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Chemical Synthesis of Complex Molecules Using Nanoparticle Catalysis

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1. INTRODUCTION

The emerging field of nanoparticle catalysis represents a burgeoning area with increasing use in chemical synthesis,[1−4] as a recent SciFinder search shows exponential growth of literature reports during the past decade (Figure 1).[5] This rapidly expanding research subject has been built upon fruitful multidisciplinary collaborations between scientists in nanosciences and organic chemistry as well as the remarkable catalytic activities and selectivities of nanometric materials. Such features closely relate to the intrinsic size and shape-dependent properties[6,7] of nanoparticles, which may be subtly tuned by selection and modifications of preparation conditions, support materials, and capping agents. In addition, although widely utilized homogeneous catalysts remain as synthetic chemists' most powerful resources, heterogeneous, nanoparticle catalysis features the possibility for catalyst recycling, continuous processing, and ease of separation,[8] thereby offering green and cost-effective alternatives. Despite the aforementioned promising attributes, nanoparticle catalysts have not yet found broad applications in complex molecule synthesis,[9,10] with most applications thus far limited to cross-couplings[11] and oxidations/reductions.[12] In this Viewpoint article, we outline select examples employing nanoparticle catalysts to create new chemical bonds, with a special emphasis on applications and opportunities in complex molecule synthesis.

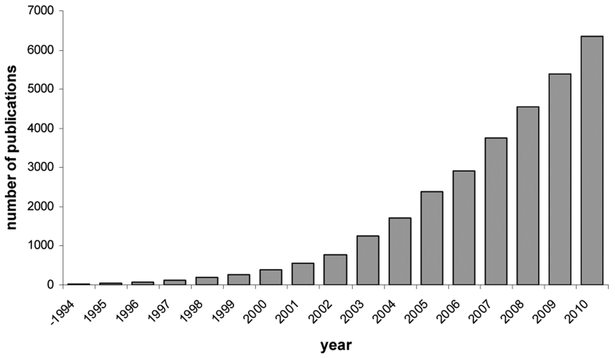
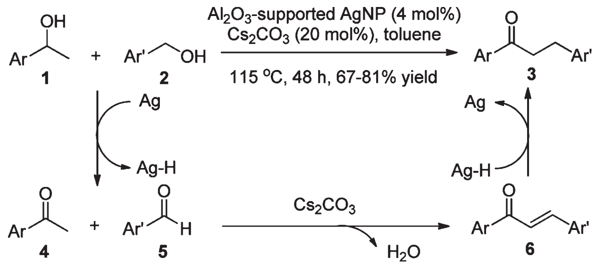


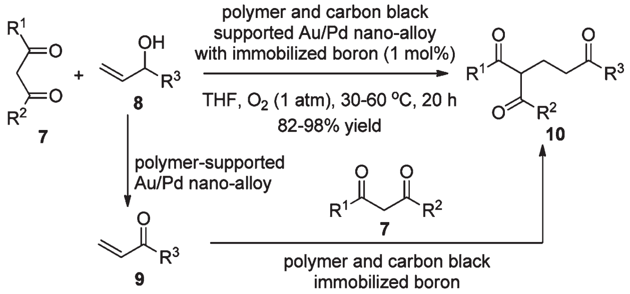
Figure 1. Publications on nanoparticle catalysis from 1994 to 2010.

