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Metal Nanoparticles for Redox Reactions

Koichiro Jitsukawa and Takato Mitsudome

Contents

Abstract Reduction and oxidation reactions (redox reactions) are fundamental and important transformation of chemicals in both laboratory and industrial chemistries. With regard to atom economy and the environmental demands, an ultimate goal of these reactions is to employ molecular hydrogen (H_2) or molecular oxygen (O_2). High-performance heterogeneous catalysts with high activity, selectivity, recoverability, and reusability are ideal for the development of green sustainable processes using H_2 or O_2. Moreover, the heterogeneous catalyst systems are the promising approach to solve the disadvantage of homogeneous ones, such as short lifetimes (low stability), risk of contaminating products with metals (low recoverability), tedious workups for reuse (low reusability), and so on. For the design of high-performance heterogeneous catalysts under liquid-phase redox reactions, metal nanoparticles (NPs) is the most promising strategy because of their unusual properties compared to bulk metal. This review provides an overview of metal NP heterogeneous catalysts developed for redox reactions using H_2 or O_2. The state-of-the-art metal NP catalysts show higher activity and selectivity for the

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chemoselective hydrogenations of carbonyl, nitro, and alkynyl compounds while retaining C=C bonds, and the aerobic oxidation of alcohols and the Wacker type oxidation of alkenes, which overcome the limitations of the conventional catalyst systems. This improved catalytic performance is due to significant advances in the precise fabrication of nanoscale metals, which has made it possible to explore novel catalysis and design metal active centers.

Keywords Catalyst · Hydrogenation · Metal · Nanoparticle · Oxidation

1 Introduction

Reduction and oxidation reactions (redox reactions) are fundamental and important transformations in both laboratory and industrial chemistries. In conventional redox reaction systems, metal hydrides, such as $NaBH_4$ and $LiAlH_4$, or heavy metal salts, such as permanganate and dichromate, have been employed as reducing or oxidizing agents. As these stoichiometric reagents have serious drawbacks, including high costs, toxicity, and producing large amounts of waste, the development of promising catalytic systems to replace these stoichiometric reactions has attracted much attention. With regard to atom economy and the environmental demands of chemical reactions, an ultimate goal of redox reactions is to employ molecular hydrogen (H_2) or molecular oxygen (O_2) [1–6]. These inexpensive reagents are abundant and can avoid the use of harmful reagents. In this context, transition metal complexes have traditionally been employed as catalysts, because they are dissolved in reaction media, which makes all active sites accessible to substrates, leading to exhibit high catalytic activities. Despite these advantages, homogeneous catalyst systems have fundamental problems, including short lifetimes (low stability), risk of contaminating products with metals (low recoverability), and tedious workups for reuse (low reusability). Although heterogeneous catalysts are the most promising approach to solving the above issues, they generally show low activity and require harsh reaction conditions and have mainly been applied in gas-phase reactions. Therefore, high-performance heterogeneous catalysts with high activity, selectivity, recoverability, and reusability would be ideal, leading to the development of green sustainable redox reaction processes using H_2 or O_2.

Using metal nanoparticles (NPs) is among the most promising strategies for the design of high-performance heterogeneous catalysts because of their unusual properties compared to bulk metal. To date, metal NP catalysts have been employed to refine petroleum, manufacture petrochemicals, clean exhaust gas, and produce renewable clean energy, especially in gas-phase reactions [7–9]. Recently, the advance of nanoengineering has enabled the precise construction of metal NP catalysts. Sophisticated metal NP catalysts, obtained by controlling particle sizes and shapes, tuning metal electronic states, and modulating metal–support interactions [10–14], have achieved high activity and selectivity in fine chemical synthesis under mild conditions. Accordingly, this review provides an overview of metal NP heterogeneous catalysts developed for redox reactions using H_2 or O_2 under liquid-phase conditions. As many reviews and reports on heterogeneous catalysts for hydrogenation [15–17] and aerobic oxidation [18–21] have been published, herein we have focused on state-of-the-art metal NP catalysts, which overcome the limitations of conventional catalysts in selective redox reactions.

2 Metal NP-Catalyzed Selective Reductions Using H_2

Selective hydrogenations are important methods in fine chemical synthesis. However, the chemoselective hydrogenation of targeted functional groups in the presence of other reducible groups is difficult. In particular, chemoselective hydrogenation in the presence of easily reducible alkene groups represents a significant challenging. To date, various approaches using metal NP catalysts to achieve high chemoselectivity have been proposed through the design of metal size, surface, shape, and components. In this section, rationally designed and developed novel metal NP catalysts for the chemoselective hydrogenation of nitro, carbonyl, and alkyne moieties while retaining easily reducible alkene groups are discussed.

2.1 Design of Core–Shell NPs

The hydrogenation of aromatic nitro compounds bearing other reducible groups is important for the direct synthesis of functionalized aniline derivatives, which are useful feedstocks in the chemical industry. In 2005, Corma et al. discovered that a Au/TiO_2 catalyst promoted the chemoselective hydrogenation of 3-nitrostyrene to give 3-aminostyrene with 98.5% conversion and 95.9% selectivity [22]. Since this pioneering report, many catalysts have been developed for the chemoselective hydrogenation of functionalized aromatic nitro compounds [23]. However, these catalysts suffer from overhydrogenation of aminostyrene to ethylaniline at high conversion levels. This is due to the chemoselectivity often being derived from preferential adsorption of the nitro moiety over the alkene moiety, resulting in alkene hydrogenation occurring prior to nitro hydrogenation at low nitro compound concentrations. Therefore, a new catalyst design strategy for the chemoselective hydrogenation of nitro compounds is needed as an alternative to the preferential adsorption method.

Au or Ag NPs and basic metal oxide support are known to cooperatively dissociate H_2 into polar hydrogen species $H^{\delta+}$ and $H^{\delta-}$, which straddle the interfacial perimeter sites [24, 25]. These polar hydrogen species show favorable reactivity with nitro groups compared to that with alkene groups [26]. Mitsudome et al. developed a novel core–shell nanostructured catalyst, $Ag@CeO_2$, for the chemoselective

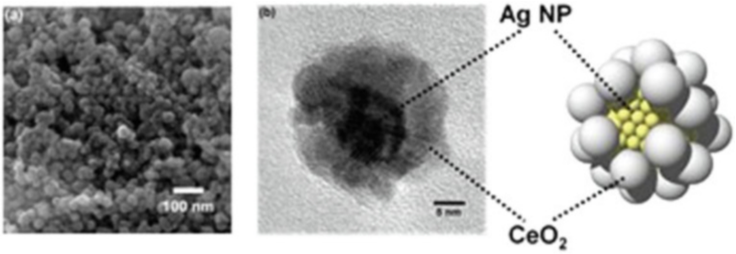


Fig. 1 Electron micrographs of Ag@CeO_2: (**a**) SEM image of Ag@CeO_2; (**b**) HRTEM image of single Ag@CeO_2 particle

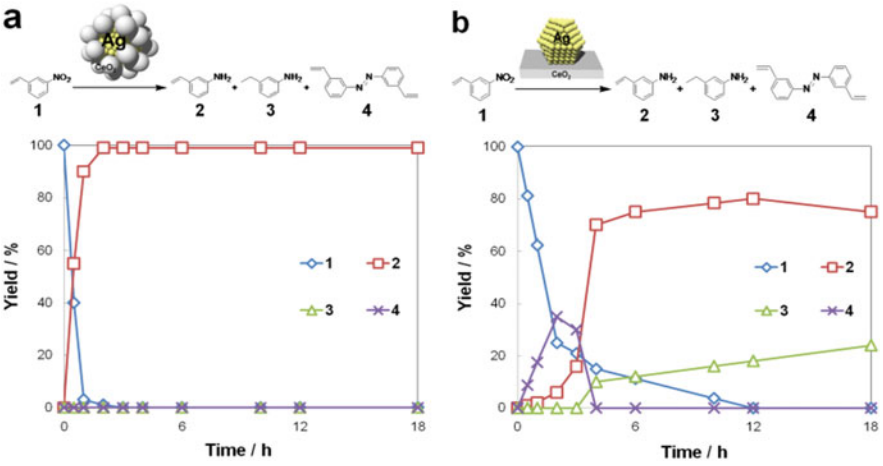


Fig. 2 Time course of 3-nitrostyrene reduction with H_2 using (**a**) Ag@CeO_2 and (**b**) Ag/CeO_2. Reprinted with permission from [27]. Copyright 2012 Wiley-VCH

hydrogenation of nitrostyrene [27]. Ag@CeO_2 comprised a core of Ag NPs with a mean diameter of 10 nm and a shell assembled from CeO_2 NPs with diameters of 3–5 nm. The shell had nanopores among the CeO_2 NPs that enabled the reactants to access AgNPs in the core (Fig. 1).

The core–shell Ag@CeO_2 catalyst structurally maximizes the interface area between the AgNPs and basic metal oxide CeO_2 while simultaneously minimizing the area of bare AgNPs. Therefore, Ag@CeO_2 is expected to enable the selective formation of polar hydrogen species at the interface between AgNPs and the basic sites of CeO_2 through heterolytic dissociation of H_2 while suppressing the unfavorable formation of nonpolar hydrogen species on bare AgNPs through homolytic dissociation of H_2, which react with alkene groups. This precise design strategy for NP catalysts enabled the selective generation of polar hydrogen species that promote complete chemoselective hydrogenation of nitro groups while retaining C=C bonds (Fig. 2). Ag@CeO_2 catalyst exhibited excellent selectivity toward the nitro hydrogenation of 3-nitrostyrene, affording 3-aminostyrene in 98% yield with >99%

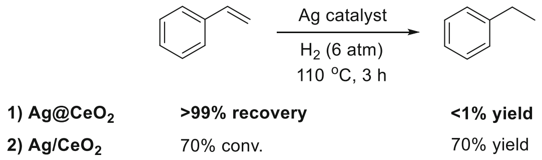


Fig. 3 Activities of Au@CeO_2 and Ag/CeO_2 toward styrene

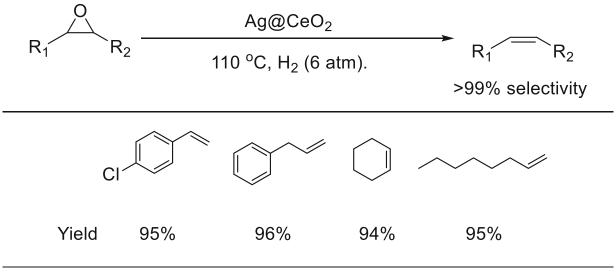


Fig. 4 Ag@CeO_2-catalyzed deoxygenation of epoxides to give alkenes using H_2

selectivity without alkene hydrogenation occurring. Interestingly, the C=C bond of 3-aminostyrene showed no hydrogenation when the reaction time was prolonged.

