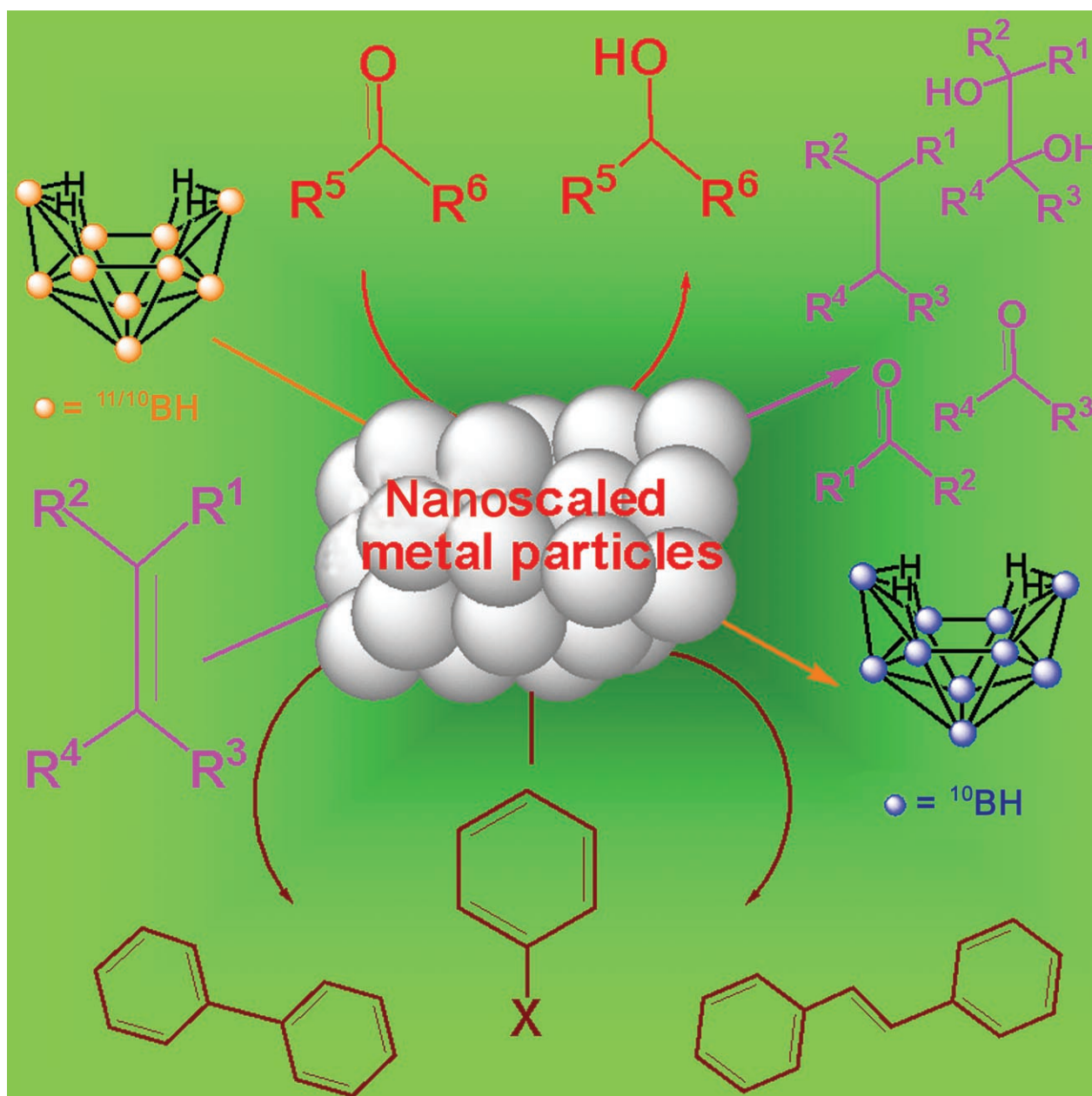


Latest Developments in the Catalytic Application of Nanoscaled Neutral Group 8–10 Metals

Yinghuai Zhu,^{*,[a]} Cjin Nong Lee,^[a] Richard A. Kemp,^[b, c] Narayan S. Hosmane,^[d] and John A. Maguire^[e]



Abstract: In the last few decades, the synthesis and catalytic application of nanoscaled particles prepared from Group 8–10 (formerly Group VIII B) elements have been widely explored and have achieved promising results. The innovative use of these nanoparticle catalysts may provide new opportunities in the efficient combination of conventionally used homogeneous and heterogeneous catalysts. Conventional homogeneous catalysts pose extraction and recycling difficulties when dealing with metal complexes and/or ligands, whereas heterogeneous catalysts generally require more pressing experimental conditions, such as high temperatures and high pressures, to be effective.

Therefore, to solve these problems, the synthesis and use of nanoparticle catalysts as replacements for conventional catalytic systems is a breakthrough owing to their improved handling and environmental and economic aspects. This Focus Review primarily addresses the catalytic applications of neutral Group 8–10 nanoparticles with an average size of less than 10 nm, and also includes a discussion of commonly used synthetic methodology.

Keywords: C–C coupling • ionic liquids • isotopic labeling • nanostructures • transition metals

1. Introduction

Homogeneous metal catalysis in synthetic organic chemistry is now so advanced that reagent combinations are available that can perform a huge spectrum of transformations thought to be impossible a few years ago.^[1] However, several practical problems can be encountered in the implementation of a homogeneous catalyst system upon scale-up and large-scale industrial utilization, particularly in the cost of catalyst components (both transition metal and ligand) and the difficulty faced in the separation and recycling of the

catalyst. On the other hand, heterogeneous catalysts have been widely used in industrial processes in applications as varied as alkylation with Y-type zeolites, hydration by silica-supported acids, and hydrogenation by various transition metals.^[2] However, for most heterogeneous catalysts, the reaction mechanisms are not known with a great deal of certainty. Furthermore, modification of the active centers of heterogeneous catalysts is difficult to achieve with precision. It is a significant challenge for current catalysis researchers to combine the advantages of both heterogeneous and homogeneous catalysis, as reported heterogenization processes such as the chemical immobilization of active organometallic catalysts or ligands onto various solid supports usually do not overcome problems such as the leaching of active centers and/or the lowering of activity.^[3]

Future advances in catalysis are highly dependent on the development of new catalytic materials with advanced design characteristics. Catalyst technology is constantly pushing towards smaller materials with improved properties, for example, activity and selectivity, to minimize waste. As a result of the development of advanced synthetic methodologies, transition-metal nanoparticles with average sizes of less than 10 nm and narrow size distributions can be conveniently prepared. Although the definition from the EU Commission acknowledges that nanotechnology can deal with objects on a scale of less than 100 nm, the transition-metal nanoparticles covered in this Focus Review are predominantly less than 10 nm in diameter.^[4] It is widely acknowledged that a smaller catalyst particle (<10 nm) leads to higher and more sustained activity relative to bulk heterogeneous catalysts; a particle of this diameter experiences no significant attrition.^[4] As a result, both the activity and the