2. REPRESENTATIVE APPLICATIONS OF NANOPARTICLE CATALYSIS IN ORGANIC SYNTHESIS

Scheme 1. AgNP-Catalyzed Coupling of Alcohols



Scheme 2. Sequential Oxidation/Michael Additions of Allylic Alcohols



2.1. Development of Tandem Reactions Based on Nanoparticle-Catalyzed Transformations. A number of notable studies have established nanoparticle-catalyzed cascade reactions, demonstrating an efficient approach to rapidly synthesize complex molecules from simple starting materials. The development of such tandem processes has also considerably broadened the utility and versatility of nanoparticle catalysis. For example, oxidations of alcohols to carbonyl compounds catalyzed by metal nanoparticles have been extensively investigated in the literature[12] and have been frequently employed in tandem reaction processes. Shimizu and co-workers (Scheme 1)[13] developed redox couplings of primary and secondary alcohols **1** and **2** catalyzed by alumina-supported silver nanoparticles (AgNPs) in combination with a mild base (cesium carbonate) to afford ketones **3**. The AgNP catalyst served dual roles in this highly creative tandem process, which entailed AgNP-catalyzed dehydrogenation of alcohols[14,15] **1** and **2** in the absence of molecular oxygen, base-mediated Claisen−Schmidt condensation of the derived carbonyl compounds **4** and **5**, and AgNP-mediated hydrogenation of the resulting α,β-unsaturated ketones **6**. Alcohols bearing α-aryl or heteroaryl groups generally afforded higher yields than alkyl-substituted substrates, likely because of the inherent limitations

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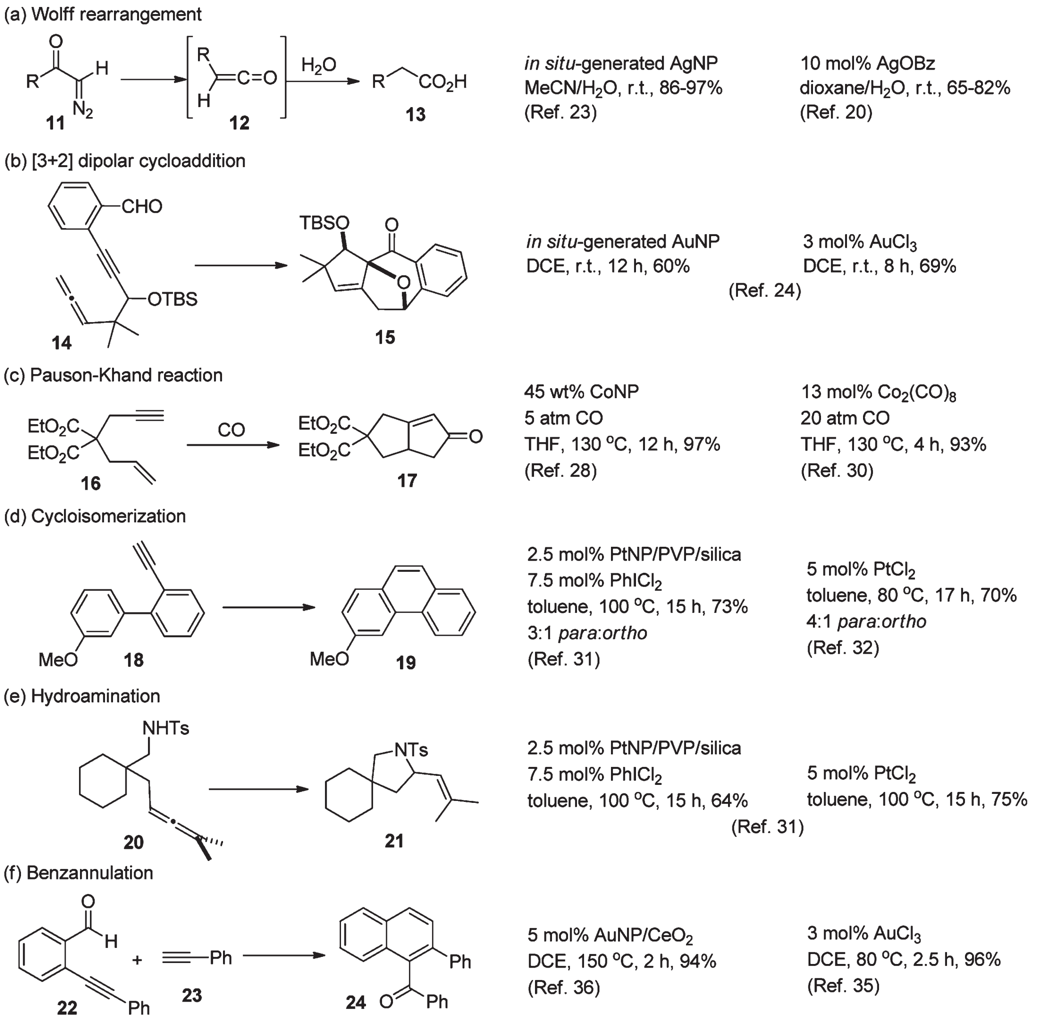
Scheme 3. Select Examples of Nanoparticle Catalysis from the Recent Literature