The efficiency of the Ag@CeO_2 core–shell structure was also demonstrated in the hydrogenation of styrene. Styrene was not hydrogenated using this catalyst but was hydrogenated using CeO_2-supported Ag NPs without a core–shell structure (Ag/CeO_2) (Fig. 3). Furthermore, the Ag@CeO_2 catalyst could be recovered through simple filtration from the reaction mixture after the reaction and reused without any loss of activity or selectivity [28].

Ag@CeO_2 also promoted the unique deoxygenation reaction of epoxides to give the corresponding alkenes. Various epoxides, including aromatic, aliphatic, and alicyclic epoxides, were smoothly converted into the corresponding alkenes with >99% selectivity (Fig. 4). This represented the first reported Ag-catalyzed chemoselective deoxygenation of epoxides to alkenes using H_2.

The design strategy of Ag@CeO_2 for the exclusive hydrogenation of a polar functional group while retaining alkene groups was further demonstrated by the selective hydrogenation of unsaturated aldehydes to give the corresponding unsaturated alcohols, which are important intermediates in fragrances and pharmaceuticals. Highly dispersed Ag@CeO_2 on a CeO_2 support (Ag@CeO_2-D), which represents a modified version of Ag@CeO_2, efficiently converted a wide range of aldehydes, including not only terpenes and aliphatic and aromatic α,β-unsaturated aldehydes but also unconjugated aldehydes, to the corresponding allylic alcohols with high selectivity at high conversion levels (Fig. 5). Ag@CeO_2 also operated well under gram-scale reaction conditions to produce unsaturated alcohols in high yields.

The semihydrogenation of alkynes is among the most important and fundamental reactions for the synthesis of (*Z*)-alkenes, which are important building blocks of fine chemicals, including bioactive molecules, flavors, and natural products

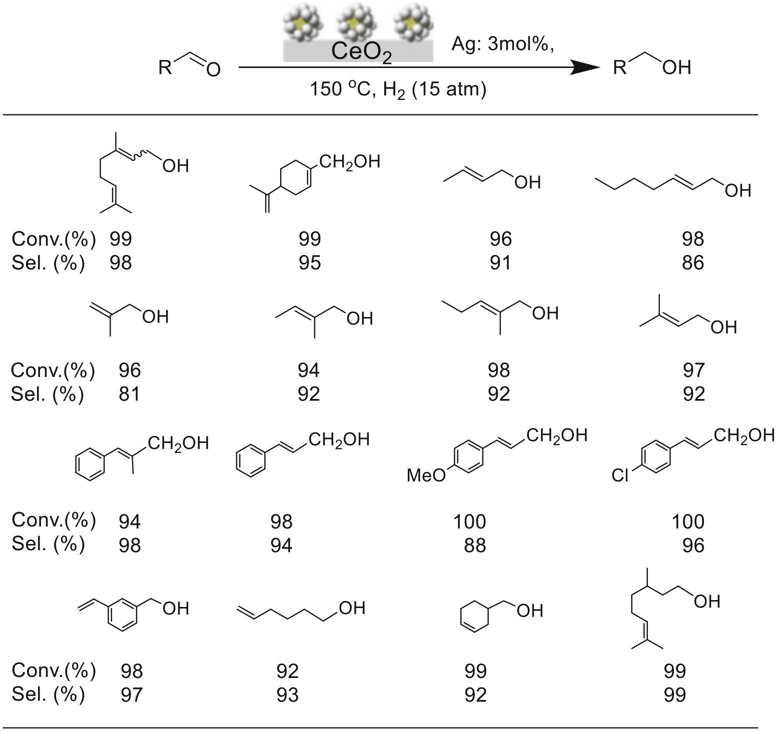


Fig. 5 Chemoselective hydrogenations of unsaturated aldehydes using Ag@CeO_2-D

[29, 30]. Although Lindlar catalyst ($Pb(OAc)_2$-treated $Pd/CaCO_3$ with large amounts of quinoline) has been widely used in these reactions [31], this method has serious drawbacks, including requiring a toxic Pb salt and large amounts of quinoline to suppress overhydrogenation of alkenes. Furthermore, when applied to terminal alkynes, Lindlar catalyst causes rapid overhydrogenation of the terminal alkene products. To establish more environmentally benign catalyst systems, a number of Pb-free catalysts involving Pd [32, 33], Fe [34, 35], Ni [36–38], Cu [39], and Ru [40] metals have been reported. Among the reported Pd NP catalysts, the addition of dimethylsulfoxide (DMSO) is a simple and effective approach alternative to Lindlar catalyst, in which DMSO drastically suppresses the overhydrogenation and isomerization of the alkene products [41]. This is caused by the suitable coordination ability of DMSO with Pd NPs, where DMSO adsorbed on the Pd NP surface inhibits the coordination of alkenes to Pd NPs, while alkynes can adsorb onto the Pd NP surfaces due to their higher coordination ability compared with that of DMSO.

Based on the above DMSO effect, Mitsudome et al. designed core–shell nanocomposites of SiO_2-supported Pd NPs covered with a DMSO-like matrix of methyl-3-trimethoxysilylpropylsulfoxide (MPSO) (Pd@MPSO/SiO_2) [42]. Pd@MPSO/SiO_2 had Pd NPs with a mean diameter of 17 nm covered by a MPSO matrix shell with a thickness of 4 nm (Pd@MPSO/SiO_2-1) or 19 nm

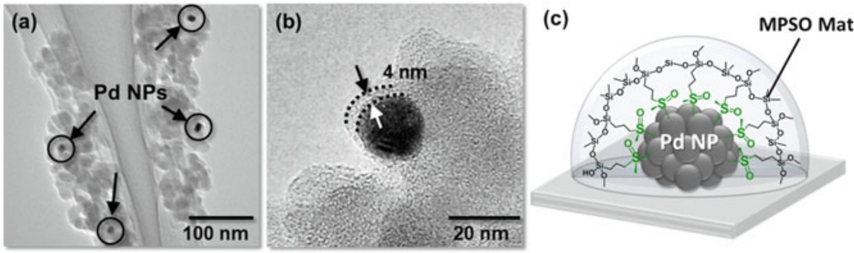


Fig. 6 TEM images of (**a**, **b**) Pd@MPSO/SiO$_2$-1 and (**c**) illustration of the core–shell structured Pd@MPSO/SiO$_2$

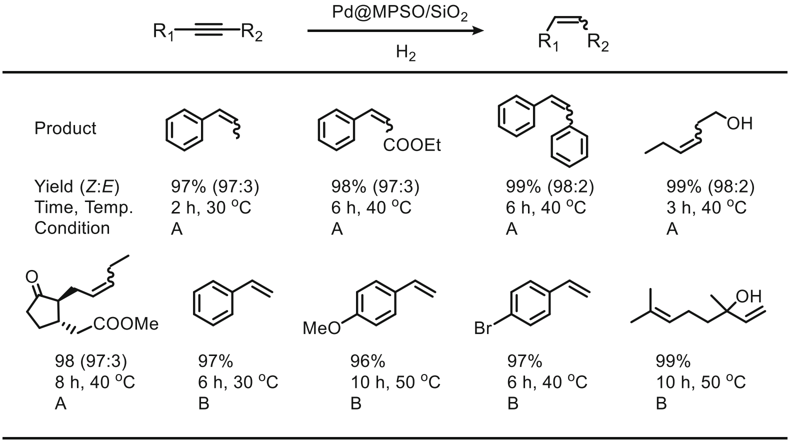


Fig. 7 Semihydrogenation of internal and terminal alkynes using Pd@MPSO/SiO$_2$. Reaction conditions: (**a**) Pd@MPSO/SiO$_2$-1 (Pd, 0.2 mol%), H_2 (1 atm); (**b**) Pd@MPSO/SiO$_2$-2 (Pd, 0.2 mol%), H_2 (1 atm)

(Pd@MPSO/SiO$_2$-2), which was controlled by the amount of MPSO. Energy-dispersive X-ray spectroscopy (EDX) of Pd@MPSO/SiO$_2$ proved the existence of sulfur and Si atoms in the shell matrix (Fig. 6). The Pd@MPSO/SiO$_2$ shell consisted of an alkyl sulfoxide network that allowed the exclusive coordination of alkynes to the Pd NP active center, promoting the selective semihydrogenation of various terminal and internal alkynes (Fig. 7).

