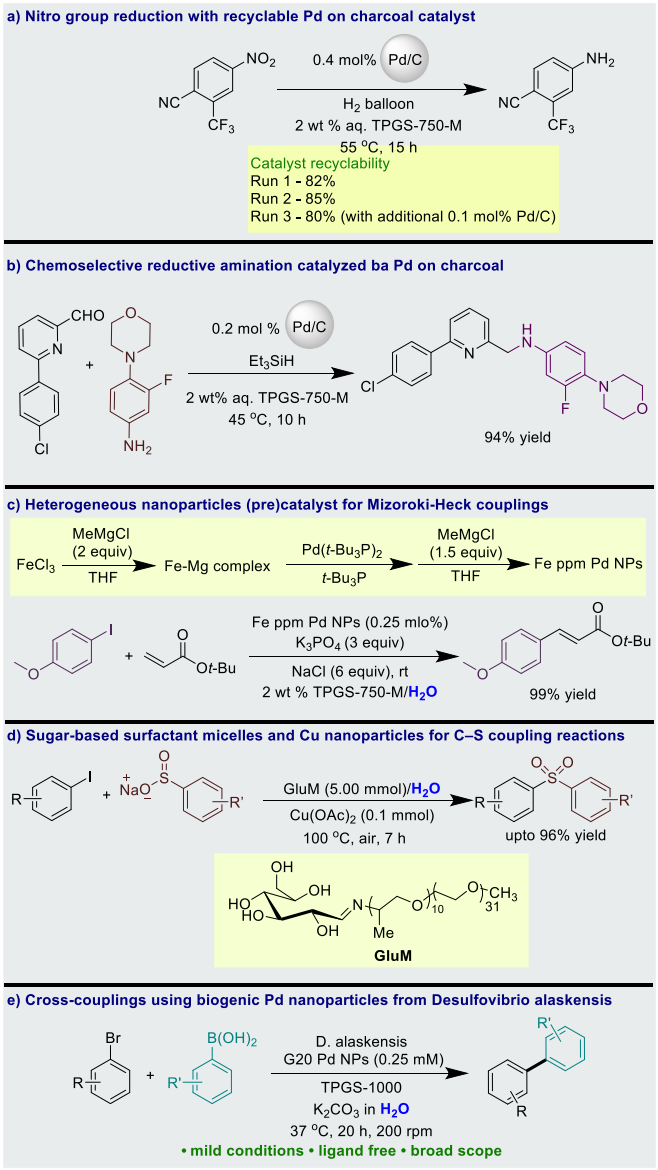


One-pot sequence catalyzed by NPs in aqueous TPGS-750-M.

The lack of a sustainable supply chain for the NPs mentioned above led us to look for more robust and more straightforward alternatives relying on existing solid catalysts. We have turned our attention to charcoal as a support and have identified charcoal-supported metals as highly effective systems [11,31,32]. Thus far, only reduction of olefins, nitro functional group [31], and reductive aminations [32] were reported relying on 0.2 to 0.4 mol% Pd loading using simple operational protocols (Figure 3a, b).

Although Pd-C catalyst offered a valuable alternative for reduction chemistry, it was ineffective for more useful cross-coupling transformations. It is likely due to this catalytic system's physical and chemical properties. The size of the solid catalyst is certainly too large for optimal micellar catalysis, and the support is improper for Pd ligation with the suitable ligands. Therefore, we continued our quest to find a more practical NPs generation that resulted in the reformation of the solid support itself, onto which the metal and ligand can be more readily added [33]. The concept was illustrated on a Mizoroki-Heck coupling and proceeded very smoothly (Figure 3c). In this case, the Fe NPs were first prepared within a sculpting process by practical reduction with a Grignard, resulting in the formation of spherical shaped NPs, followed by the addition of Pd(*t*-Bu_2P)$_2$ and extraneous ligand, once again reduced with a Grignard, and aging. Nanorods of 100 to 200 nm length were then obtained, which smoothly catalyze the desired cross-coupling with as little as 0.25 mol% Pd. We were able to store the spherical Fe NPs and further dope them with various metals and ligands just before use for the desired transformation. We are particularly excited by this novel preparation of NPs that should greatly facilitate the technology for application in industrial laboratories and on the scale.

