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Nanosilver As A New Generation of Silver Catalysts in Organic Transformations for Efficient Synthesis of Fine Chemicals

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Among the metal-based nanoparticles, silver nanoparticles catalysis has been of great interest in organic synthesis and has expanded rapidly in the past ten years because of nanosilver catalysts' unique reactivity and selectivity, stability, as well as recyclability in catalytic reactions. As can be seen from the research results reported in this critical review, the application of heterogeneous silver-based nanoparticles to general organic reactions has proved to be an effective strategy in the development of highly efficient organic transformations in term of efficiency and selectivity. In particular, this review revealed the powerful potential of nanosilver catalysis in total synthesis of natural products and pharmaceutical molecules.

1. Introduction

As it is known to all, the chemical community has witnessed an explosion of investigation and interest in the field of nanoscience and nanotechnology in the past decades.[1] The numbers of publications dealing with metal nanoparticles (1-100 nm) has increased almost exponentially over the past 20 years. Such research is highly multidisciplinary infiltrating in the field of physics, medicine, chemistry, biology, material science and engineering, etc. Especially in the past years, the preparation and application of metal nanoparticles in catalysis (nanocatalysis) has attracted emerging attention from chemists.[2] One of the key driving forces is the potential for increased efficiency and selectivity from nanoparticle catalyst, in combination with the advantages of such heterogeneous supports as well as the environmentally benign synthetic procedure and catalyst recovery.[3] Among the metal-based nanoparticles, nanosilver plays an important role in catalysis, which has been extensively explored in many organic transformations to the synthesis of fine chemicals.

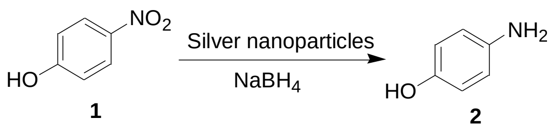
Catalysis is currently the subject of intense investigation and one of the most important researches that is in progress from a variety of viewpoints.[4] According to incomplete statistics, more than 80% of globally produced valuable chemicals are made using catalytic organic transformations.[4,5] And particularly, research effort to the field of catalysis is expected to continue increasing as the benefits of catalytic and atom-economic synthesis of chemicals.[5] Thus the development of highly efficient and practical catalysts displaying extremely high activity and selectivity are highly desirable. Consequently, many metal-based catalysts have attracted much attention and are widely-used in various organic reactions because of its good catalytic activities and controllable selectivities. Among many metal catalysts, silver is an extremely useful noble metal and has some outstanding characteristics such as antimicrobial activity, environmental friendliness.[6] And more importantly, silver is particularly suitable for industrial catalysis and heterogeneous catalysis because of its relatively low prices, for example, less than 1/50 of gold or platinum, and about 1/25 of palladium.[7] Although the ease of accessibility of the nanosilvers when compared to other metals has been realized widely,[6-8] research into the catalytic activities of silver nanoparticles for organic reactions is at an early stage and still remains a synthetic challenge for modern organic synthesis.[9] Owing to the rapidly expanding and exciting research of nanosilver chemistry, we hope that the review of nanosilver-promoted organic transformations will help to promote the future development of nanocatalysis. In this critical review, we highlighted the recent progress of silver nanoparticles –catalyzed organic reactions and provided an overview and comprehensive information of the recently reported preparation protocols of fine chemicals with nanosilver catalysis.

2. Reduction of Nitroaromatics, Carbonyl compounds, and Reductive transformations

Reduction plays a crucial role in organic chemistry and synthesis. A large number of organic syntheses and industrial application of valuable compounds involve reduction at some stage.[10] In this context, silver nanoparticles have been widely exploited for use in different reduction of functional molecules, such as nitroaromatics, carbonyl compounds, and reductive amination or its related transformations.

2.1 Reduction of nitroaromatics

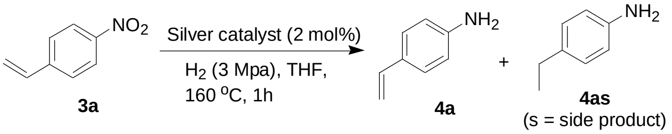
The nanosilver-catalyzed reduction of nitroaromatics has received enormous attention due to their potential applications in the field of organic synthesis and environmental sciences. Especially, because of its wide utilization in industrial application including analgesic and antipyretic drugs, photographic develops, and corrosion inhibitors,[11] the reduction of 4-nitrophenol in aqueous medium is a model reaction for the catalytic evaluation of silver nanoparticles in the past years. Meanwhile, it is well-known that 4-nitrophenol can cause water and environment pollution that is of great public concern. Thus there are many reports on the nanosilver-catalyzed reduction of 4-nitrophenol and related kinetic studies (Scheme 1).[12] From the viewpoint of organic synthesis, this reaction is quite simple and represents brief information for nanosilver catalysis for preparation of fine chemicals. The silver nanoparticles on various supporters including silver nanoshell-coated cationic polystyrene beads[12a], silver nanoparticle/brush-gel hybrid film[12b], silver nanotubes[12c], nanosilver/silica nanotubes[12d,13], nanosilver/porous silicon[12e,14] have been found to be effective catalysts in this reaction. Besides, recent progress in this context further supported the importance of such reaction in the evaluation of catalytic activity of silver nanoparticles, which showed great potential for practical application for water treatment.[15] Brawny silver-hydrogel-based nanocatalyst,[16] metal-organic framework-based silver nanoparticles[17], semi-IPN hydrogel-based silver nanoparticles[18], bimetallic gold/silver core-shell nanoparticles or other Ag-based bimetallic nanoparticles[19], zeolite Y-dispersed silver nanoparticles[20], silver/reduced graphene oxide or N-doped graphene hybrid nanocomposite[21], superparamagnetic silver/halloysite nanotube/Fe_3O_4 nanocomposites[22],silver nanoparticles supported on polymer material[23], and etc., have been designed and prepared for the reduction of 4-nitrophenol, which exhibit a hot topic of nanocatalysis. However, most of research works in this reaction only deal with the simple examination of various silver nanoparticles that supported varied type of inorganic or organic supporters. In this review, we will leave out detailed investigation on the evaluation of catalytic reduction of 4-nitrophenol because of its application is far from organic synthesis or the practical synthesis of fine chemicals.