The design of bimetallic catalysts comprising a core of Pd NPs and a Ag nanolayer shell provides another strategy for core–shell metal NP arrangement for the selective semihydrogenation of alkynes. Unmodified Pd NP catalysts have intrinsically high activity for alkyne hydrogenation but low selectivity for alkene products owing to the overhydrogenation of alkenes to alkanes. Ag NP catalysts, in contrast, exhibit low activity for hydrogenation despite having inherent high alkene selectivity [43–45]. Mitsudome et al. envisioned that the design of core-Pd/shell-Ag nanocomposite catalysts (Pd@Ag) could avoid the trade-off between activity and selectivity for Pd and Ag NPs in semihydrogenation [46]. The construction of a

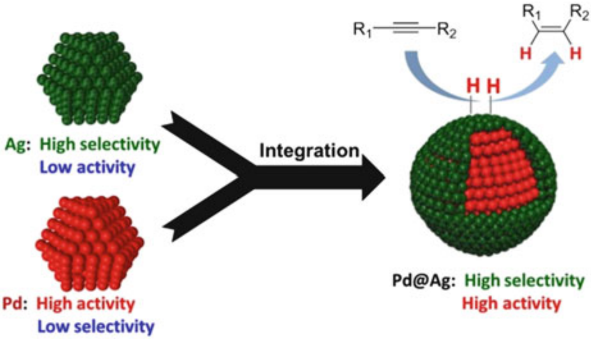


Fig. 8 Design concept of complementary bimetallic core-Pd/shell-Ag catalyst for selective semihydrogenation of alkynes

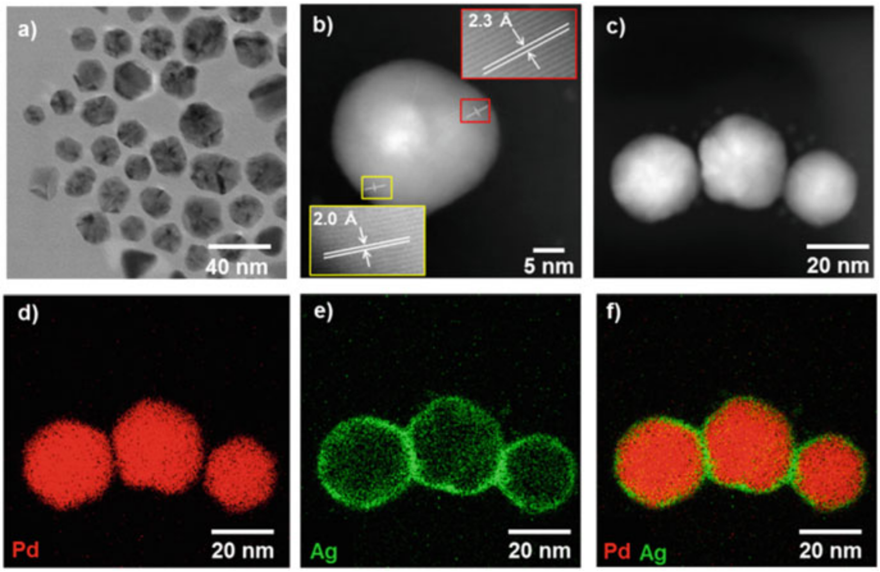


Fig. 9 Compositional and structural analysis of Pd@Ag. (**a**) TEM image; (**b**, **c**) HAADF-STEM images; (**d**, **e**) elemental mapping images of (**d**) Pd and (**e**) Ag; and (**f**) composite overlay image formed from (**d**) and (**e**). Reprinted with permission from [46]. Copyright 2016 American Chemical Society

core–shell nanocomposite would significantly improve the low activity of Ag NPs owing to a ready supply of hydrogen from the core of Pd NPs to Ag nanolayer shell in a synergistic manner. Meanwhile, coating the core Pd NPs with a Ag nanolayer would suppress overhydrogenation of alkenes at the Pd surface (Fig. 8). This cooperative catalysis between the Pd core and Ag shell was expected to lead to the selective semihydrogenation of alkynes under mild reaction conditions.

According to the above catalyst design concept, Pd@Ag comprising of Pd NPs with a mean diameter of 26.2 nm in the core and a Ag nanolayer with a thickness of approx. 1 nm as the shell was synthesized (Fig. 9) and demonstrated excellent alkene

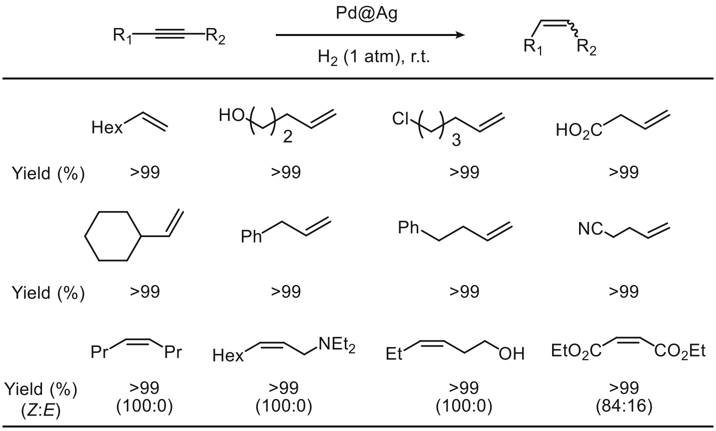
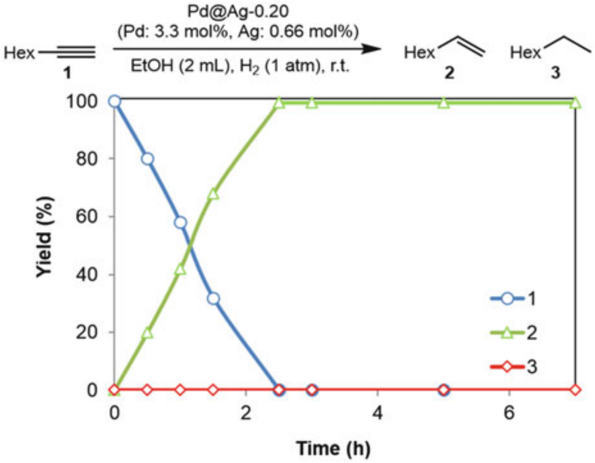


Fig. 10 Pd@Ag-catalyzed semihydrogenation of alkenes under ambient conditions

Fig. 11 Time profile of semihydrogenation of 1-octyne using Pd@Ag



selectivity for a wide range of alkynes under mild reaction conditions (room temperature and 1 atm of H_2) (Fig. 10). Notably, Pd@Ag successfully inhibited the overhydrogenation of alkenes even after the full conversion of alkynes. This result was quite different from those obtained using other previously reported catalysts, in which rapid overhydrogenation of alkenes occurred at a high alkyne conversion level (Fig. 11). Furthermore, Pd@Ag was separable from the reaction mixture and reusable without a loss of catalytic activity or selectivity. Furthermore, Pd@Ag was also suitable for use in a column flow reactor, demonstrating its practical utility.

2.2 Nitrogen or Sulfur Modification of Metal NP Surface

Although heterogeneous metal NP catalysts have many advantages over homogeneous catalysts, such as high stability and easy separation and reuse, fine-tuning the active metal center remains difficult. Beller et al. reported the heterogenization of well-defined organometallic complex catalysts via immobilization and pyrolysis on activated carbon [47]. The synthetic scheme for novel cobalt oxide NPs is shown in Fig. 12. The deposition of cobalt(II) acetate–phenanthroline complex onto commercially available carbon followed by pyrolysis under inert conditions provided cobalt oxide NPs coated with *N*-doped graphene (Co oxide–N/C).

The synthesized novel *N*-ligated Co oxide NPs showed high chemoselectivity for nitroarenes bearing easily reducible moieties including alkenes, alkynes, aldehydes, and ketones (Fig. 13). Furthermore, this heterogeneous Co catalyst was reusable without a significant decrease in activity during the recycling experiments, although an initial loss of activity was observed.

Beller et al. also showed that the convenient pyrolysis heterogenization method of well-defined organometallic complex catalysts could be applied to the most earth-abundant metal, iron [48], because the development of efficient and cost-effective catalyst systems is greatly needed in current chemical research. The pyrolysis of iron–phenanthroline complexes adsorbed on carbon at 800°C provided stable Fe_2O_3 NPs surrounded by a nitrogen-doped carbon layer (Fe-phen/C-800). The Fe-phen/C-800 catalyst promoted more than 80 examples of structurally diverse nitroarenes, giving the corresponding functionalized anilines in good to excellent yields under industrially acceptable conditions (Fig. 14).

One rational design approach toward metal NP catalysts involves metal modification with self-assembled monolayers (SAMs) to create a favorable surface environment for selective formation of the desired products [49, 50]. SAMs are organic assemblies of molecules containing a headgroup that noncovalently bind to the metal, producing ordered and stable monolayer films on the metal surface. A unique property of SAM modification is the formation of highly ordered assembly structures on metal surfaces, where modifiers with different tail structures can finely tune the metal surface environment to facilitate specific interactions between reactants and metal NPs.

Medlin et al. showed that SAMs on metal NP surfaces can act as “molecular recognition monolayers” to give the reactant a desirable orientation, which greatly improves the catalytic performance for hydrogenation reactions [51]. For example, in the hydrogenation of cinnamaldehyde, modification of a Pt NP catalyst with 3-phenylpropanethiol significantly improved the selectivity for cinnamyl alcohol to over 95% compared with 25% selectivity using uncoated Pt catalysts [52]. This high chemoselectivity was attributed to the favorable orientation of cinnamaldehyde in the vertical configuration through aromatic stacking interactions between the modifier and reactant. The proposed adsorption mechanism on SAMs is shown in Fig. 15. This represents the first successful demonstration of using specific

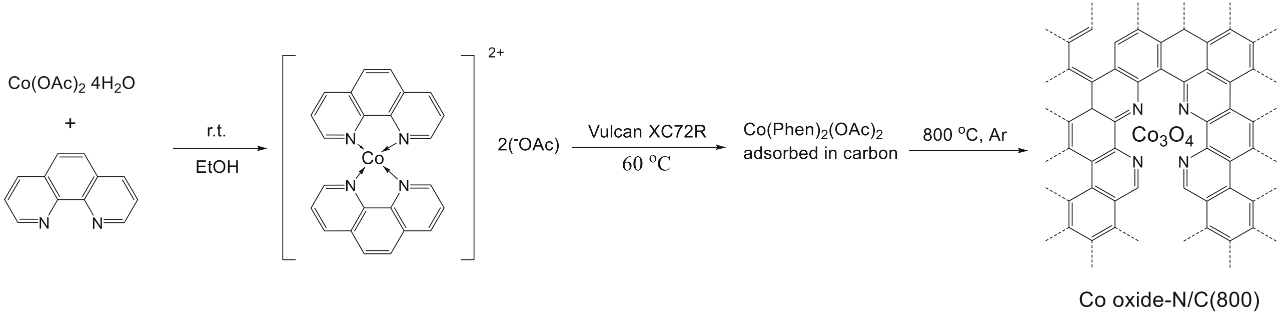


Fig. 12 Synthetic scheme for Co oxide–N/C

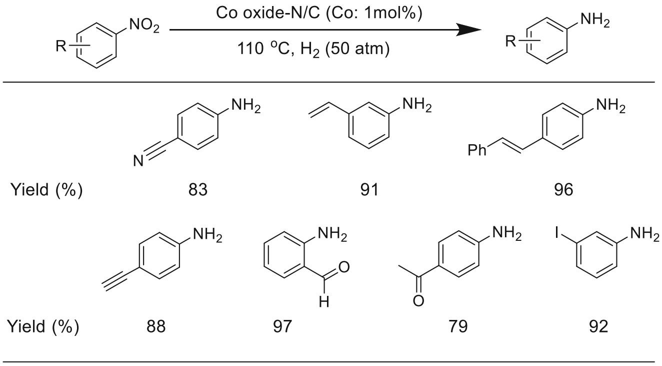


Fig. 13 Chemoselective hydrogenation of substituted nitroarenes using Co oxide–N/C