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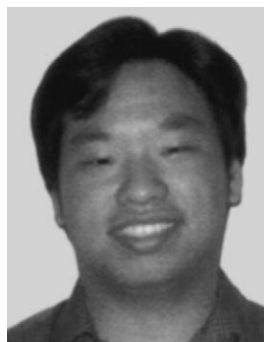
stability of a solid catalyst system suspended in the liquid phase can benefit greatly from the use of smaller catalyst particles. In recent years, the preparation and stabilization of nanoscale metal particles (<10 nm) has attracted much attention as the materials prepared have intriguing chemical and physical properties as well as a myriad of potential applications.^[4] With advances in the methods of fabricating nanomaterials, it has been possible to prepare “soluble” analogues of heterogeneous catalysts that might have properties intermediate between those of bulk metal and single metal particles. This characteristic is due to the high surface areas and high density of active sites.^[5] The application of transition-metal nanoparticles as catalysts for organic transformations has attracted widespread interest as nanoparticle-based catalytic systems can exhibit superior catalytic activities relative to the corresponding bulk materials.^[6] For example, Miyaura–Suzuki cross-coupling and Heck reactions are very versatile and useful tools in organic synthesis, and palladium complexes are important catalysts for these two reaction types. However, the relatively high price of the palladium complexes required has greatly limited the industrial implementation of the corresponding homogeneous reactions; some of the phosphine ligands are also air- and moisture-sensitive. Furthermore, similarly to other homogeneous-catalyst systems, the removal of ligands and ligand-degradation products derived from homogeneous catalysts often complicates workup and production isolation.^[7] Therefore, to avoid these issues, heterogeneous palladium catalysts have been developed over the last decade.^[8] Highly dispersed and stable Pd⁰ nanoparticles have been prepared on various supports such as mesoporous silica, dendrimers,

Abstract in Chinese:

近年来，第八副族金属纳米颗粒的合成及应用引起广泛关注。应用金属纳米颗粒催化剂利于综合均相及多相催化过程的可利因素。均相催化活性高，但回收及再利用较困难。多相催化剂易循环利用，但往往需要苛刻条件如高温，高压。且活化中性修饰较难，反应机理往往不太清楚。本综述主要概括第八副族金属纳米颗粒（<10 纳米）的制备及典型应用范例。



Yinghuai Zhu was born in China in 1969. He received his PhD in 1997 from Nankai Univ. in organometallic chemistry. He continued his studies as a Postdoctoral Fellow in boron chemistry with Prof. Narayan S. Hosmane at Northern Illinois Univ. and Prof. John A. Maguire at Southern Methodist Univ. in 2000. He joined the Institute of Chemical and Engineering Sciences in 2002 and is currently a Research Scientist. His research focuses on the design and synthesis of complexes as efficient catalysts for important organic reactions and biological applications.



Cjin Nong Lee was born in Singapore in 1982. He is now an undergraduate student in materials engineering at Nanyang Technological University. He joined Dr. Yinghuai Zhu's team in 2007 as part of an industrial attachment at the Institute of Chemical Engineering Sciences.



Richard Kemp received his PhD in 1982 from The Univ. of Texas, Austin under the direction of Prof. Alan H. Cowley in synthetic main-group chemistry. He then spent the next two decades working in industry at Shell Chemical Co. and Union Carbide Corp. in homogeneous and heterogeneous catalysis. Since 2001, he has been Professor of Chemistry at the Univ. of New Mexico as well as Principal Member of the Technical Staff at Sandia National Laboratories in Albuquerque, New Mexico. His current research interests are in the fundamental reaction chemistry of CO₂ and selective oxidation catalysis.



Narayan Hosmane was born in Gokarn, Southern India. He obtained a PhD in inorganic/organometallic chemistry in 1974 from the Univ. of Edinburgh (Prof. Evelyn Ebsworth). After a brief postdoctorate at Queen's Univ., Belfast (Prof. Frank Glockling), he eventually worked at several universities in the USA, including with Prof. Russell Grimes at the Univ. of Virginia. He finally moved to Northern Illinois Univ. in 1998, where he is now Distinguished Research Professor of Chemistry and Biochemistry. His research interests are in main-group organometallic chemistry and nanomaterials as drug-delivery vehicles for B and Gd neutron-capture therapy in cancer treatment.



John A. Maguire is Professor of Chemistry at Southern Methodist Univ. (SMU). He received his BS in chemistry from Birmingham Southern College in 1958 and his PhD in physical chemistry in 1963 from Northwestern Univ. He joined Southern Methodist Univ. as Assistant Professor of Chemistry and is now Professor of Chemistry. From 1976 to 1981 he was Associate Dean and then Dean of University College at SMU. His research interests are in the bonding, structure, and reactivity of carborane cage compounds. In 2002 he was appointed University Distinguished Teaching Professor.

ionic liquids, polymers, and so on, and these nanoparticles maintain high activities.^[9] The nanoparticles are also easily recovered by recycling processes such as magnetic attraction.^[10] As the length of this Focus Review is limited, nano-sized crystallographically ordered inorganic solids such as zeolitic aluminosilicates, transition-metal oxides, and immobilized homogeneous catalysts will not be included in this report. However, the synthesis and stabilization of neutral Group 8–10 (formerly Group VIII B) metal nanoparticles (G8-10NPs) will be briefly described, and their catalytic applications in organic reactions will be discussed in more detail.

2. Current Synthesis and Stabilization Methodologies of G8-10NPs

Several reviews and books have been published with regard to the synthesis, stabilization, and application of transition-metal-derived nanoparticles.^[11–14] It is well-recognized that the exact preparation process, as well as the stabilizer and support used, can have critical influences on the morphology, size distribution, and electronic properties of the nanoparticles produced,^[15–17] all of which are strongly related to their catalytic performance.^[14–17] One popularly used method of preparing catalytic G8-10NPs is the reduction of transition-metal salts or ligand-coordinated complexes in the presence of stabilizers, such as functional polymers, surfactants, or ionic liquids, to avoid particle aggregation.^[14,18,19] Conventional reductants include hydrogen, alcohols, borohydrides (e.g., NaBH_4 or KBH_4), formic acid, hydrazine, lithium, and others.^[11–14,20–28] For instance, well-dispersed ruthenium(0) nanoparticles with a mean diameter of around 2.4 nm and a narrow size distribution were successfully prepared in our laboratory by the reduction of precursor $[\text{CpRuCp}^*\text{-RuCp}^*]\text{PF}_6$ ($\text{Cp} = \text{C}_5\text{H}_5$, $\text{Cp}^* = \text{C}_5\text{Me}_5$) stabilized by the presence of an ionic-liquid agent, trihexyltetradecylphosphonium dodecylbenzenesulfonate.^[18] The Ru^0 nanoparticles stabilized with ethylene glycol were easily extracted into ionic liquids to form two layers. Owing to differences in the densities of the ionic liquids and ethylene glycol, the ionic liquid containing nano- Ru^0 could be either the top or the bottom layer of the biphasic mixture (Figure 1 a and b). For supported metal nanoparticles, commonly used methods of synthesis include 1) adsorption of previously prepared colloidal metal nanoparticles onto a high-surface-area solid support material,^[16] 2) use of impregnation techniques to immobilize suitable precursors followed by decomposition in situ by hydrogenation, thermolysis, photolysis, and so on,^[15–31] and 3) direct grafting of transition-metal nanoparticles onto the support.^[32,33] Notably, the nanoparticle size, shape, and stability, all of which play important roles in determining catalytic performance, can be precisely controlled by simple modification of the preparation conditions. Examples include reduction temperature, reaction time, concentration, and type of stabilizer and solution used.^[16] With the above methods, we prepared magnetic-nanoparticle-supported, ul-