(a) Wolff rearrangement

in situ-generated AgNP
MeCN/H_2O, r.t., 86-97%
(Ref. 23)

10 mol% AgOBz
dioxane/H_2O, r.t., 65-82%
(Ref. 20)

(b) [3+2] dipolar cycloaddition

in situ-generated AuNP
DCE, r.t., 12 h, 60%

3 mol% $AuCl_3$
DCE, r.t., 8 h, 69%

(Ref. 24)

(c) Pauson-Khand reaction

45 wt% CoNP
5 atm CO
THF, 130 °C, 12 h, 97%
(Ref. 28)

13 mol% $Co_2(CO)_8$
20 atm CO
THF, 130 °C, 4 h, 93%
(Ref. 30)

(d) Cycloisomerization

2.5 mol% PtNP/PVP/silica
7.5 mol% $PhICl_2$
toluene, 100 °C, 15 h, 73%
3:1 *para*:*ortho*
(Ref. 31)

5 mol% $PtCl_2$
toluene, 80 °C, 17 h, 70%
4:1 *para*:*ortho*
(Ref. 32)

(e) Hydroamination

2.5 mol% PtNP/PVP/silica
7.5 mol% $PhICl_2$
toluene, 100 °C, 15 h, 64%

5 mol% $PtCl_2$
toluene, 100 °C, 15 h, 75%

(Ref. 31)

(f) Benzannulation

5 mol% AuNP/CeO_2
DCE, 150 °C, 2 h, 94%
(Ref. 36)

3 mol% $AuCl_3$
DCE, 80 °C, 2.5 h, 96%
(Ref. 35)

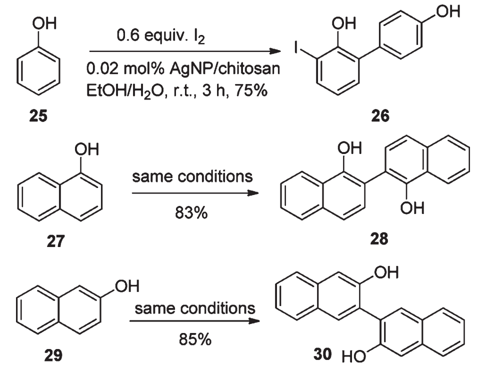
of the Claisen–Schmidt condensation. In addition, the supported AgNP catalyst displayed a high turnover number (TON) of up to 800 and remained active after two recycles.

Kobayashi and co-workers (Scheme 2)[16] demonstrated a tandem aerobic oxidation–Michael addition process involving oxidation of allylic alcohol **8** followed by 1,4-addition of 1,3-dicarbonyl derivative **7** to Michael acceptor **9**. This multicatalytic reaction[17] was built upon authors' earlier studies on polymer incarcerated gold nanoparticles (AuNPs)[18] and a polymer/carbon black-incarcerated boron catalyst that promotes alcohol oxidation and Michael addition, respectively. The latter catalyst was prepared from $NaBH_4$ and PEGylated polystyrene to afford an immobilized boron species which was characterized as a tetravalent borate. The addition of porous carbon black as a support material optimized the catalyst preparation by reducing polymer cross-linking. Accordingly, a hybrid, heterogeneous catalyst containing polymer-incarcerated, bimetallic Au/Pd nanoclusters and boron was created and showed excellent dual catalytic activities after six recycles. The new catalyst also exhibited a broad substrate scope, including cyclic, aliphatic, and aromatic-substituted starting materials. Since the heterogeneous support materials may minimize possible interactions and side reactions among multiple catalysts, the development of hybrid, supported catalysts containing orthogonal components should find broad applications in the synthesis of complex molecules.