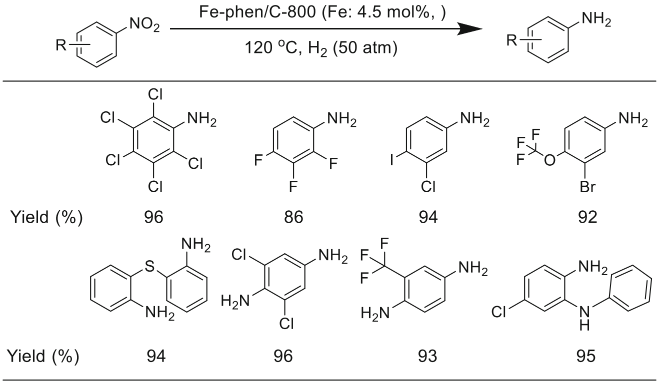


Fig. 14 Fe-phen/C-800-catalyzed selective hydrogenation of substituted nitroarenes

noncovalent interactions to orient the reactant to promote aldehyde-selective hydrogenation.

Pt catalysts are not chemoselective for the hydrogenation of nitro groups in nitro aromatic compounds bearing other reducible groups. However, the thiol-modification approach transforms nonchemoselective Pt catalysts into highly chemoselective Pt catalysts for the hydrogenation of 4-nitrostyrene to 4-aminostyrene [53]. The TiO_2-supported Pt NPs with a mean diameter of 1.4 nm treated with some thiols, such as thioglycerol, 1,6-hexanedithiol, and α-lipoic acid, gave 100% selectivity for aminostyrene at conversion levels close to 100%. In contrast, an unmodified Pt/TiO_2 catalyst provided C=C bond-hydrogenated products, 4-ethylnitrobenzene, and 4-ethylaniline. Therefore, thiol modification produced a 100% switch in selectivity to 4-aminostyrene.

As shown above, surface modification through SAMs construction on the metal NP surface is a powerful method to improve the selectivity of hydrogenations. However, the modifiers often suppressed diffusion and the adsorption of reactants and protected active sites, unavoidably resulting in the low activity of metal NPs.

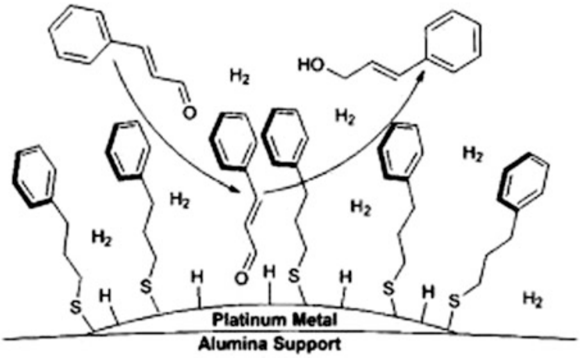


Fig. 15 Proposed adsorption model depicting favorable orientation of cinnamaldehyde induced by 3-phenylpropanethiol SAM modifiers. Reprinted with permission from [58]. Copyright 2014 American Chemical Society

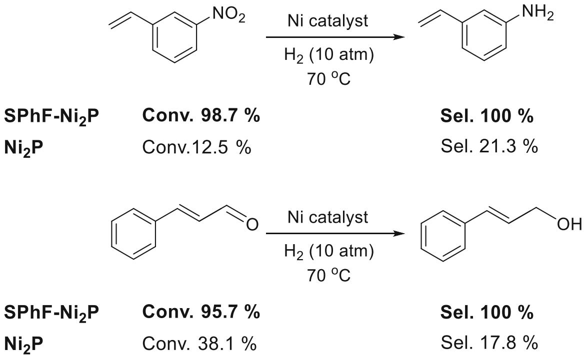


Fig. 16 Performance-boosting effect of SPhF modification on chemoselective hydrogenation

Therefore, high selectivity is usually achieved at the expense of activity, resulting in a trade-off relationship between the activity and selectivity. Therefore, the development of surface-modified metal NPs with both high selectivity and activity is a great challenge in chemoselective hydrogenation.

Recently, Zou et al. succeeded in breaking the trade-off between activity and selectivity in chemoselective hydrogenations using Ni NPs modified by *p*-fluorothiophenol (SPhF) [54]. SPhF-chelated dinickel phosphide nanosheets (SPh-Ni_2P) with activity nearly 12-fold higher than that of unmodified Ni_2P in the hydrogenations of 3-nitrostyrene and cinnamaldehyde selectively gave 3-aminostyrene and cinnamyl alcohol, respectively. Furthermore, the selectivity for desired products significantly improved from 38.1% and 21.3% to nearly 100%. Importantly, the effect of SPhF modification has broad applicability to other metal catalysts, such as Pt, Pd, and commercially available metal catalysts. For example, commercial catalysts like Raney Ni modified with SPhF exhibit twice higher activity with enhanced selectivity from 21–23% to nearly 100% in the above hydrogenations (Fig. 16). Experimental results and density functional theory calculations showed that both the steric and electronic effects of SPhF modification can provide superior catalytic performance. Namely, the confined flat adsorption of ordered SPhF-arrays onto the metal surface and downshifted d-band center of the catalysts lead to prohibited undesired hydrogenation of the alkene group and accelerative H_2 activation, respectively.

3 Metal NP-Catalyzed Selective Oxidations Using O_2

The selective oxidation of organic compounds is a fundamental challenge in synthetic chemistry. Although the economic and environmental advantages of molecular oxygen as a chemical oxidant are apparent, few reports on the selective introduction of oxygen functions into organic compounds exist because oxygenation often involves radical reactions that are difficult to control. The oxidation reactivity of organic compounds greatly varies depending on their structures. For example, in the oxidation of ethylene using silver catalyst, ethylene oxide is produced using molecular oxygen through a silver-superoxo intermediate. In contrast, when the substrate is changed from ethylene to propylene, propylene is not converted to propylene oxide but completely oxidized to CO_2 and H_2O. This is attributed to the low bond dissociation energy of the allylic C–H bond. Preferential dissociation of the allylic C–H bond in organic compounds generally induces unselective reactions or combustion. Therefore, only limited compounds with tertiary or benzylic C–H bonds can undergo selective oxygenation reactions.

The Wacker oxidation of alkenes is an important oxygenation reaction. The Wacker oxidation is conducted under an oxygen atmosphere, but the carbonyl oxygen introduced into the product is derived from water, not molecular oxygen. Molecular oxygen reoxidizes the metal and is not added into the substrate. An oxygen nucleophile from water attacks the positively charged C=C double bond through coordination to the metal center to form methyl ketones. Alternatively, the resulting metal–hydrogen species generated from the substrate through dehydrogenation is oxidized by molecular oxygen, completing the catalytic cycle. In this reaction, high selectivity for methyl ketone products can be achieved because the radical character of oxygen is not involved.

Some oxidation reactions that use molecular oxygen as an oxidant give low selectivity for oxygenated compounds, while oxidations involving dehydrogenation give high selectivity. In this section, we describe metal NP-catalyzed selective oxidation reactions involving dehydrogenation, in which molecular oxygen acts as an oxidant but is not incorporated into the substrate.

3.1 Aerobic Oxidation of Alcohols Using Pd NPs

There have been numerous reports on the catalytic oxidation of alcohols under an oxygen atmosphere [55]. In particular, Pd had been used as a metal center both in homogeneous and heterogeneous systems [56]. PdHAP, in which a mononuclear Pd species is adsorbed to hydroxyapatite (HAP), was reduced to a Pd NP (~5 nm)

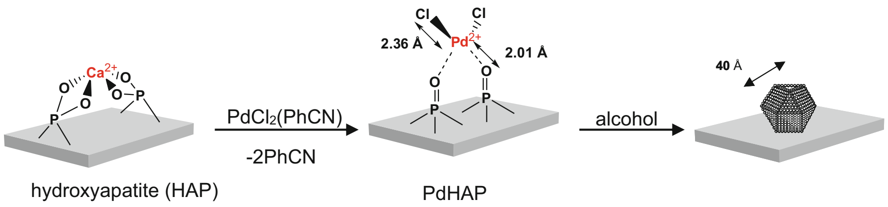


Fig. 17 PdHAP preparation method

Fig. 18 PdHAP-catalyzed aerobic oxidation of 1-phenylethanol under solvent-free conditions

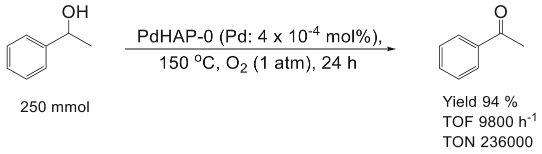
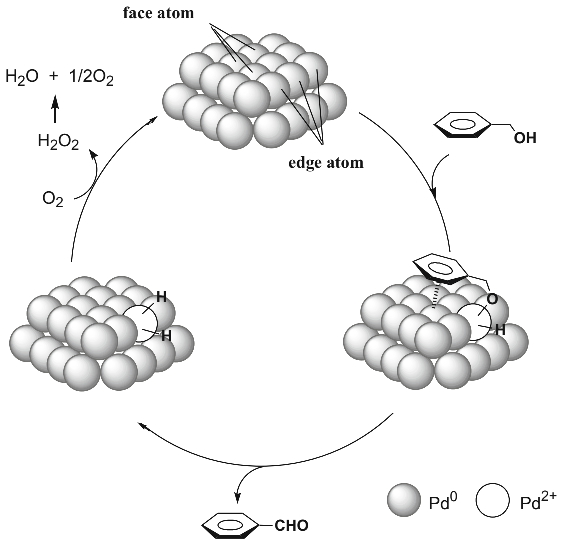


Fig. 19 Proposed reaction mechanism for the PdHAP-catalyzed aerobic oxidation of alcohols. Reprinted with permission from [58]. Copyright 2004 American Chemical Society



during alcohol oxidation (Fig. 17), catalyzing the aerobic oxidation of a wide range of alcohols without any need for additives [57, 58]. The use of HAP as catalyst supports has the following advantages: (1) well-defined monomeric active species can be immobilized on their surface owing to its high ion-exchange ability and adsorption capacity; (2) the nonporous structure can help overcome the problems regarding mass transfer limitations; and (3) weak acid–base properties prohibit side reactions induced by the support itself.