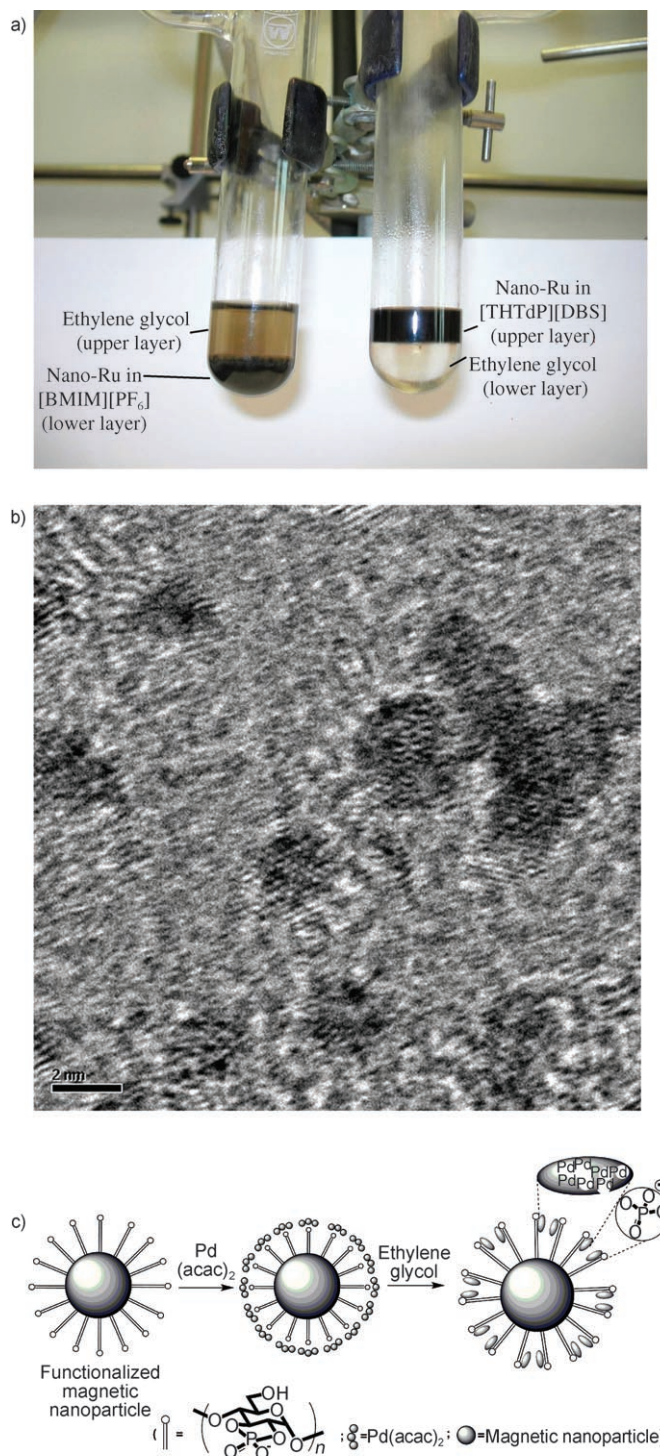


Figure 1. Ionic-liquid systems and Pd-supported magnetic nanoparticles. a) Ru nanoparticles in different ionic liquids.^[18] b) TEM picture of Ru nanoparticles.^[18] c) Synthesis of magnetic-nanoparticle-supported palladium nanoparticles.^[19] acac = acetylacetonate, BMIM = 1-*N*-butyl-3-methylimidazolium, DBS = dodecylbenzenesulfonate, THTdP = trihexyltetradecylphosphonium.

trasmall Pd^0 particles (< 1 nm) as catalysts. In this case, immobilized phosphate functional groups were used as stabilizing ligands (Figure 1 c).^[19] By utilizing recent developments

in materials chemistry, supports other than traditional mesoporous silica, alumina, or active carbon can now be used. New macromolecules, such as carbon nanotubes (CNTs;

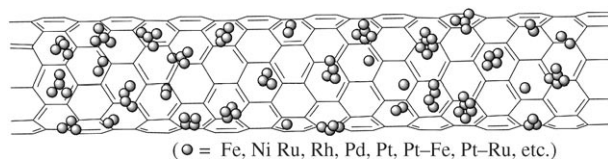


Figure 2. Carbon nanotubes as nanocatalyst support.

Figure 2), which might offer high chemical stability, high surface area, and good thermal stability,^[34–39] and dendrimers,^[40,41] have been used as supports for transition-metal nanoparticle catalysts with promising performances to date.

Other methods, such as UV photolysis,^[42] thermal decomposition,^[43] metal-vapor deposition,^[44] electrochemical reduction,^[45] sonochemical decomposition,^[46] microwave irradiation,^[47] and rapid expansion of solutions of supercritical fluids^[48] have also been successfully used to prepare G8-10NP-based catalysts.

Bi- and multimetallic G8-10NPs can be prepared similarly by using the above-mentioned synthetic routes for homometallic nanoparticles. In this area, significant contributions have been made, in particular, by Johnson and co-workers.^[29] Several types of bimetallic nanoparticles such as Ru₆Pd₆, Ru₃Pd, and related molecules have been prepared by the thermolysis of appropriate carbonylate precursors. These new nanoparticle catalysts have been used in organic reactions such as olefin hydrogenation.^[29]

3. Catalytic Applications of G8-10NPs

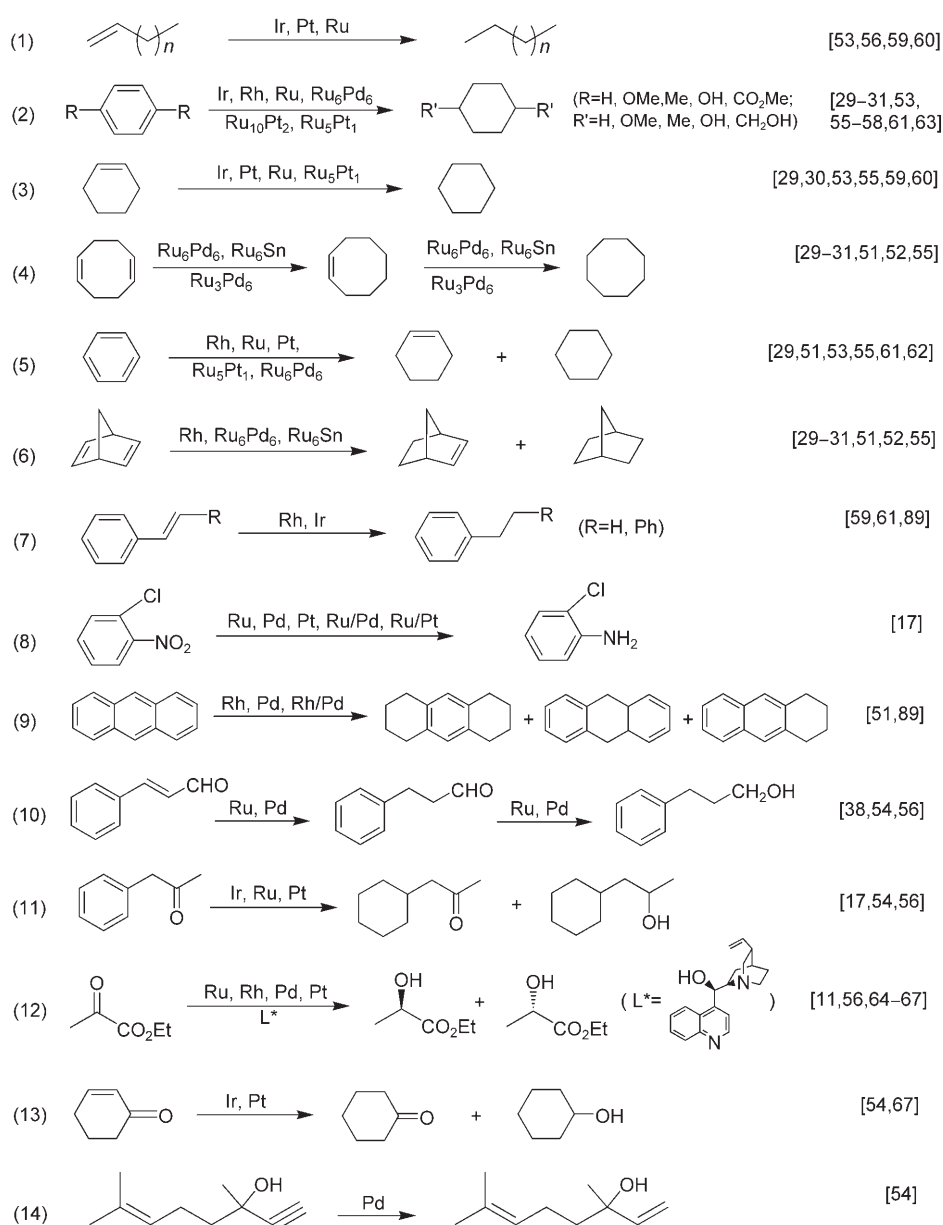
In recent years, the synthesis and application of metal nanoparticles to organic synthesis has been attracting more and more attention. Metal nanoparticles may have advantages and be developed into highly effective, selective, and environmentally benign catalysts. On the basis of a report from Business Communication Co., the global market for nanocatalysts, including enzymes, zeolites, and transitional-metal nanocatalysts, is expected to reach US\$5.0 billion in 2009.^[49] By now, thousands of research articles, review papers, and books have been published that discuss the range of catalytic applications of G8-10NPs in organic-molecule transformations.^[11–17,50–52] It is widely recognized that the catalytic performance of transition-metal nanoparticles is critically influenced by the exact reaction conditions used, such as size and shape of particles, support, and stabilizers, reaction temperature, reaction media, and the like.^[14–17] For example, Pt⁰ nanoparticles can have either tetrahedral, cubic, or spherical shapes, with average sizes of 4.8 ± 0.1, 7.1 ± 0.2, and 4.9 ± 0.1 nm, respectively.^[16] Platinum nanoparticles have been utilized to catalyze one-electron-transfer reactions between hexacyanoferrate(III) and thiosulfate ions to form hexacyanoferrate(II) and tetrathionate ions.^[16] Under the reaction