2.2. Conversion of Homogeneous to Heterogeneous Reactions Employing Nanoparticle Catalysis. Another productive strategy for development of nanoparticle catalysis has taken advantage of the homogeneous transition metal catalysis. Reactions known to be catalyzed by transition metal complexes can also be facilitated by metal nanoparticles containing the same metal. This hypothesis has been proven true in many cases, as highlighted in Scheme 3 with direct comparisons of nanoparticles and transition metal catalysts made for each reaction. In addition, heterogeneous nanoparticle catalysts have exhibited the capability of offering superior catalytic activities through artful design and modifications. It should be noted, nonetheless, that minimizing the possibility of nanoparticle leaching has become increasingly crucial to establish truly heterogeneous catalysis.[19]

In situ-generated nanoparticles in solution have shown remarkable catalytic properties in complex molecule synthesis. For example, the Wolff rearrangement has been conventionally initiated by thermal energy, UV light, and transition metal catalysis, including silver(I) salts.[20] Sudrik and co-workers (Scheme 3a)[21−23] found that AgNPs also served as an effective catalyst for rearrangement of diazo compounds **11** to form ketene intermediates **12**,

Scheme 4. AgNP-Catalyzed Oxidative Coupling of Phenols

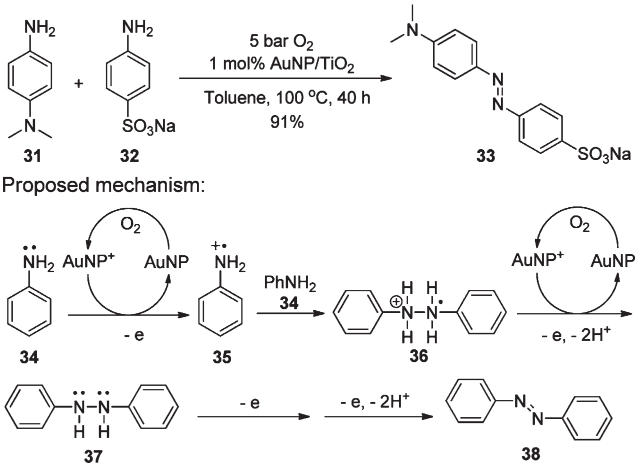


which further reacted with water to afford carboxylic acids **13**. The catalytically active AgNPs were generated in situ by chemical (e.g., triethylamine) or electrochemical reduction of silver(I) precursors. Another example by Han and co-workers (Scheme 3b)[24] showed that both in situ-generated AuNPs and homogeneous $AuCl_3$[25−27] catalyzed tandem alkyne activation/benzopyrylium formation/[3 + 2] dipolar cycloaddition of **14** to construct natural product-like polycycle **15** in a single step. In both studies, nanoparticles were unambiguously characterized by a number of instrumental analyses, including UV−vis spectroscopy, powder X-ray diffraction, and transmission electron microscopy. However, using in situ-generated nanoparticles as catalysts has complicated accurate evaluations of the reactions' heterogeneity and nanoparticles' activity in terms of catalyst loading and TON. In light of the notable reaction complexity achieved in their studies, future investigations are warranted on related reactions employing supported nanoparticle catalysts.

In 2001, Chung and co-workers (Scheme 3c),[28] reported Pauson−Khand reactions catalyzed by cobalt nanoparticles (CoNPs). Building upon earilier studies using mesoporous silica and charcoal-supported cobalt catalysts,[29,30] the CoNP catalyst exhibited improved activity for the intramolecular Pauson−Khand reaction of enyne **16** under a pressurized CO atmosphere. In addition, four catalyst recycles were conducted without particle agglomeration or loss of activity. Extending the CoNP catalyst to intermolecular reactions between norbornadiene and terminal alkynes afforded near quantitative yields.