Typically, PdHAP promoted well in the aerobic oxidation of 1-phenylethanol under solvent-free conditions, showing a remarkably high TON of up to 236,000 with an excellent TOF of approximately 9,800 h^{-1} (Fig. 18).

A possible reaction pathway is shown in Fig. 19. Initially, oxidative addition of an alcohol O–H bond to the coordinately unsaturated Pd^0 species at the edge of the NP

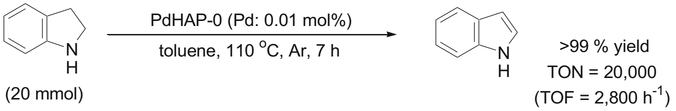


Fig. 20 PdHAP-catalyzed dehydrogenation of indoline

affords a Pd-alcoholate species, which undergoes β-hydride elimination to produce the corresponding carbonyl compounds and Pd-hydride species. The hydride species mediated on the Pd NPs was oxidized by O_2 along with the formation of O_2 and H_2O through H_2O_2 as an intermediate. The kinetic isotope effect for the intramolecular competitive oxidation of α-deuterio-*p*-methylbenzyl alcohol gave a k_H/k_D value of 2.0, indicating that the elimination of β-hydride from the Pd-alcoholate species might be the rate-determining step.

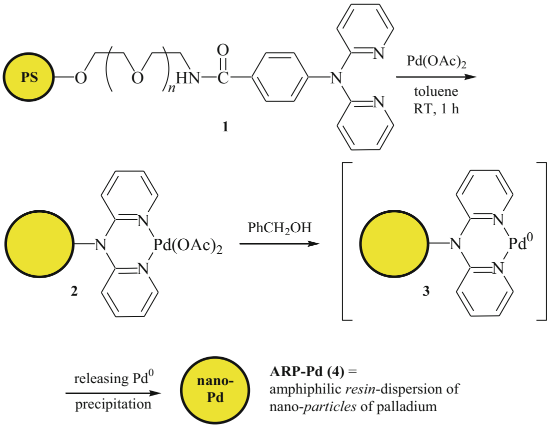
Interestingly, the PdHAP catalyst also promoted dehydrogenation of various indolines to indole, which serves as an important and versatile intermediate for the synthesis of pharmaceuticals and agrochemicals [59]. The applicability of PdHAP was demonstrated in a 20-mmol scale reaction of indole, as shown in Fig. 20. Dehydrogenation was completed within 6 h to afford **2** in 99% yield, in which the TON based on Pd approached up to 20,000 with an excellent TOF of approximately 2,800 h^{-1}. These TON and TOF values were significantly higher than those reported for other catalytic systems.

Pd NPs supported on inorganic materials often give undergo leaching from the support or aggregate to generate inactive larger NPs during the reaction. Park et al. found that small Pd NPs with a diameter of 2–3 nm entrapped into an aluminum hydroxide matrix showed high catalytic activity and durability in the oxidation of alcohols [60]. The oxidation of 1-phenylethanol under solvent-free conditions proceeded smoothly in the presence of 0.005 mol% aluminum hydroxide-entrapped Pd NPs at 150°C, giving acetophenone in 98% yield. This highly dispersed Pd NP catalyst was also reusable at least ten times without activity loss.

Kantam et al. reported the aerobic oxidation of alcohols at room temperature under aerobic conditions using nanocrystalline magnesium oxide-supported Pd NPs (NAP-Mg-Pd(0)) [61]. Although most Pd NP catalysts require high temperatures (65–150°C) for alcohol oxidation, these Pd NPs with a diameter of 5–7 nm highly dispersed on the surface of NAP-Mg showed a wide substrate scope for alcohols under mild conditions through a cooperative effect between the basic support and active metal NPs. Benzylic, allylic, aliphatic, and alicyclic alcohols were oxidized at room temperature under air, giving the corresponding carbonyl compounds from good to excellent yields. This NAP-Mg-Pd(0) catalyst was able to be recycled four times without loss of catalytic efficiency.

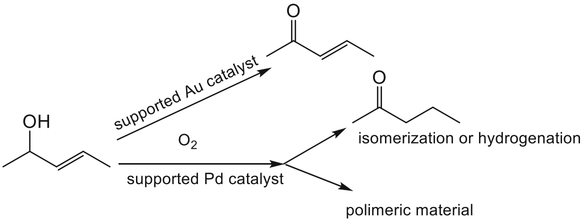
From both a practical and economic standpoint, using water in organic reactions has significant advantages, including the low cost, abundance, safety (nonexplosive, non-flammable, and nontoxic), easily controlled reaction temperatures owing to the high heat capacity of water, and ease of phase separation [62–65]. Uozumi et al. synthesized polymer-supported Pd NPs with a mean diameter of 9 nm (ARP-Pd) via

Fig. 21 Preparation of amphiphilic resin-dispersed Pd NPs (ARP-Pd)



ARP-Pd (4) = amphiphilic *resin*-dispersion of nano-*particles* of palladium

Fig. 22 Differences in product distribution for the aerobic oxidation of allylic alcohols catalyzed by Au and Pd catalysts



the reduction of a polystyrene-polyethylene glycol (PS-PEG) resin-supported bipyridyl palladium(II) complex, which efficiently promoted the aerobic oxidation of alcohols in aqueous media (Fig. 21) [66]. ARP-Pd was used in aqueous media to show that that alcohols as substrates would diffuse into the hydrophobic ARP-Pd matrix to give a highly concentrated reaction field, where the active Pd NPs in the polymer matrix would efficiently oxidize the trapped alcohols.

Pd NP catalysts generally show low chemoselectivity for the oxidation of allylic alcohols to α,β-unsaturated carbonyl compounds compared with Au NPs, which was due to the formation of other byproducts arising from the isomerization and hydrogenation of C=C bonds and/or polymerization (Fig. 22) [67]. The different stabilities and steady-state concentrations of the metal hydrides (Au–H and Pd–H) are probably the cause of such a result. The Au–H species generated during oxidation is much more reactive with O_2 than the Pd–H species, preventing C=C bond hydrogenation or isomerization.

3.2 Bimetallic NP-Catalyzed Alcohol Oxidation

A combined system composed of plural metal species exhibit interesting catalytic activity compared with single metal species. Au–Pd/TiO_2 showed a wide substrate

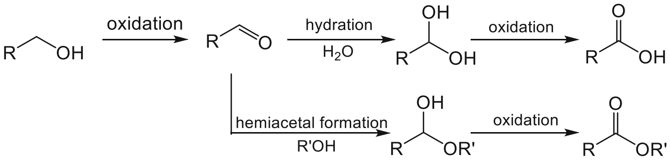


Fig. 23 Two reaction pathways for alcohol oxidation

scope with high TOFs in the aerobic oxidation, in which the choice of metal oxide support significantly influenced the product distribution in the oxidation of benzyl alcohol [68]. The side reaction, involving disproportionation of two molecules of benzyl alcohol to produce benzaldehyde and toluene, occurred when using TiO_2-, Nb_2O_5-, and activated carbon-supported Au–Pd NPs. In contrast, MgO- and ZnO-supported Au–Pd NPs were superior to the above catalysts for the selective oxidation of benzyl alcohol, giving benzaldehyde in more than 99% selectivity. Similarly, Kobayashi et al. reported that polymer-incarcerated Au–Pt alloyed bimetallic NPs (PI Pt/Au) exhibited higher catalytic activity than single metal Au or Pt NPs in the aerobic oxidation of alcohols [69]. PI Pt/Au worked well without additional base in water at room temperature, although PI Au, as a single metal species, required a large amount of K_2CO_3 to promote oxidation, in which water acted as a hydrogen transporter in the hydrophobic polystyrene surroundings, therefore aiding α-hydrogen abstraction.

The same group also developed carbon black-stabilized polymer-incarcerated bimetallic catalysts (PI-CB catalysts) [70]. Notably, PI-CB containing Au and Pt NP catalysts (PI-CB/Au–Pt) showed high catalytic activity and selectivity in the oxidation of primary aliphatic alcohols to the corresponding aldehydes under mild reaction conditions. This high catalytic activity could not be obtained using monometallic PI-CB catalysts, such as PI-CB/Au and PI-CB/Pt. The reactivity and selectivity were strongly dependent on the combination of metals and solvent system, with the overoxidation of 1-octanol to octanoic acid suppressed under neutral conditions. Furthermore, PI-CB/Au–Pd showed completely different activity and selectivity compared with PI-CB/Au–Pt, with direct oxidative methyl ester formation catalyzed by PI-CB/Au–Pd proceeding in methanol/H_2O in the presence of K_2CO_3. The oxidation to carboxylic acids or esters is dependent on hydration of, or hemiacetal formation from, the aldehyde (Fig. 23).