conditions, tetrahedral and cubic platinum nanoparticles strive to resemble spherical platinum nanoparticles because the latter have the lowest surface energy. “Near-spherical” nanoparticles are of modest catalytic activity and are most stable.^[16] It is difficult to compare fully and judge detailed catalytic performances for various reactions. In this Focus Review, we discuss generally examined organic transformations, including hydrogenation, C–C bond formation, redox reactions, and other unique reactions with G8-10NPs.

3.1. Catalytic Hydrogenation

3.1.1. Catalytic Hydrogenation of Alkenes, Alkynes, and Carbonyl Compounds

The catalytic hydrogenation of various unsaturated C=C, C≡C, and C=O bonds with G8-10NP catalysts have been widely investigated.^[11,17,51] Selected hydrogenation reactions that have been examined catalytically are listed in Scheme 1. The scheme indicates that different alkenes, alkynes, ketones, and aldehydes can be reduced to the corresponding alkanes and alcohols under mild conditions: low hydrogen pressures (≈1 atm) and low temperatures (at or near room temperature).^[11,17,51] When multiple unsaturated C–C bonds exist within the same molecule, such as in arenes and 1,5-cyclooctadiene, the molecule does not have to be hydrogenated fully. Partial hydrogenation can be achieved in high yields to produce cyclohexene and cyclooctene, respectively.^[38,50,51,53] For unsaturated ketones and aldehydes, the C=C bonds can be selectively hydrogenated to the saturated carbonyl compounds. As an example, with Pd MWCNTs (multi-walled carbon nanotubes) as the catalyst, it is possible to convert cinnamaldehyde into hydrocinnamaldehyde in yields as high as 78 % (Scheme 1, Equation (10)).^[38,54] Notably, bimetallic nanoparticles used as catalysts usually result in higher activities than the corresponding monometallic nanoparticles under the same reaction conditions.^[11,52] As an example, in the hydrogenation of either 1-hexene or 1-dodecene, the turnover frequency (TOF) for a bimetallic Pd–Ru nanoparticle catalyst is more than 10 times higher than for monometallic Ru and Pd nanoparticles alone.^[55] The improved activity may result from the active interaction of the bimetallic composition. Besides composition, the size and shape of metallic nanoparticles also play important roles in ultimate catalytic performance.^[16] Interestingly, substantial particle agglomeration has not generally been observed for G8-10NP catalysts. Normally, G8-10NP catalysts can be reused many times, even thousands of times, without dramatically losing catalytic performance.^[11,56–61] With the appropriate support and stabilizer, leaching of G8-10NP catalysts can be significantly decreased or even avoided.^[18,19,59] Importantly, by using G8-10NPs such as nano-Pt⁰, -Ru⁰, -Rh⁰, and -Ir⁰ as catalysts, the complete hydrogenation of arenes can be successfully achieved to produce saturated substituted cyclohexanes under mild conditions.^[53,54,60,62,63] For example, benzene was hydrogenated to cyclohexane with 100 % conversion by utilizing



Scheme 1. Catalytic hydrogenation of C=C, C≡C, and C=O groups. The references from which the examples are taken are given in square brackets on the right.

Pt⁰ nanoparticle catalysts with 2–3-nm diameters at 75 °C under 4 atm H₂ pressure in the absence of solvent.^[60]

Another interesting investigation is the asymmetric hydrogenation of C=O and C=N bonds with G8-10NP catalysts to produce optically pure alcohols and amines, respectively. It is well-recognized that the reduction of aldehydes, ketones, and imines to chiral alcohols and amines has been very established, and many notable homogenous and heterogeneous catalysts that give high yields (>95%) in these reductions already exist. However, problems are again faced with catalyst recycling and product separation. It was reported that the enantioselective hydrogenation of ethyl pyruvate to (*R*)-ethyl lactate (Scheme 1, Equation (12)) was achieved with 100% conversion and enantiomeric excesses (*ee*) of up

to 72% by using layered-double-hydroxide (LDH-Mg-Al)-supported Pt⁰ nanoparticle catalysts in the presence of the chiral inductor cinchonidine.^[64] The catalyst was recovered and reused for several cycles with no significant drop in activity.^[64] In another example, Pt⁰ nanoparticles (≈2.7-nm diameter) stabilized with the surfactant salt *N,N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium chloride also showed efficient activity for the asymmetric hydrogenation reaction in Scheme 1, Equation (12) in biphasic media under hydrogen pressure.^[65] The nano-Pt⁰ catalysts were recovered and used for additional runs with total conservation of activity and an enantioselectivity for (*R*)-ethyl lactate of up to 55% *ee* in aqueous media.^[65] Furthermore, a higher *ee* of 97% was reached by using Al₂O₃-supported Pt⁰ nanoparticle catalysts in MeOH/AcOH.^[65] Pd⁰ nanoparticles stabilized by chiral bisphosphine BINAP (2,2'-bis(diphenylphosphanyl)-1,1'-binaphthyl), with an average size of (2.0 ± 0.5) nm, were reported to be efficient catalysts for the asymmetric hydrosilylation of styrene and related olefins under mild conditions to give enantiometric excesses of 95% in approximately 90% yields. This catalyst is more active than the phosphine complex [Pd(PPh₃)₄].^[66]