Toste, Somorjai, and co-workers (Scheme 3d, e)[31] recently reported the design and synthesis of electrophilic platinum nanoparticles (PtNPs), which were capped with either polyamidoamine dendrimers or polyvinylpyrrolidone (PVP) and further deposited onto mesoporous silica. The supported PtNPs initially showed no catalytic activity until the authors creatively devised an oxidative treatment of the nanoparticles employing a hypervalent iodine-based oxidant ($PhICl_2$). This mild oxidant selectively oxidized more than 25% of the Pt(0) atoms in the supported nanoparticles to higher oxidation states, as confirmed by X-ray photoelectron spectroscopy (XPS), thereby converting the PtNPs into highly active electrophilic catalysts. This novel heterogeneous catalyst enabled a range of cyclization reactions, including the hydroarylation of alkyne **18**[32] and hydroamination of allene **20** via π-bond activation. In addition, the heterogeneity of the oxidized PtNP catalyst was unambiguously established by the "filtrate transfer" test.[33] This work is of particular impact because of the crafty postsynthetic modifications that induced the desired properties onto otherwise inactive nanoparticle catalysts.[34]

Scheme 5. AuNP-Catalyzed Synthesis of Aromatic Azo Compounds

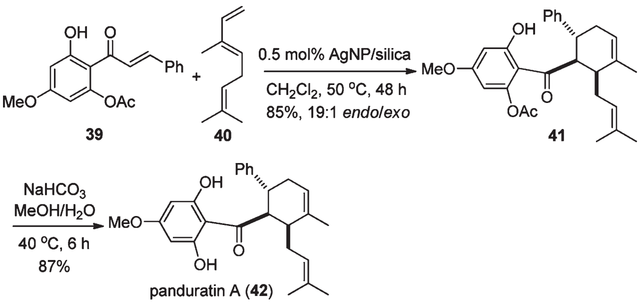


Inspired by an $AuCl_3$-catalyzed intermolecular benzannulation between *o*-alkynylbenzaldehydes and alkynes,[35] Garcia, Corma, and co-workers (Scheme 3f)[36] developed a reusable cerium oxide-supported AuNP catalyst that is now commercially available. The catalyst efficiently facilitated the formation of naphthalene **24** from precursors **22** and **23** in near quantitative yield[37] and was validated to be heterogeneous by both the "filtrate transfer" test[33] and elemental analysis of the reaction solution. A series of in-depth control experiments led to interesting observations that product **24** was obtained in 94% yield using the optimal catalyst containing 4.5 wt % (wt %) of AuNPs supported on CeO_2, in comparison with only 67% yield with 1.8 wt % AuNP/CeO_2 (both reactions were conducted under the otherwise same conditions with 5 mol % catalyst loading based on the amount of AuNPs). The same trends were also observed employing other support materials. The authors reasoned that most support materials can also function as adsorbents of organic molecules. Therefore, a higher amount of support materials was added to reactions when using catalysts with lower AuNP content, which caused decreased yields.

2.3. Exploration of Novel Activities of Nanoparticle Catalysts. In contrast to the homogeneous catalysis that has been extensively applied to a wide range of reaction types,[38] the identification of new catalytic activities of nanoparticles is highly underdeveloped. A brief survey of known nanoparticle-catalyzed transformations[1] has revealed that most of these reactions involve redox processes, which is echoed by the distinctive electrochemical properties of nanoparticles, including size and shape-dependent redox potentials[6] and multiple available oxidation states.[39,40] On the basis of these promising characteristics, nanoparticle catalysis should offer broad opportunities for mining new chemical transformations; in particular, those that enable the synthesis of otherwise challenging complex molecules.

Chattopadhyay and co-workers (Scheme 4)[41] reported oxidative couplings of phenols catalyzed by chitosan-supported AgNPs. In the presence of molecular iodine as an oxidant, unsubstituted phenol (**25**) underwent an iodine-incorporated, oxidative C−C coupling to afford biphenyl **26** in 75% yield. The products of the AgNP-catalyzed oxidative couplings were highly regioselective and substrate-dependent, with α- (**27**) and

Scheme 6. AgNP-Catalyzed Diels−Alder Cycloaddition of 2′-Hydroxychalcones



β- (**29**) naphthols affording exclusive 2,2′- (**28**) and 3,3′- (**30**) binaphthols, respectively, under the same conditions. The formation of binaphthol **30** differed in the regioselectivity for oxidative coupling of **29** using homogeneous catalysis.[42−46] These intriguing observations implied subtle mechanistic variations related to specific phenol starting materials, which warranted further investigation. In addition to the above notable features, the novel AgNP-catalyzed reactions showcased low catalyst loading and mild reaction conditions.