Au@NiOx NP catalyst with a core–shell structure was developed for the oxidative esterification of aldehydes with alcohols [71]. The Au@NiOx NP catalyst, in which 20 mol% Au in the core was covered by nickel oxide (NiOx) supported on silica-alumina-magnesia, provided an environmentally benign method for ester synthesis, because the side product was water and molecular oxygen is the ideal oxidant. In this method, the reaction with various aldehydes and primary alcohols gave the corresponding esters with good selectivity. Typically, this catalyst can promote aerobic esterification of acrolein with methanol, providing methyl methacrylate as an important raw material for polymer chemistry.

3.3 Base Metal NP-Catalyzed Alcohol Oxidation

From an economic efficiency standpoint, some non-noble transitional metals catalysts, such as Co [72–75], Mn [76, 77], Fe [78–80], V [81], and Cu [82, 83], have been explored in the aerobic oxidation of alcohols. Yingwei et al. reported that Co NPs stabilized by N-doped carbon composite (Co/C–N) acted as highly efficient heterogeneous catalysts for the synthesis of carbonyl compounds from the aerobic oxidation of alcohols [84]. Co/C–N could be synthesized by the one-pot thermal decomposition of Co-containing metal–organic frameworks (MOFs). Co NPs with a particle size of 9.8 ± 2.6 nm were highly dispersed on N-doped carbon. Importantly, N-doping into Co/C–N played a dual role, not only in enhancing the basic properties, which is crucial for promoting the activity of the liquid-phase aerobic oxidation of alcohols, but also in reducing the Co particle size. The Co/C–N catalyst showed a broad substrate scope for both aryl and alkyl alcohols in water under an atmospheric pressure of air and base-free conditions. Furthermore, the Co/C–N catalyst could be separated from the reaction system using an external magnetic field and reused. The Co NPs with surface-oxidized CoO species incorporated into N-doped carbon were applicable to the esterification of primary alcohols under mild conditions with air or 1 bar of O_2 [85, 86]. A broad substrate scope was observed for aromatic and aliphatic alcohols, as well as diols, giving their corresponding esters in good to excellent yields (Fig. 24).

Based on the above results, a possible reaction mechanism for the oxidative esterification of alcohols over Co–CoO incorporated into N-doped carbon is illustrated in Fig. 25. Firstly, alcohols are oxidized to aldehydes by O_2 through the abstraction of β-hydride from alcohols. Secondly, aldehydes and methanol undergo a condensation reaction to give hemiacetal species. Finally, the hemiacetal intermediate is oxidized by Co catalyst giving an ester product.

Although heterogeneous catalysts of inexpensive and reusable transition metals are attractive alternatives to homogeneous catalysts, the relatively low activity of

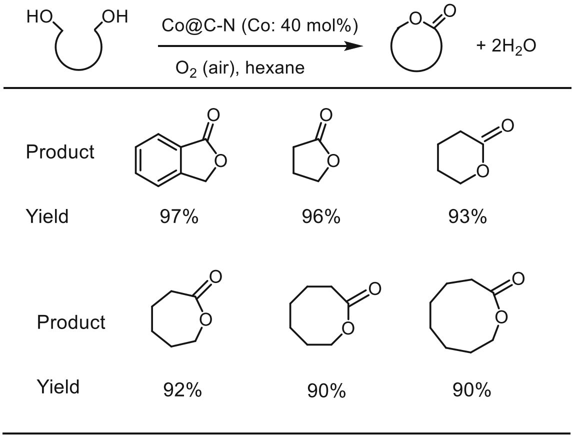


Fig. 24 Lactonization of various diols using Co NP catalyst

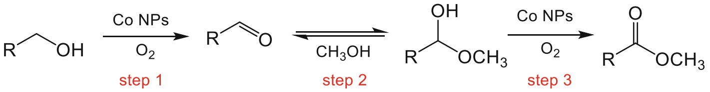


Fig. 25 Proposed reaction pathway for direct oxidative esterification of alcohols using Co NP catalysts

transition metal NPs represents a hurdle to their practical application. Li et al. reported that a nitrogen-rich carbon-coated cobalt NPs (Co@NC) catalyst, synthesized by direct polycondensation in the presence of g-C_3N_4 powder, exhibited a high TOF of 8.12 for the direct base-free aerobic oxidation of benzyl alcohols to methyl benzoate. This TOF was 30-fold higher than those of state-of-the-art transition metal-based nanocatalysts previously reported [87].

Nitrogen-rich carbon, which has a higher band potential than that of metallic Co materials, will accept electrons from Co NPs until their Fermi level reaches equilibrium, described as the Mott–Schottky effect. The resulting electron-poor Co NPs sufficiently attract and activate O_2 for proton removal from the Co–H intermediates to accelerate the whole reaction process. N-doped carbon could also act as a strengthened Lewis base to accelerate the deprotonation process of alcohols. Conclusively, the Co@NC-x-based Mott–Schottky catalysts not only boosted the oxidative power of the Co NPs but also enabled the reaction to proceed in the absence of bases, constituting an overall mild and additive-free catalytic system.

Continuous flow technology has attracted much attention because it can maximize catalyst efficiency in the simple workup procedure. Heterogeneous catalysts also have a significant advantage in the application to the use in column flow reactor. Kappe et al. found that iron oxide NPs stabilized on a mesoporous aluminosilicate support acted as highly efficient catalysts for the selective aerobic oxidation of a primary alcohol in continuous flow reactor [88]. In a single pass of the reactor, benzyl alcohol as a model substrate was selectively converted to benzaldehyde. This catalyst was highly stable and did not leach from support under the investigated conditions, providing solid evidence for the participation of a heterogeneous iron species in the catalytic cycle.

3.4 Wacker-Type Oxidation Using Pd NPs

Ethylene and palladium chloride react in the presence of water under atmospheric conditions to produce a stoichiometric amount of acetaldehyde with simultaneous formation of the precipitates of Pd (0) (Pd black) [89]. When copper dichloride ($CuCl_2$) is added to this system, in situ-formed Pd(0) species are reoxidized to Pd (II) by Cu(II), and then O_2 oxidizes the resulting Cu(I) back to Cu(II), thereby allowing this catalytic cycle. This method is called the Wacker process, which is limited to the synthesis of acetaldehydes through ethylene oxidation [90]. Using *N*, *N*-dimethylformamide (DMF) as a solvent in this process allowed the substrates to

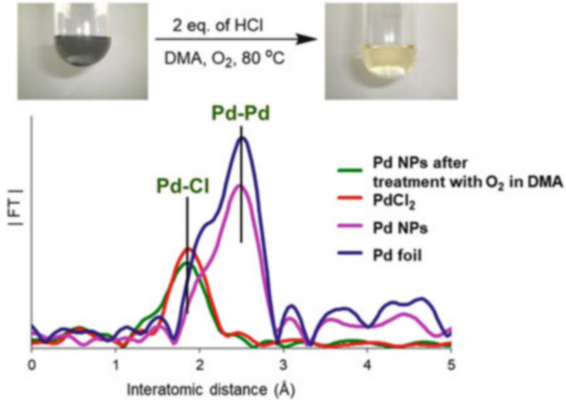


Fig. 26 Direct oxidation of colloidal Pd NPs coordinated by *N*,*N*-dimethylacetamide (DMA) by O_2

be extended to the terminal alkenes. This process, the Wacker–Tsuji reaction, is an effective means of selective methyl ketone synthesis from a wide range of terminal alkenes [91].

Recently, Mitsudome et al. found that colloidal Pd NPs in *N*,*N*-dimethylacetamide (DMA) solution can be directly oxidized by O_2 as sole oxidant to homogeneous Pd(II) species in the presence of hydrochloric acid (Fig. 26). Pd K-edge XAFS analysis proved that the peak attributed to the Pd–Pd bond in the Fourier transforms (FT) of k^3-weighted EXAFS disappeared and that a new peak derived from the Pd–Cl bond appeared after treating Pd NPs with DMA in the presence of two equivalents of HCl at 80°C under O_2 at atmospheric pressure.

This unique phenomenon would be applicable to developing the Cu-free Wacker oxidation system because in situ-generated Pd(0) species from the reaction of Pd (II) with alkenes can be facilely reoxidized to Pd(II) by O_2 without the necessity of Cu [92]. In fact, the Cu-free Wacker oxidation of various terminal alkenes could proceed using a $PdCl_2$/DMA catalyst system, affording the corresponding methyl ketones under O_2 at atmospheric pressure without substrate isomerization (Fig. 27).

This $PdCl_2$-DMA-O_2 system can be used for the oxidation of not only terminal alkenes but also internal alkenes, where various internal alkenes were efficiently converted to the corresponding ketones with 99% selectivity (Fig. 28) [93]. Although the conventional Wacker oxidation suffers from limited reactivity toward internal alkenes, this catalyst system overcame this limitation and provided a new and efficient methodology for catalyzing the oxidation of internal alkenes to carbonyl compounds.

The regioselective introduction of ketone oxygen functions was also possible using substrates containing functional groups [94]. Various nonenyl acetates were tested in this system, as shown in Fig. 29, and the ketone oxygen atom was selectively introduced into the carbon distal from the acetoxy group.