Furthermore, high regioselectivities have also been achieved with G8-10NP catalysts. For instance, hydrogenation of cyclohexenone in the reaction shown in Scheme 1, Equation (13) can be well-controlled to produce cyclohexanone in 90% yield by using Ir⁰ nanoparticle ((2.3 ± 0.4)-nm diameter) catalysts with a selectivity of 83:16 (ketone/alcohol) under mild conditions.^[54] With Pt⁰ nanoparticles (0.6–2.6-nm diameter), an even higher selectivity of 92:5 (ketone/alcohol) was reached with 56% conversion for the same reaction.^[67] The C≡C bond can also be selectively hydrogenated in the presence of a C=C bond (Scheme 1, Equation (14)).^[54] For nano-Pd⁰ catalysts with an average diameter of 1–3 nm supported on nanostructured polymers, both high activity (>98% conversion) and selectivity (>95%) were achieved

for the reaction in Scheme 1, Equation (14).^[54] Interestingly, in results based on varying the support, high hydrogenation selectivities were also reached by using structurally related olefins such as allyl alcohol, 1-penten-3-ol, and 3-methyl-penten-3-ol. By using Pd⁰ nanoparticles of diameter 1–3 nm embedded in polyelectrolyte films of poly(acrylic acid) and polyethylenimine as catalysts, a high chemoselectivity ratio of 435:94:23 for the three alcohols mentioned above was reached in methanol/water (4:1 v/v).^[54] The selectivities are about two to three times higher than that with dendrimer-encapsulated Pd⁰ nanoparticles, which suggests that the polyelectrolyte films provide highly restricted access to the catalytic sites of the nanoparticles.^[54] From the limited reported data, it can be seen that G8-10NP catalysts are not as effective for enantio- and regioselective hydrogenation reactions relative to current homogeneous catalysts. However, given their potential advantages in catalyst recycling and other environmental factors, it is highly desirable to develop these G8-10NP catalysts further to improve their performance.

3.1.2. Catalytic Dehydrogenation of Alkanes and Alcohols

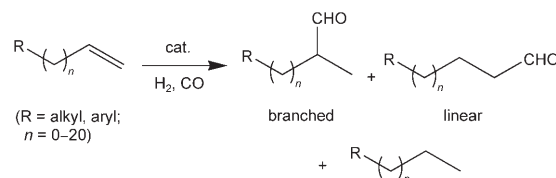
Dehydrogenation is the reverse process of hydrogenation. Although the same catalysts can be used for both processes, the detailed reaction conditions such as temperature, pressure, and even solvents might well be different. Besides the hydrogenation reactions shown above, G8-10NPs have also been reported to be effective catalysts for the dehydrogenation of alkanes and alcohols to produce the corresponding alkenes. These reports are quite important because of potential applications in new alternative-energy research, such as those seen in the hydrogen-energy economy. Pt⁰ nanoparticles (<1-nm diameter) were reported as efficient catalysts for the dehydrogenation of cyclohexane to produce hydrogen with the highest H₂-producing rate of 1060 mmol (g Pt)⁻¹ min⁻¹ at 328 °C.^[68] In this report, bimetallic Pt⁰–Rh⁰ nanoparticle catalysts of 4–5-nm diameter demonstrated higher activities than monometallic Pt⁰ nanoparticles of 2–3-nm diameter under the same conditions, as with the hydrogenation catalysts seen above.^[68] Catalysts prepared from either nanoscale Pt⁰ or Fe⁰–Co⁰ deposited in microchannel reactors are also active for the dehydrogenation of cyclohexene.^[68] Another recent example revealed that Pd⁰ or Ni⁰ nanocatalysts are highly active for the dehydrogenation of CH₄ to produce H₂. These catalysts decreased the decomposition temperature of CH₄ to 400–500 °C.^[69]

Notably, catalytic hydrogen production from ethanol steam reforming has promise as a clean energy source (C₂H₅OH + 3H₂O → 2CO₂ + 6H₂). This area is attracting more and more attention from both academic and industrial laboratories.^[70] Compared with other possible hydrogen sources, such as methanol, gasoline, natural gas, or ammonia, ethanol is less toxic, can be stored more easily and handled more safely, and can be obtained by fermentation of biomass. High activities for the catalytic steam reforming of ethanol have been found with Rh⁰, Ru⁰, Co⁰, Ni⁰, Pd⁰, and Pt⁰ nanoparticle catalysts.^[70–75] For these catalysts, oxide sup-

ports play an important role in setting catalytic performance. For instance, the activities of the catalysts decreased in the order Rh > Co > Ni > Pd on a MgO support.^[71] For Co⁰ nanoparticle catalysts, high activities for steam reforming of ethanol were found when either Al₂O₃ or SiO₂ supports were used.^[72] In general, high temperatures, low pressures, and high water-to-ethanol ratios in the feed favor hydrogen production; however, low temperatures favor the formation of by-products such as acetaldehyde and ethyl acetate.^[70–75] In the future, the problems of fast catalyst coking and by-product formation would need to be overcome before effective scale-up can occur.

3.2. Catalytic Hydroformylation

Catalytic hydroformylation (Scheme 2) plays a key role in both academic and industrial research. Currently, there are three types of commercially applied processes for hydrofor-



Scheme 2. Hydroformylation of α -olefins.

mylation:^[76] a phosphine-modified, cobalt-based system derived from [HCo(CO)₄], a rhodium-based catalyst system, and a biphasic homogeneous hydroformylation. Rhodium-derived catalysts are much more expensive than cobalt catalysts and have higher activities and linear product selectivities with smaller substrates. The most significant problem of using a rhodium catalyst such as [Rh^I(CO)₂(acac)] is the catalyst-recovery step. In general, even though current industrial processes have reached high standards of performance, both the rhodium and cobalt catalyst systems are expensive, and there is a desire to minimize these costs. Interestingly, G8-10NPs are also active catalysts for olefin hydroformylation. Nano-Pd⁰ catalysts supported on silica-gel composites are active for ethylene hydroformylation.^[77] In this case, the very fine nanoparticles of Pd⁰ (<2 nm in diameter) lead to higher activity (TOF = 16.1 × 10⁻² min⁻¹) than the relatively large particles of Pd⁰ of 5–7-nm diameter (TOF = (1.77–2.23) × 10⁻² min⁻¹) when evaluated at 373 K in a fixed-bed-type reactor.^[77] The hydroformylation of 1-alkenes can also be performed under solvent-free conditions by using Rh⁰ nanoparticle catalysts.^[78] There is a strong influence of the particle size on the hydroformylation reaction. When 5.0-nm Rh⁰ particles were used in the hydroformylation of 1-alkenes, aldehydes were generated as products without any hydrogenation of alkenes. With 1-hexene, a high linear/branched ratio of 25:1 was achieved by addition of the Xantphos ligand (9,9-dimethyl-4,5-bis(diphenylphosphanyl)-xanthene).^[78] Larger nanoparticles of Rh⁰ (15 nm) produced

only small amounts of aldehydes compared to experiments with smaller Rh⁰ (5.0 nm) nanoparticles, a result similar to those observed with a classical heterogeneous Rh/C catalyst precursor.^[78] Nano-Co⁰ particles with an average size of around 7.5 nm supported on carbon nanotubes have been reported to show high activity and regioselectivity for the hydroformylation of 1-octene. A high conversion of 65.4% was achieved with selectivity to the C₉ aldehyde of 81.2% at 5.0 MPa of CO/H₂ pressure at 130 °C.^[79]

3.3. Catalytic C–C Bond Formation

The formation of C–C bonds is a key methodology in synthetic organic chemistry for constructing new molecules. Generally used reactions include the Miyaura–Suzuki coupling reaction, the Heck reaction, carbene cycloaddition, and the like. Although the technology involved has been widely explored and excellently developed, there is still a desire to discover new methodologies for C–C cross-coupling reactions to impact the economics favorably and to aid in industrial implementation. Improved properties might include lower catalyst amounts coupled with higher and more reliable yields. Notably, most of the catalytic C–C cross-coupling reactions reported so far are ligand-based reactions.^[80] One main disadvantage of this approach is that additional steps are needed for attaching and removing the ligands. Furthermore, removal of the leached metals from the reaction solution is also critical to lower the possible toxicity of the product. Therefore, recycling of both ligand and metal is highly desirable for decreasing raw-material costs and engineering a “greener” process through lowering of the amount of waste chemicals for disposal, thus leading to less metallic pollution for both products and environment.