Figure 3



(a, b) Nitro group reduction and reductive amination catalyzed by Pd/C catalyst in aqueous TPGS-750-M. (c-e) NPs for cross-couplings.

In the meantime, several peers embraced the concept and developed independent solutions to cross-couplings, or reductions, essentially relying on a similar approach [34-37]. The methodology that enables C-S coupling using Cu NPs in a carbohydrate-based surfactant (Figure 3d) has particular interest and relevance [38]. The surfactant can be readily obtained via condensation of glucose to a PEG-amine that most likely stabilizes the NPs. The latter are formed by i*n situ* reductions of $Cu(OAc)_2$ to catalytically more active Cu_2O via the reducing nature of the sugar derivative. The resulting catalyst performs moderately, requiring 3 mol% catalyst loading and elevated temperature (100 °C). Characterization data revealed the average 50 nm-sized micelles and Cu NPs of 1.35 nm sitting within the PEG region at the outer surface of micelles or inside the micelles (dynamic phenomenon).

Wallace and co-workers reported another unique compartmentalization approach. The authors have explored *in situ* produced NPs by microorganisms to catalyze Suzuki-Miyaura cross-coupling reactions (Figure 3e) [39]. Such micellar catalysis using biogenic Pd NPs is fascinating. It opens up opportunities for compatible bio and chemo-catalysis in a very effective and sustainable manner, such as no need for ligand, low catalyst loading, and mild reaction temperatures.

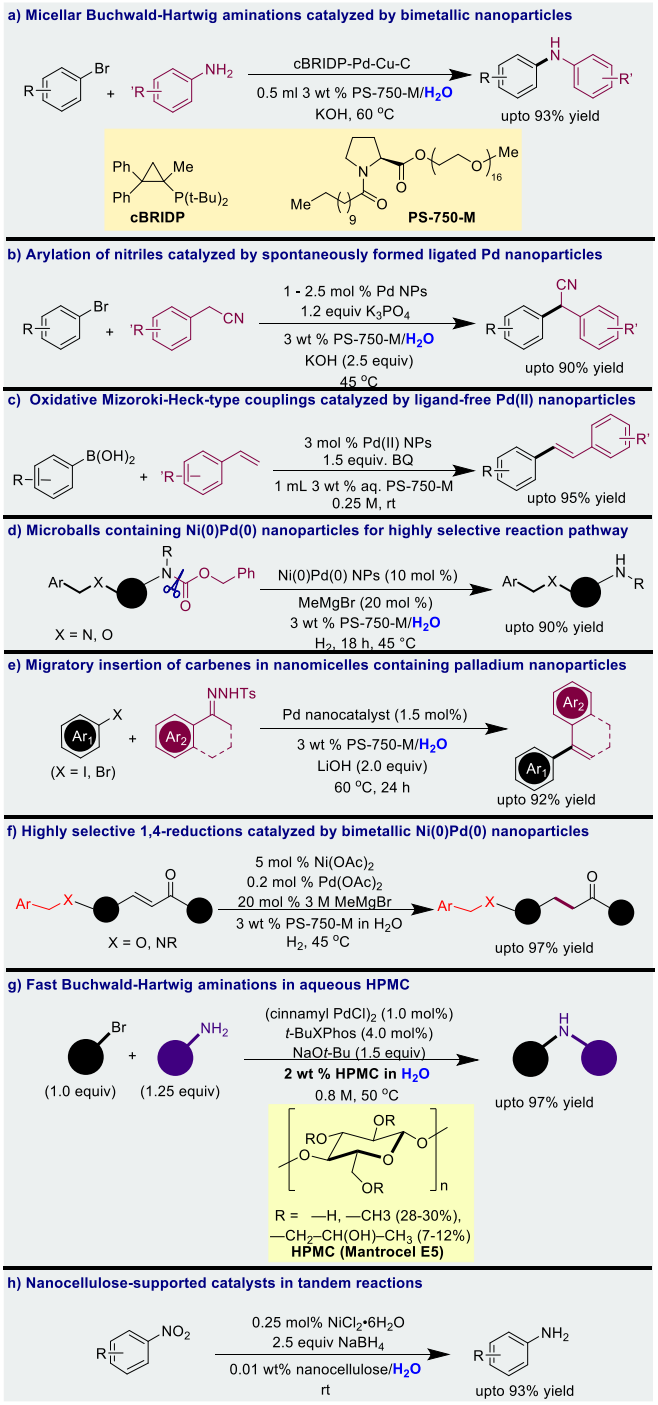
Proline-Based Rationally Designed Surfactant for NPs Catalysis. Handa and co-workers have designed novel functional surfactants that facilitate the preparation and stabilization of catalytic NPs. The appendage of an additional relatively polar proline moiety between the hydrophilic and lipophilic fragments offers the opportunity to chelate with metals and template the formation of NPs. The proline-derived PS-750-M surfactant chelate and forms microscopic aggregates within its very polar proline core [16,40]. With the surfactant in hand, we learned how to fully harness its structural and chemical properties on practical transformations while understanding how chemistry in the micelles of PS-750-M works. The proline fragment of the amphiphile preferentially ligates Pd, Cu, Ni, and combinations thereof are used as is or deposited onto a surface, such as charcoal. The use of polymetallic catalytic systems was beneficial in minimizing the extent of aggregation and increasing the catalytic activity. With such an approach, efficient and robust synthetic protocols for Suzuki-Miyaura couplings of (iso)quinolines [19], Buchwald-Hartwig or Sonogashira cross-couplings [11], alpha arylation of nitriles [41], oxidative Mizoroki−Heck-type couplings [42], selective hydrogenolysis [43], and selective reductions [44] have been reported. Besides, the reactivity of carbenes and carbanions has been thoroughly investigated [20] (Figure 4a-f). In all cases, the size of the NPs catalyst ranged from below 1 to 2.5 nm. For the Buchwald-Hartwig aminations, charcoal, as the surface, plays a crucial role in anchoring the two metals. Cu and Pd were found to be bridged with a phosphine ligand, most likely via a $2e^-$–3c bond. The design of the catalyst offered remarkable recyclability and stability of the catalyst with negligible metal leaching. For the alpha arylation of nitriles, an exciting protocol for the spontaneous in-situ generation of the NPs was developed. Due to its operational simplicity and robustness, it will find resonance soon.