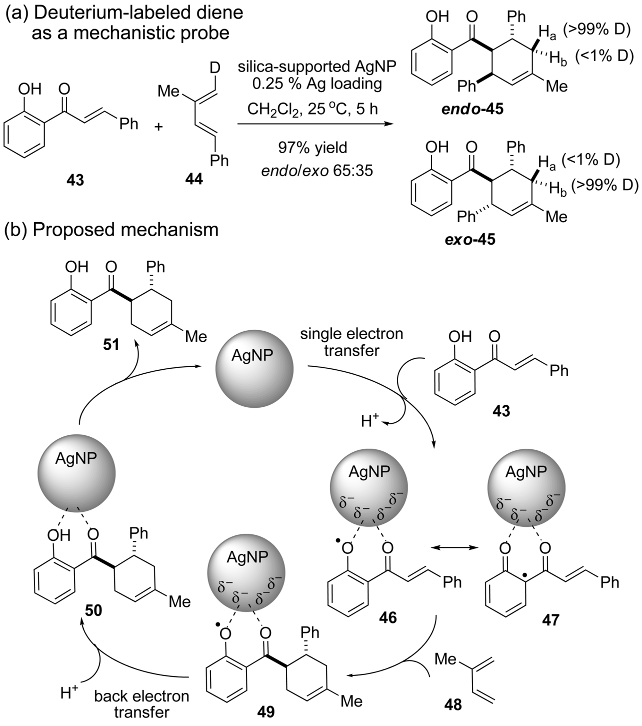
Aromatic azo compounds have broad industrial applications, including drugs, dyes, and food additives.[47] Corma, Garcia, and co-workers (Scheme 5)[48] developed a catalytic, oxidative synthesis of azobenzenes directly from anilines, which represented a major improvement in comparison with traditional synthetic methods.[49−51] Employing the commercially available titanium dioxide-supported AuNPs as catalyst and molecular oxygen as terminal oxidant, a number of symmetrically substituted azobenzenes were prepared in >90% yield, regardless of the electron-donating or -withdrawing substitutions of the starting materials. Notably, the reaction between equimolar electron-rich (**31**) and electron-poor (**32**) anilines afforded unsymmetrical product **33** (methyl orange) in 91% yield in a single step.

The proposed reaction mechanism entailed AuNP-mediated single-electron transfer (SET) of aniline **34** to generate radical cation **35**, followed by formation of intermediate **36** through the coupling between **35** and aniline **34**. Key supporting evidence included electron paramagnetic resonance (EPR) data for radical trapping of **35**.[52] Subsequent AuNP-mediated, stepwise oxidative electron transfer processes afforded hydrazine **37** and, finally, the desired azobenzene **38**.

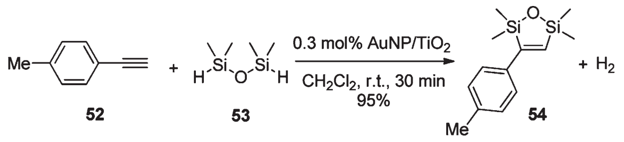
Porco and co-workers (Scheme 6)[53] recently demonstrated the utility of silica-supported AgNPs as an active catalyst for Diels−Alder cycloadditions of 2′-hydroxychalcones, a biomimetic and straightforward access to the core structure shared by over 50 biologically active natural products.[54] In this study, the authors accomplished the total synthesis of panduratin A (**42**), establishing the first example of a natural product synthesis employing nanoparticle catalysis. The key AgNP-catalyzed cycloaddition step was carried out using 0.5 mol % catalyst loading with chalcone **39** and the acid-labile trans-*β*-ocimene (**40**) in 85% yield and 19:1 d.r., thereby showcasing the catalytic activity and selectivity that has not been achieved by other methodologies.[55] Final acetate deprotection of cycloadduct **41** afforded the natural product **42** in 87% yield.