To overcome this problem, both palladium complexes and particles, which are the most popular catalysts in the Miyaura–Suzuki cross-coupling and Heck reactions, have been immobilized on various supports.^[81] The detailed progress in using G8-10NP catalysts for these types of reactions are discussed individually in the following sections.

3.3.1. Miyaura–Suzuki Coupling Reaction

This reaction was discovered in 1979 by Akira Suzuki; since then, the coupling reaction has been widely used in organic synthesis to form C–C bonds.^[82,83] Homogeneous catalysts have been primarily developed for this reaction. However, the limitations imposed by expensive catalysts and ligands, as well as the toxicity of phosphine-based ligands, have made the process difficult to scale up. To overcome these barriers, the exploration of new catalyst systems that combine high efficiency and ease of reuse is a highly attractive but daunting challenge. Palladium is the most commonly used catalyst for the cross-coupling reaction. Over the last few years, Pd⁰ nanoparticles have been immobilized on various supports with excellent results in terms of activity.^[19,24,84] A report from Cho et al. revealed that the cross-linked resin-supported Pd⁰ nanoparticles with average diameters of (7.4 ± 1.4) nm show high activity for the Miyaura–Suzuki

coupling reaction between substituted aryl bromides and aryl boric acids in water.^[81] A yield of 99% was achieved in 10 min with microwave irradiation for 4-acetylphenyl bromide and phenyl boric acid.^[24] Significantly, the catalyst is reusable with minimal palladium leaching in the filtrate (0.09 ppm from inductively coupled plasma with optical emission spectroscopy (ICP-OES)). We successfully immobilized ultrafine Pd⁰ nanoparticles (<1.0 nm) onto magnetic nanoparticles enriched with phosphate functional groups and demonstrated that these catalysts are effective for both the Miyaura–Suzuki cross-coupling and Heck coupling reactions (Figure 3).^[19] These supported catalysts can be well-

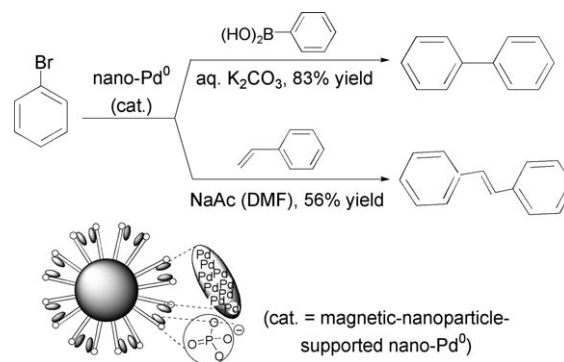


Figure 3. Magnetic-nanoparticle-supported ultrafine Pd particles as catalyst.^[19] DMF = *N,N*-dimethylformamide.

dispersed in both aqueous and organic phases to produce a false homogeneous catalyst system. Furthermore, this unique catalyst was easily separated from the reaction medium by magnetic attraction.

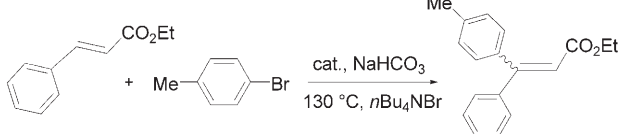
3.3.2. Heck Reaction

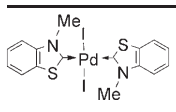
The Heck coupling reaction is a powerful method of preparing *trans* olefins. Aryl or vinyl halides with various functional groups have been shown to react with activated alkenes under Heck reaction conditions. Some articles detailing this chemistry have been published.^[85,86] As with the Suzuki coupling reaction, Pd–phosphine catalysts are normally used for the Heck reaction. Because of the adverse environmental effects related to phosphines, phosphine-free catalytic systems are desired. A number of Pd⁰ nanoparticles have shown both high efficiency and convenient recyclability.^[19,84,87–89] By using Pd⁰-nanoparticle-core dendrimers as catalysts, in which the average diameter of the Pd⁰ nanoparticles is 2.0 nm, Heck reactions of iodobenzene with styrene and ethyl acrylate were successfully achieved with TOFs of 1738 and 1066 h^{−1}, respectively.^[84] Compared with commercially available Pd/C catalysts (10 wt % Pd/C from Aldrich), in which 53% conversion was achieved for the Heck coupling reaction between iodobenzene and styrene to produce *trans*-stilbene after 24 h, the CNT-supported Pd⁰ nanoparticles showed a yield of 94% after 3 h under the same conditions.^[89] On the basis of a report by Caló et al., Pd⁰ nanoparticles are effective catalysts for Heck coupling between 1,1-

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and 1,2-disubstituted alkenes, such as *trans*-ethyl cinnamate, *n*-butyl methacrylate, and α -methylstyrene, and aryl bromides to produce trisubstituted alkenes and their isomers (Table 1).^[87,88,89] In the cases discussed, tetrabutylammonium

Table 1. Arylation of *trans* cinnamates.^[87]

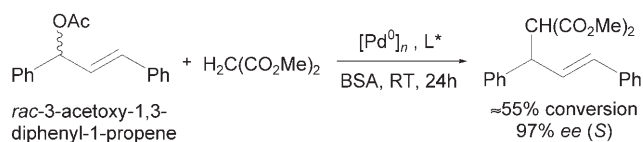


Catalyst	<i>t</i> [h]	Yield [%]	<i>E/Z</i>
	7	97	59:41
Pd(OAc) ₂ /PPh ₃	15	95	58:42
Pd ⁰ nanoparticles (2–6 nm)	1	95	< 99:1

acetate plays an important role in both catalyst formation and stereospecificity.