Authors have also shown that the PS-750-M could readily replace phosphine ligands in the NPs catalysis for cross-couplings [42,45]. Remarkably, the cross-couplings of water-sensitive acid chlorides have been cleanly achieved. Using state-of-the-art NMR, IR, and SERS spectroscopies, the authors displayed that the amphiphile PS-750-M binds with the Pd NPs surface through amidic and ester carbonyls. NMR spectroscopy further revealed the integration of Pd NPs with the aqueous micelles. Besides the broad substrate scope, excellent functional group tolerance, and scalability, these NPs were equally effective for cross-couplings between (hetero)aryl halides and boronic acids.

Cellulose-Based Additives for Efficient Catalysis in Water. Recently, a series of disclosures on the impressive hydrophobic effect of food additive polymer HPMC on the reaction rates and selectivity has also appeared in the literature from Braje and Handa [8]. The presence of hydrophobic pockets in the aqueous HMPC enabled compartmentalization within the reaction mixture that caused excellent catalytic activity and selectivity. Notably, extremely fast reaction rates were reported under these reaction conditions. The organometallic catalyst spontaneously and instantaneously transformed into NPs. The ultrasmall NPs were reported with

an average size of 1.5 nm. The extraordinarily active NPs enabled cross-couplings of various substrates in < 5 minutes (Figure 4g). A similar strategy was also recently reported by Diner and co-workers [46]. The authors reported the formation of Ni boride NPs and their use in nitro reduction using nanocellulose (Figure 4h).

Figure 4



(a-h) Highly selective and efficient transformations mediated by NPs and aqueous nanomicelles of PS-750-M. (g-i)Cellulose-based additives for efficient catalysis.

Summary. In this brief account, we have highlighted our journey and the contribution of other groups to the field of sustainable chemistry in water using soft and dispersed matters. It is not an exhaustive overview of the literature but rather a report on recent and potentially impactful developments from an industrial perspective.

Credit Author Statement

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Seyedesahar Miraghaee – Writing
Sachin Handa – Supervision, writing, and advising
Fabrice Gallou – Supervision, writing, and advising

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