This breakthrough in the limitations of the conventional Wacker oxidation was attributed to the development of a Cu-free catalyst system because Cu strongly

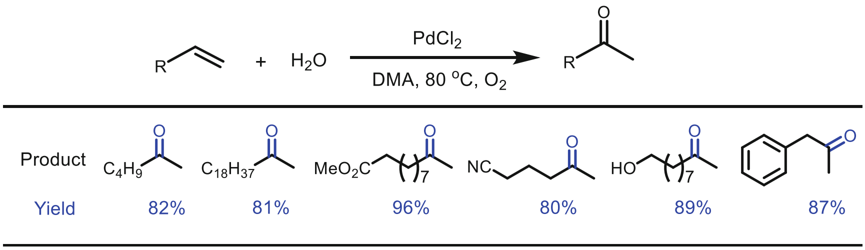


Fig. 27 O_2-coupled Wacker oxidation system without copper

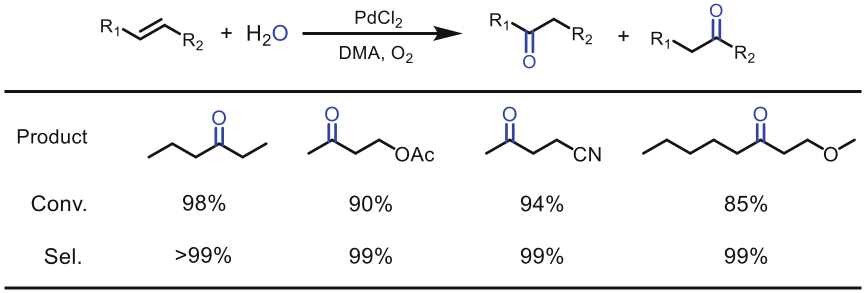


Fig. 28 Cu-free Wacker oxidation of internal alkenes

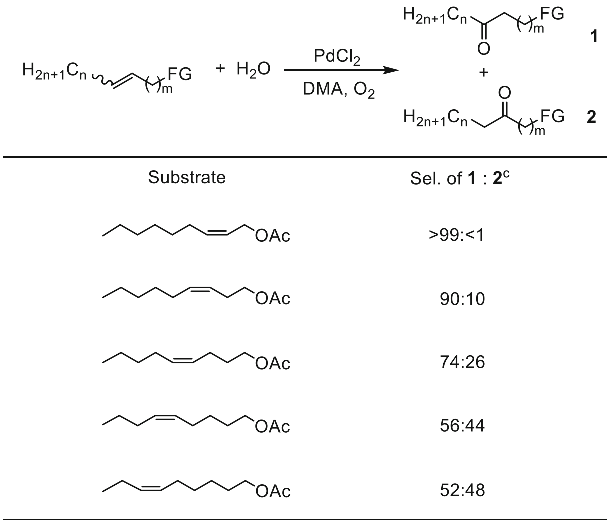


Fig. 29 Wacker-type oxidation of nonenyl acetates

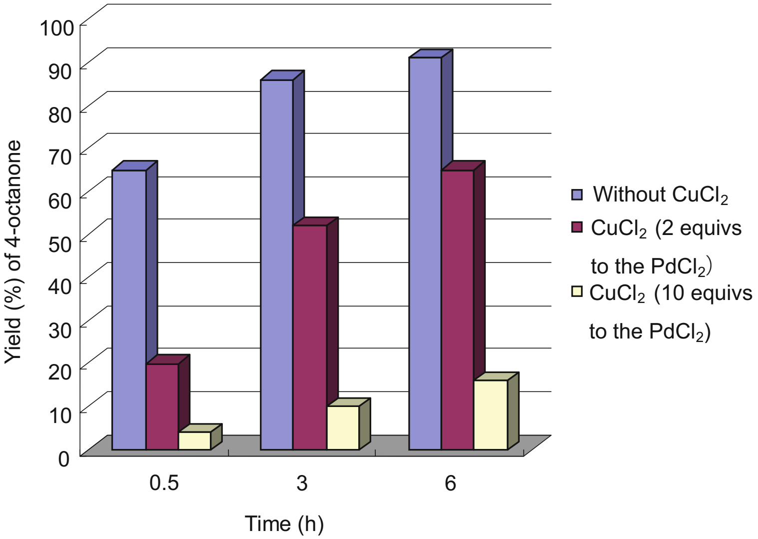


Fig. 30 Effect of $CuCl_2$ amounts on the oxidation of 4-octene. Reprinted with permission from [93]. Copyright 2010 Wiley-VCH

suppresses the oxidation of internal alkenes. As shown in Fig. 30, the reactivity of the internal alkene for oxidation was strongly suppressed by adding $CuCl_2$ to the $PdCl_2$-DMA-O_2 system, while that of the terminal alkene was not suppressed. This was probably due to the formation of a bulky Pd/Cu complex [95], which is difficult to coordinate to internal alkenes.

In the previous Wacker reaction, molecular oxygen acted to reoxidize palladium through the redox cycle of Cu(I) and Cu(II) and was not incorporated into the substrate. In this $PdCl_2$-DMA-O_2 system, $^{18}O_2$ was not incorporated into the product ketones, and the oxygen atom introduced into the ketone was derived from water. The selective oxygenation of alkenes to ketones was achieved using oxygen nucleophiles derived from water. Interestingly, methanol can be used as a nucleophile instead of water. In this case, using the $PdCl_2$-DMA-O_2-methanol system, the oxidation of α,β-unsaturated carbonyl compounds gave β-methoxy-α,β-unsaturated compounds that were easily hydrolyzed to the corresponding β-carbonyl compounds, as shown in Fig. 31 [96].

The $PdCl_2$-DMA-O_2-methanol-TsOH-H_2O system realized the simple oxidation process of converting α,β-unsaturated carbonyl compounds to β-carbonyl compounds (Fig. 32). As described above, this reinvestigation of the Wacker process provides a new and highly selective oxygenation method for converting various internal alkenes to ketones.

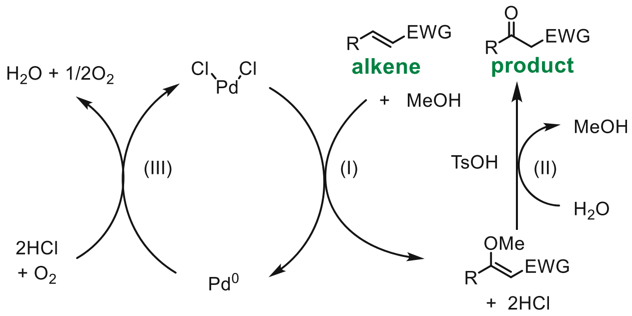


Fig. 31 Reaction pathway and reaction formulas of the $PdCl_2$-DMA-MeOH-TsOH catalyst system

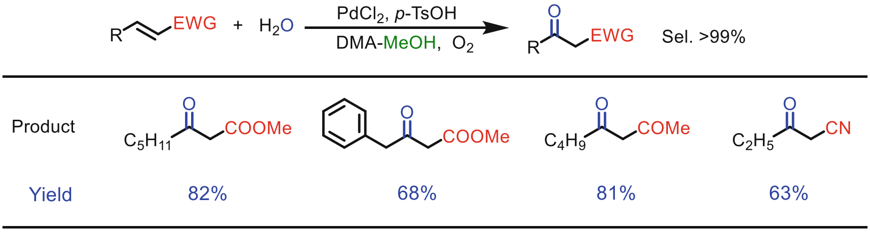


Fig. 32 Wacker-type oxidation of α,β-unsaturated carbonyl compounds to β-carbonyl compounds using $PdCl_2$-DMA-O_2-methanol-TsOH-H_2O system

4 Summary

The selective transformation of organic compounds through reduction and/or oxidation is a fundamental challenge in synthetic chemistry. This review focused on recently developed high-performance metal NP catalysts for selective reduction and oxidation under liquid-phase conditions using molecular hydrogen and molecular oxygen, respectively. Traditional heterogeneous catalysts, including metal NP catalysts, have significant intrinsic advantages of easy separation and robustness but generally show lower catalytic performance (activity and selectivity) and require harsh reaction conditions, such as high temperature, compared with homogeneous catalysts. Compared with premodern heterogeneous catalysts, the state-of-the-art metal NP catalysts introduced here have higher activity and selectivity for the chemoselective hydrogenations of carbonyl, nitro, and alkynyl compounds while retaining C=C bonds and the aerobic oxidation of alcohols and the Wacker oxidation of alkenes. This improved catalytic performance is due to significant advances in the precise fabrication of nanoscale metals, which has made it possible to explore novel catalysis and design metal active centers. The rapid expansion of characterization methods for the nanostructured catalysts has also greatly contributed to catalytic improvement. Spectroscopic analysis, especially operand analysis, enabled deep understanding of the role of supports and the relationship between structure and activity, leading to the development of more sophisticated catalysts with high performance. Although the catalytic performance of heterogeneous metal NP catalysts has been greatly advanced in the last decade, research on heterogeneous catalysts for fine chemistry is still in the development stage. The development of more efficient metal NP catalysts that promote selective hydrogenation and aerobic oxidation using lower amounts of active metals under milder reaction conditions without any additives and solvents remains vital. We believe that advances in both nanotechnology for the fine-tuning of metal NPs and a deep understanding of the complicated structure of heterogeneous catalysts play key roles in the development of next-generation metal NP catalysts for selective redox reactions in environmentally friendly fine chemistry.

References

1. Trost BM (1991) Science 254:1471
2. Anastas PT, Warner JC (1998) Green chemistry, theory and practice. Oxford University Press, Oxford
3. Sheldon RA, Wallau M, Arends IWCE, Schuhardt U (1998) Acc Chem Res 31:485
4. Clark JH (1999) Green Chem 1:1
5. Sheldon RA (2000) Green Chem 2:G1
6. Anastas PT, Bartlett LB, Kirchhoff MM, Williamson TC (2000) Catal Today 55:11
7. Hagen J (1999) Industrial catalysis: a practical approach. Wiley, Weinheim
8. Ertl G, Knözinger H, Schüth F, Weitkamp J (2008) Handbook of heterogeneous catalysis. 2nd edn. Wiley, Weinheim
9. Astruc D (2008) Nanoparticles and catalysis. Wiley, Weinheim
10. Tauster SJ, Fung SC, Baker RT, Horsley JA (1981) Science 211:1121
11. Schubert MM, Hackenberg S, van Veen AC, Muhler M, Plzak V, Behm RJ (2001) J Catal 197:113
12. Bell AT (2003) Science 299:1688
13. Tian N, Zhou Z-Y, Sun S-G, Ding Y, Wang ZL (2007) Science 316:732
14. Somorjai GA, Park JY (2008) Angew Chem Int Ed 47:9212
15. Astruc D, Lu F, Aranzaes JR (2005) Angew Chem Int Ed 44:7852
16. Johnson BF (2003) Top Catal 24:147
17. Mitsudome T, Kaneda K (2013) Green Chem 15:2636
18. Mallat T, Baiker A (2004) Chem Rev 104:3037
19. Zhan BZ, Thompson A (2004) Tetrahedron 60:2917
20. Matsumoto T, Ueno M, Wang N, Kobayashi S (2008) Chem Asian J 3:196
21. Vinod CP, Wilson K, Lee AF (2011) J Chem Technol Biotechnol 86:161
22. Serna P, Corma A (2006) Science 313:332
23. Serna P, Corma A (2015) ACS Catal 5:7114
24. Mitsudome T, Noujima A, Mikami Y, Mizugaki T, Jitsukawa K, Kaneda K (2010) Angew Chem Int Ed 49:5545
25. Noujima A, Mitsudome T, Mizugaki T, Jitsukawa K, Kaneda K (2011) Angew Chem Int Ed 50:2986
26. Shimizu K, Miyamoto Y, Satsuma A (2010) J Catal 270:86
27. Mitsudome T, Mikami Y, Matoba M, Mizugaki T, Jitsukawa K, Kaneda K (2012) Angew Chem Int Ed 51:136
28. Mitsudome T, Matoba M, Mizugaki T, Jitsukawa K, Kaneda K (2013) Chem Eur J 19:5255