3.3.3. Carbene Cycloaddition, Vinyl Esterification, and Alkylation

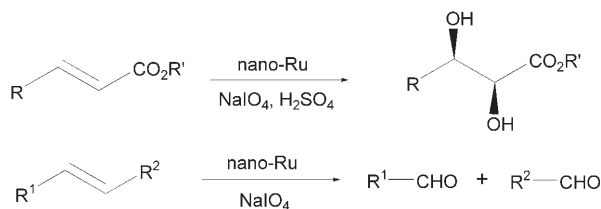
Beside the above well-studied reactions, Pd⁰ nanoparticles are also known to be effective catalysts for carbene cycloaddition, vinyl esterification, and alkylation. Ultrasmall (<1 nm) Pd⁰ particles were produced from the reduction of Pd(OAc)₂ in the presence of diazomethane.^[90] These Pd⁰ particles are active catalysts for the cyclopropanation of cyclohexenone by diazomethane.^[90] Silica-supported Pd⁰ particles with an average size of 10 nm in diameter were prepared by hydrogen reduction of [PdCl₄]²⁻ precursors. The catalyst is reported to be active for the synthesis of vinyl acetate from ethylene and acetic acid in the presence of oxygen.^[91] Another example with regard to the use of Pd⁰ nanoparticles in C–C formation is the catalytic asymmetric allylic alkylation reaction. In this case, the chiral xylofuranside diphosphite (L*) stabilized Pd⁰ particles with an average size of around 4 nm were prepared by reaction of [Pd₂(dba)₃] (dba = dibenzylideneacetone) with hydrogen at room temperature in a solution of THF containing the chiral ligand. In the presence of KOAc and *N,O*-bis(trimethylsilyl)acetamide in dichloromethane, the chiral-ligand-stabilized Pd⁰ nanoparticle catalysts revealed a high selectivity to the (*S*)-3-(dimethyl malonate)-1,3-diphenyl-1-propene product in the reaction of *rac*-3-acetoxy-1,3-diphenyl-1-propene with dimethyl malonate. The *S* product was formed with conversions as high as 55% and around 97% *ee* after 24 h at room temperature by using a Pd/L*/substrate ratio of 1:0.2:100 (Scheme 3).^[92] The reaction primarily proceeded with one substrate enantiomer, thus demonstrating a high degree of kinetic resolution in this system. As opposed to the homogeneous-catalyst processes, the Pd⁰ nanoparticle catalyst system excels in being recyclable and easily extracted from the reaction solution.^[93]



Scheme 3. An example of asymmetric alkylation.^[92] BSA = *N,O*-bis(trimethylsilyl)acetamide.

3.4. Redox Reactions

Selective catalysts are important for both partial oxidation of organic molecules and total oxidation of inorganic compounds. Ru⁰ nanoparticles with an average diameter of around 4 nm were prepared by reduction at 150 °C of RuCl₃·*x*H₂O in 1,2-propanediol in the presence of sodium acetate.^[94] The Ru⁰ nanoparticles had been successfully immobilized onto calcium hydroxyapatite by treating the Ru⁰ colloidal solution with calcium hydroxyapatite. The supported Ru⁰ nanoparticles were highly efficient for *cis* dihydroxylation of ethyl *trans*-cinnamate and oxidative cleavage of alkenes to produce aldehydes (Scheme 4).^[94] Nanostructured-



Scheme 4. Partial oxidation of C=C bonds.^[94]

polymer-supported Pt⁰ nanoparticles are highly effective for the oxidation of alcohols. In the presence of oxygen with the Pt⁰ nanoparticle catalyst, *L*-sorbose was oxidized to 2-keto-*L*-gulonic acid with conversions of 73–80% and selectivities of 75–94%.^[54]

In polymer-electrolyte fuel cells, the purification of hydrogen by the preferential catalytic oxidation of CO at low temperatures is an important practical process. It was reported that Pt⁰ nanoparticles (≈2.5 nm) supported on mesoporous silica (FSM-16) gave unprecedented selectivity (95% CO conversion) and durability (within 96 h) in the preferential oxidation of CO below 423 K.^[95] By using the isotopic tracer technique in IR spectroscopy, it was found that gas-phase O₂ is not directly utilized for the CO oxidation; rather, oxygen atoms of the mesoporous silica are incorporated into CO₂. These results suggest that CO oxidation is promoted by the attack of the surface OH groups onto CO adsorbed on Pt without the formation of water (Figure 4).^[95] In some oxidation processes, Pt⁰ and Pd⁰ nanoparticles have been synthesized by the combustion method and were shown to have higher catalytic activities. For the CO + O₂ reaction, 100% CO conversion occurred below 300 °C over α -Al₂O₃-supported Pt⁰, Pd⁰, and Ag⁰ nanoparticles with average sizes of 7, 12, and 20 nm, respectively, whereas 90% conversion was observed over Au⁰ (≈15 nm) at 450 °C.^[96] Similarly, for the removal of NO, which is an important aspect of the pu-

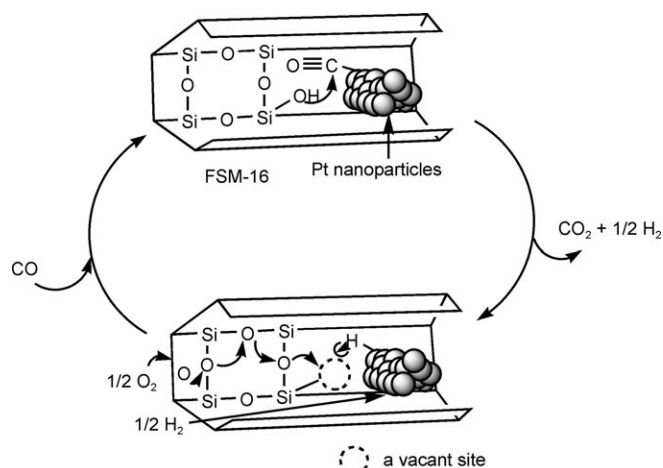


Figure 4. Preferential oxidation over Pt/FSM-16.^[95]

rification of industrial exhaust gases, 100% NO conversion was seen over 1% Pd/Al₂O₃ and 1% Pt/Al₂O₃ below 400 °C for the NO + CO reaction. Approximately 90% NO was converted into N₂ above 650 °C by using 1% Ag/Al₂O₃ and 1% Au/Al₂O₃.^[96] On the other hand, NO was selectively reduced by CH₄ to N₂, CO_x, H₂, and H₂O over γ -Al₂O₃-supported Ru⁰ nanoparticles.^[97] The amount of methane consumed increased with increasing temperature. When small particles of Ru⁰ (average size 4.8–7.6 nm) were used as catalysts, as the reaction temperature was raised from 450 to 600 °C, the concentrations of H₂ and CO increased from 0.16 to 0.42% and from 0.2 to 0.86%, respectively. In contrast, the concentrations of CO₂ and H₂O decreased with increasing reaction temperature. However, with larger Ru nanoparticles (average size 5 nm), CH₄ was selectively oxidized by NO to CO₂ and H₂O at 450 °C.^[97]

G8-10NP catalysts also play an important role in fuel-cell catalysis. Direct-oxidation methanol fuel cells have many advantages over other energy-generating devices, such as high efficiency of energy conversion, benign environmental effects, high energy densities, and availability of the fuel. With Ru⁰-decorated Pt⁰ nanoparticles, the obtained Pt⁰/Ru⁰ catalyst containing a Ru packing density of 0.4–0.5 was twice as active as the commercial 50:50 Pt/Ru alloy catalyst.^[98] This result is considered to be consistent with the “ensemble effect”, because on the decorated surface there is a static/dynamic distribution of island sizes that leaves enough room for ensemble availability. Another advantage is the maximization of Ru edge sites to secure the most effective CO removal. Well-dispersed Pt⁰/Ru⁰ nanoparticles with 2–3-nm diameters supported on MWCNTs exhibited a higher MeOH oxidization current of 26 mW mg⁻¹, and thus a higher performance, for direct MeOH fuel cells.^[99] Under the same conditions, a current power of around 21 mW mg⁻¹ was produced by using a commercially available E-TEK Pt–Ru/C catalyst.^[99]