In addition, a series of mechanistic studies were conducted, including EPR measurements of radical trapping (confirming SET processes between AgNPs and 2′-hydroxychalcones) and deuterium-labeling experiments between chalcone **43** and deuterium-labeled diene **44** (Scheme 7a), supporting a concerted cycloaddition mechanism. These results suggested a working mechanism (Scheme 7b) starting with proton removal and SET from the adsorbed chalcone **43** to AgNPs. The resulting AgNP-stabilized phenoxyl radical **46** and its resonance form, **47**, can further undergo concerted cycloaddition with diene **48** to generate intermediate **49**, which afforded cycloadduct **51** via back electron transfer, protonation, and product desorption.

Scheme 7. Mechanistic Evidence and Proposed Mechanism for AgNP-Catalyzed Diels-Alder Cycloadditions



Scheme 8. AuNP-Catalyzed Synthesis of Dihydrooxadisiloles via Oxidative, Formal [3 + 2] Cycloadditions



Stratakis and co-workers (Scheme 8)[56] have reported a AuNP-catalyzed dehydrogenative, formal [3 + 2] cycloaddition between tetramethyldisiloxane **52** and acetylene **53**, which was conducted at room temperature with 0.3 mol % catalyst loading, leading to the production of dihydrooxadisole **54** in 95% isolated yield. The substrate scope of the methodology was established employing a range of functionalized aromatic, aliphatic, and internal alkynes. Generally, most reactions were completed within an hour, regardless of the electron-donating or -withdrawing substitutions of the alkynes. In comparison, starting materials **52** and **53** underwent alkyne hydrosilylation catalyzed by homogeneous *t*-Bu$_3$P-modified Pt(0) catalyst,[57] thereby highlighting the unique catalytic activity of the AuNPs.

3. SUMMARY AND FUTURE OUTLOOK

In this Viewpoint article, we have briefly summarized the utility of nanoparticle catalysis in organic synthesis through a critical overview based on recent literature examples. With increasing research endeavors being devoted to this field, new methodology development based on nanoparticle catalysis is emerging as a valuable addition to chemists' existing tools for complex molecule synthesis.

As outlined in this article, an evaluation of the possibility of catalyst leaching is crucial for the investigation of supported nanoparticle catalysts. Current studies employ mainly the "filtrate transfer" test,[33] elemental analysis of the reaction solution, or both to determine catalyst leaching. In addition to these indirect methods, real-time monitoring of catalyst surface using in situ X-ray absorption spectroscopy techniques provides unambiguous proof of catalyst heterogeneity.[58−60] Although there is no strict rule for the nanoparticle-catalyzed reactions, the absence of evidence against catalyst leaching may lead to questioning of reaction heterogeneity as well as the identity of actual catalytic species.

Future development of nanoparticle catalysis may also significantly benefit from further understanding of reaction mechanisms that will ultimately require interdisciplinary collaborations; for example, between organic chemists and material scientists. Such mechanistic studies may include experiments on reaction kinetics, theoretical modeling, catalyst surface characterization, and validation of reaction intermediates.

In the future, we anticipate further discovery of new nanoparticle catalysts, including bimetallic and hybrid systems,[61,62] and their applications in complex molecule synthesis in an effort to identify novel chemical reactions and tandem reaction sequences. Such opportunities should offer a strong stimulus to the continuing efforts in this vigorously advancing area.

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(33) The "filtrate transfer" test refers to the following experimental conditions: (1) initiate a nanoparticle-catalyzed reaction under normal conditions; (2) interrupt the reaction before completion by removing the heterogeneous catalyst (usually by filtration or centrifugation); (3) treat the filtrate under normal reaction conditions without any heterogeneous catalyst; and (4) if the reaction conversion in the filtrate remains unchanged over the usual reaction completion time, then the active catalyst is considered to be heterogeneous with minimal leaching.

(34) This strategy has been extended to palladium nanoparticles, which exhibit superior catalytic activity for electrophilic reactions compared with homogeneous Pd catalysts. See: Huang, W. Y.; Liu, J. H. C.; Alayoglu, P.; Li, Y. M.; Witham, C. A.; Tsung, C. K.; Toste, F. D.; Somorjai, G. A. *J. Am. Chem. Soc.* **2010**, *132*, 16771.

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