29. Derrien ML (1986) Catalytic hydrogenation. In: Červený L (ed) Studies in surface science and catalysis, vol 27. Elsevier, Amsterdam, p 613
30. Piringer OG, Baner AL (2008) Plastic packaging: interactions with food and pharmaceuticals. 2nd edn. Wiley, Weinheim
31. Lindlar H (1952) Helv Chim Acta 35:446
32. van Laren MW, Elsevier CJ (1999) Angew Chem Int Ed 38:3715
33. Yabe Y, Yamada T, Nagata S, Sawama Y, Monguchi Y, Sajiki H (2012) Adv Synth Catal 354:1264
34. Armbrüster M, Kovnir K, Friedrich M, Teschner D, Wowsnick G, Hahne M, Gille P, Szentmiklósi L, Feuerbacher M, Heggen M, Girgsdies F, Rosenthal D, Schlögl R, Grin Y (2012) Nat Mater 11:690
35. Torres Galvis HM, Bitter JH, Khare CB, Ruitenbeek M, Dugulan AI, de Jong KP (2012) Science 335:835
36. Brown CA, Ahuja VK (1973) J Chem Soc Chem Commun 38:553
37. Studt F, Abild-Pedersen F, Bligaard T, Sørensen RZ, Christensen CH, Nørskov JK (2008) Science 320:1320
38. Carenco S, Leyva-Pérez A, Concepción P, Boissière C, Mézailles N, Sanchez C, Corma A (2012) Nano Today 7:21
39. Semba K, Fujihara T, Xu T, Terao J, Tsuji Y (2012) Adv Synth Catal 354:1542
40. Niu M, Wang Y, Li W, Jiang J, Jin Z (2013) Catal Commun 38:77
41. Takahashi Y, Hashimoto N, Hara T, Shimazu S, Mitsudome T, Mizugaki T, Jitsukawa K, Kaneda K (2011) Chem Lett 40:405
42. Mitsudome T, Takahashi Y, Ichikawa S, Mizugaki T, Jitsukawa K, Kaneda K (2013) Angew Chem Int Ed 52:1481
43. Sárkány A, Révay Z (2003) Appl Catal A Gen 243:347
44. Vilé G, Baudouin D, Remediakis IN, Copèret C, Lòpez N, Pèrez-Ramìrez J (2013) ChemCatChem 5:3750
45. Oakton E, Vilé G, S. Levine D, Zocher E, Baudouin D, Pèrez-Ramìrez J, Copèret C (2014) Dalton Trans 43:15138
46. Mitsudome T, Urayama T, Yamazaki K, Maehara Y, Yamasaki J, Gohara K, Maeno Z, Mizugaki T, Jitsukawa K, Kaneda K (2016) ACS Catal 6:666
47. Westerhaus FA, Jagadeesh RV, Wienhofer G, Pohl MM, Radnik J, Surkus AE, Rabeah J, Junge K, Junge H, Nielsen M, Bruckner A, Beller M (2013) Nat Chem 5:537
48. Jagadeesh RV, Surkus AE, Junge H, Pohl MM, Radnik J, Rabeah J, Huan HM, Schunemann V, Bruckner A, Beller M (2013) Science 342:1073
49. Schwartz DK (2001) Annu Rev Phys Chem 52:107
50. Love JC, Estroff LA, Kriebel JK, Nuzzo RG, Whitesides GM (2005) Chem Rev 105:1103
51. Schoenbaum CA, Schwartz DK, Medlin JW (2014) Acc Chem Res 47:1438
52. Kahsar KR, Schwartz DK, Medlin JW (2014) J Am Chem Soc 136:520
53. Makosch M, Lin WI, Bumbálek V, Sá J, Medlin JW, Hungerbühler K, van Bokhoven JA (2012) ACS Catal 2:2079
54. Gao R, Pan L, Wang H, Yao Y, Zhang X, Wang L, Zou J-J (2019) Adv Sci 6:1900054
55. Mitsudome T, Kaneda K (2013) Oxidation of alcohols using nano-catalysts. In: Nanocatalysis: synthesis and applications. Wiley, Weinheim, pp 287–332
56. Stahl SS (2004) Angew Chem Int Ed 43:3400
57. Mori K, Yamaguchi K, Hara T, Mizugaki T, Ebitani K, Kaneda K (2002) J Am Chem Soc 124:11572
58. Mori K, Hara T, Mizugaki T, Ebitani K, Kaneda K (2004) J Am Chem Soc 126:10657
59. Hara T, Mori K, Mizugaki T, Ebitani K, Kaneda K (2003) Tetrahedron Lett 44:6207
60. Kwon MS, Kim N, Park CM, Lee JS, Kang KY, Park J (2005) Org Lett 7:1077
61. Layek K, Maheswaran H, Arundhathi R, Kantam ML, Bhargava SK (2011) Adv Synth Catal 353:606
62. Chanda A, Fokin VV (2009) Chem Rev 109:725

63. Minakata S, Komatsu M (2009) Chem Rev 109:71
64. Grieco PA (1998) Organic synthesis in water. Blackie, London
65. Li CJ, Chan T-H (1997) Organic reaction in aqueous media. Wiley, New York
66. Uozumi Y, Nakao R (2003) Angew Chem Int Ed 42:194
67. Abad A, Almela C, Corma A, García H (2006) Chem Commun 30:3178
68. Sankar M, Nowicka E, Tiruvalam R, He Q, Taylor SH, Kiely CJ, Bethell D, Knight DW, Hutchings GJ (2011) Chem Eur J 17:6524
69. Miyamura H, Matsubara R, Kobayashi S (2008) Chem Commun 17:2031
70. Kaizuka K, Miyamura H, Kobayashi S (2010) J Am Chem Soc 132:15096
71. Suzuki K, Yamaguchi T, Matsushita K, Iitsuka C, Miura J, Akaogi T, Ishida H (2013) ACS Catal 3:1845
72. Zhu J, Faria JL, Figueiredo JL, Thomas A (2011) Chem Eur J 17:7112
73. Zhu J, Kailasam K, Fischer A, Thomas A (2011) ACS Catal 1:342
74. Shimizu K-I, Kon K, Seto M, Shimura K, Yamazaki H, Kondo JN (2013) Green Chem 15:418
75. Zhang G, Vasudevan KV, Scott BL, Hanson SK (2013) J Am Chem Soc 135:8668
76. Sun HY, Hua Q, Guo F-F, Wang Z-Y, Huang WX (2012) Adv Synth Catal 354:569
77. Raisanen MT, Al-Hunaiti A, Atosuo E, Kemell M, Leskela M, Repo T (2014) Cat Sci Technol 4:2564
78. Song H, Kang B, Hong SH (2014) ACS Catal 4:2889
79. Li R, Zhao J, Yang F, Zhang Y, Ramella D, Peng Y, Luan Y (2017) RSC Adv 7:51142
80. Rajabi F, Pineda A, Naserian S, Balu AM, Luque R, Romero AA (2013) Green Chem 15:1232
81. Hanson SK, Baker RT, Gordon JC, Scott BL, Sutton AD, Thorn DL (2009) J Am Chem Soc 131:428
82. Chen C, Liu B, Chen W (2013) Synthesis 45:3387
83. Liu L, Ma J, Ji L, Wei Y (2008) J Mol Catal A Chem 291:1
84. Cuihua B, Aiqin L, Xianfang Y, Hongli L, Yingwei L (2016) Green Chem 18:1061
85. Zhou YX, Chen YZ, Cao L, Lu J, Jiang HL (2015) Chem Commun 51:8292
86. Wei Z, Hongli L, Cuihua B, Shijun L, Yingwei L (2015) ACS Catal 5:1850–1856
87. Su H, Zhang KX, Zhang B, Wang HH, Yu QY, Li XH, Antonietti M, Chen JS (2017) J Am Chem Soc 139:811
88. Obermayer D, Balu AM, Romero AA, Goessler W, Luque R, Kappe CO (2013) Green Chem 15:1530
89. Phillip FC (1894) Am Chem J 16:255
90. Smidt J, Hafner W, Jira R, Sieber R, Sedlmeier J, Sabel A (1962) Angew Chem Int Ed Engl 1:80
91. Tsuji J (1984) Synthesis 1984:369
92. Mitsudome T, Umetani T, Nosaka N, Mori K, Mizugaki T, Ebitani K, Kaneda K (2006) Angew Chem Int Ed 45:481
93. Mitsudome T, Mizumoto K, Mizugaki T, Jitsukawa K, Kaneda K (2010) Angew Chem Int Ed 49:1238
94. Mitsudome T, Yoshida S, Tsubomoto T, Mizugaki T, Jitsukawa K, Kaneda K (2013) Tetrahedron Lett 54:1596
95. Hosokawa T, Nomura T, Murahashi S-I (1998) J Organomet Chem 551:387
96. Mitsudome T, Yoshida Y, Mizugaki T, Jitsukawa K, Kaneda K (2013) Angew Chem Int Ed 52:5961