Another well-developed fuel cell is the proton-exchange-membrane fuel cell, also known as the polymer-electrolyte-membrane fuel cell. The distinguishing advantages of this

type of fuel cell include lower operating temperatures and pressure ranges. However, a special polymer-electrolyte membrane is required. It is well-known that the performance of catalysts can be improved by producing a high loading of nanosized particles with uniform distributions over large-surface-area carbon supports.^[25] Carbon-supported Pt nanoparticles with an average size of 2.8 nm and a high loading of 39.5 wt% can be produced. As catalysts for fuel cells, it was found that, by operating in ambient O₂ at 70 °C, this system can deliver a high performance of more than 0.6 V at 1.44 A cm⁻².^[100] Monodispersed Pt⁰ nanoparticle (2–3 nm) catalysts supported on MWCNTs can also improve the power performance of polymer-electrolyte-membrane fuel cells. The power density (mW cm⁻²) of such fuel cells fabricated by electrophoretic deposition of Pt⁰ nanoparticles supported on MWCNTs was increased by approximately 36% compared to the same Pt loading (0.16 (mg Pt) cm⁻²) of Pt/C nanocatalysts.^[101] Furthermore, γ -Al₂O₃-supported Ru⁰ nanoparticles with an average size of 5 nm revealed unusually high activity for ammonia synthesis from hydrogen and nitrogen.^[16,102]

Another important, well-developed application is the direct formation of hydrogen peroxide (H₂ + O₂ → H₂O₂) catalyzed by G8-10NPs. H₂O₂ can be used in countless applications owing to its controlled, yet adaptable, stability. The hydrogen peroxide market has an annual world production of 3 million metric tons, and demand is growing at a steady pace of around 4% annually.^[103] Currently, hydrogen peroxide is produced on a large scale by the anthraquinone oxidation process with a high yield per cycle.^[104] However, many disadvantages exist in the current process, such as side reactions and complicated purification technology, so this route is not considered a green method. Thus, novel, cleaner methods for the direct catalytic synthesis of hydrogen peroxide from hydrogen and oxygen are highly desired with regard to minimizing operating costs. In recent research, Pd⁰ nanoparticles with average diameters of around 5 nm supported on resins functionalized with SO₃H groups demonstrated high catalytic performance with 46% yield.^[105] This catalyst system is very stable and reusable.^[105] The use of a multichannel microchemical reactor with a packed-bed catalyst such as Pd/Al₂O₃, Pd/SiO₂, or Pd/C may improve the implementation of this chemically simple and environmentally benign direct synthetic process.^[106] Interestingly, by using supercritical CO₂ as the reaction medium, H₂O₂ could also be synthesized directly from O₂ and H₂ over Pd- or Pt-loaded titanium silicate in high yields of up to 31.7% with an H₂O₂ selectivity of 56.1%.^[107]

3.5. Isotope-Exchange Reactions

Boron neutron-capture therapy (BNCT) is based on the nuclear reaction that occurs when ¹⁰B is irradiated with low-energy thermal neutrons to yield high-linear-energy-transfer alpha particles and recoiling ⁷Li nuclei.^[108,109] Clinical interest in BNCT has focused primarily on the treatment of high-grade gliomas and either cutaneous primaries or cerebral

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metastases of melanoma, as well as head, neck, and liver tumors more recently.^[110]

Over the past 20 years, various boron delivery agents have been designed and synthesized. However, to date, there is no single boron delivery agent that fulfils all the criteria of high tumor boron concentration, high selectivity towards tumor cells, and low toxicity. One of the problems is that only the ^{10}B isotope, which is of minor abundance ($\approx 20\%$), is therapeutically effective. To reach higher ^{10}B concentrations in the tumors, ^{10}B -enriched compounds are needed; thus, the search for convenient and effective methods of preparing such compounds is an extremely important area of both pharmacological and academic research interests. Decaborane(14) ($\text{B}_{10}\text{H}_{14}$) is one of the most useful precursor boron hydrides in the synthesis of high-boron-containing compounds. We developed a catalytic isotope-exchange method to prepare ^{10}B -enriched decaborane(14).^[18] Well-dispersed Ru^0 nanoparticles were successfully prepared by a reduction reaction of the precursor $[\text{Cp}^*\text{RuCp}^*\text{PF}_6]$ stabilized in the ionic-liquid agent trihexyltetradecylphosphonium dodecylbenzenesulfonate. The resulting Ru^0 nanoparticles were shown to catalyze the isotope-exchange reaction between ^{10}B -enriched diborane and naturally abundant $\text{B}_{10}\text{H}_{14}$ to produce highly ^{10}B -enriched ($\approx 90\%$) decaborane(14) products (Figure 5).

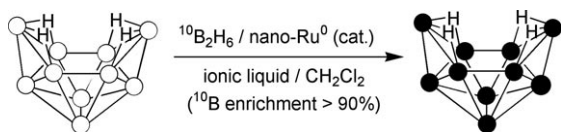


Figure 5. Nano-Ru-catalyzed isotope exchange.^[18] $\circ = {}^{11}\text{B}$, $\bullet = {}^{10}\text{B}$.

As with the homogeneous catalyst system $[\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Me})(\text{CH}_2\text{Cl}_2)][\text{BAR}_f]$ ($[\text{BAR}_f] = [\text{B}\{3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2\}_4]$),^[111] active-carbon-supported Pd^0 nanoparticles are efficacious for the catalytic isotope exchange between H_2 and D_2O in situ to produce D_2 gas. The nearly pure D_2 gas can be used to produce deuterated substrates that contain reducible functionalities within the molecules.^[112] Besides Pd^0 nanoparticles, high performances for H/D isotope exchange were also found by using Pt, Rh, Co, and Ni nanoparticle catalysts, and the detailed preparative applications of the H/D-exchange reaction was reviewed recently.^[113]

4. Summary and Perspectives

In conclusion, in research into metal-nanoparticle-based catalysis, the preparation and stabilization of nanoparticles with controlled size and composition, such as alloys or core-shell particles, are of great interest and provide significant challenges. Changes in composition can help to control reactivity in catalytic and optical applications.^[114] Generally, the particle size is closely related to the exact preparation process used. With regard to activity alone, in most cases metallic-nanoparticle-derived catalysts cannot yet compete with

homogeneous catalysts. However, with the great advancements in nanotechnology in modern science, the need for environmentally benign catalysts, and the economic considerations of the future, the field of G8-10NP catalysts is promising and is ripe for advancement. Presently, there are many existing novel methods of synthesizing and stabilizing G8-10NP catalysts. Compared with conventional heterogeneous catalysts, G8-10NP catalysts can be more effective in the synthesis of desired products, mainly due to their large surface areas.^[6] Even though G8-10NP catalysts are becoming more and more effective, they have still not been developed adequately. Therefore, it may take decades to replace the existing conventional catalysts with nanoparticle catalysts for large-scale industrial reactions. For instance, adequate size control of nanoparticles is still lacking, and only for commonly used nanocatalysts such as Ni^0 nanoparticles has adequate research been done.^[23] Furthermore, G8-10NPs that contain stabilizers might make the materials unsuitable for applications involving electron transfer and catalysis because the stabilizers can strongly modify physical and chemical properties.

Scale-up problems would also need to be addressed. The synthesis should be reproducible and consistent, and the characterization and physical properties should be studied.^[57] G8-10NP catalysts have to be scaled-up effectively to affect industrial production and further impact our society and standard of living.^[115] Even though there are studies that indicate the validity of using G8-10NP catalysts, there are also technical issues that need to be improved with regard to catalyst recycling. For instance, it was found that Pd^0 nanoparticle catalysts require effective agents to remove them from the reaction solutions.^[116] These reagents might be as harmful and expensive as those required to remove homogenous complexes from the reaction mixture, thus eliminating any advantage in catalyst removal of nanoparticles over homogeneous catalysts. There are still many as-yet-unknown effects and incompatibilities of the use of metal-nanoparticle catalysts, therefore, more research and evaluation must be done to improve this breakthrough catalysis technology further.

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