Scheme 1. Catalytic reduction of 4-nitrophenol by silver nanoparticles

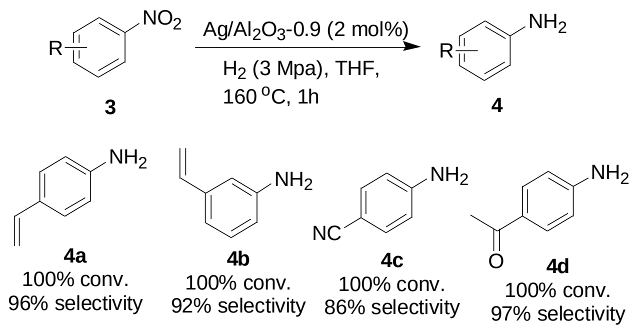
Although the reduction of 4-nitrophenol has been investigated widely in the past years with nanosilver catalysis, there are few reports on the substrate scope of nanosilver-catalyzed reduction of reduction of nitroaromatics and thus it is desired to be a synthetically useful research topic in organic synthesis. It is no surprise that the reduction of various nitroaromatics to the synthesis of aromatic amines catalyzed by silver nanoparticles. In 2010, Shimizu and coworkers reported their findings on the size- and support-dependent silver cluster catalysis for chemoselective reduction of nitroaromatics (Scheme 2 and Table 1).[24]

Table 1. Hydrogenation of 4-nitrostyrene (**3a**) by various supported silver catalysts[24]



Entry	Catalyst	Particle size of Ag (nm)	Conv.(%)	Selectivity	
				4a	4as
1	Ag/Al_2O_3	0.7	99	88	3.9
2	Ag/Al_2O_3	0.9	100	96	3
3	Ag/Al_2O_3	1.1	100	95	2.9
4	Ag/Al_2O_3	3.4	31	73	2.6
5	Ag/Al_2O_3	25	31	0	0
6	Ag/WO_3	2.6	11	98	0
7	Ag/SnO_2	2.4	3	79	0
8	Ag/CeO_2	0.9	59	74	0

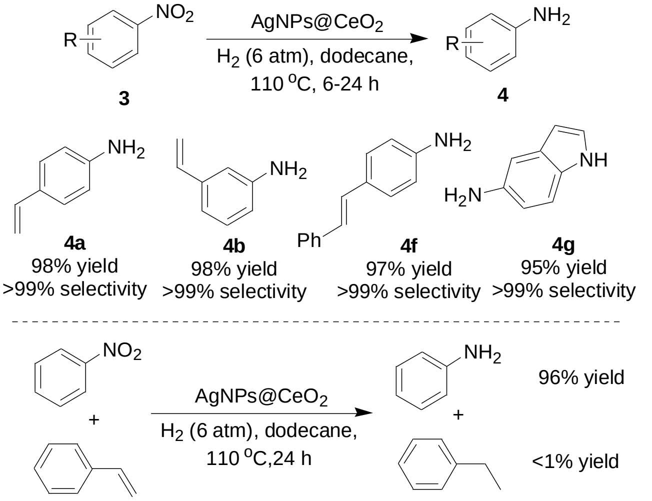
On the basis of experimental results on the screening of supported nanosilver catalyst systems for hydrogenation of 4-nitrostyrene (Table 1), the silver nanoparticle on θ-Al_2O_3 (with surface area of 112 m^2g^{-1}), Ag/Al_2O_3-0.9 (0.9 refers to 0.9 nm, and 5 wt% of silver for this catalyst, S = 105 m^2g^{-1}) was found to be a highly efficient silver catalyst in this reaction. Under the optimized reaction conditions, the reduction of a series of nitroaromatic compounds containing alkene, nitrile, amide, or ketone groups led to high selective hydrogenation of nitro-group to amine at 100% conversions (Scheme 2).[24] And more importantly, other functional groups including alkene, nitrile, amide, and ketone groups, could tolerate under the reaction conditions. Only trace amount of by-products with transformation of above functional groups except nitro moiety were detected in every case (86-97% selectivity). The novel silver nanoparticles based on polydopamine (PDOP) coating and electroless plating of silver on nanoporous anodic alumina membranes (AAO) with various pore sizes (20-200 nm) for catalytic reduction of 2-nitrophenol was reported by Demirel and coworkers[25] in 2011. The results indicated that the silver nanoparticles on nanoporous alumina membranes (AAO) and polystyrene (PS) nanotubes exhibited significantly higher catalytic activities than individual silver nanoparticles (AgNPs). It was found that hese material coating played crucial role in this reduction reaction. Subsequently in 2013, porous cross-linked lysozyme crystals (CLLC) was also proved to be a novel bio-nanocomposite material for silver nanoparticles, and the resulting nanosilver catalyst exhibited high catalytic activity in the reduction of nitroaromatic compounds, including 4-nitrophenol.[26]



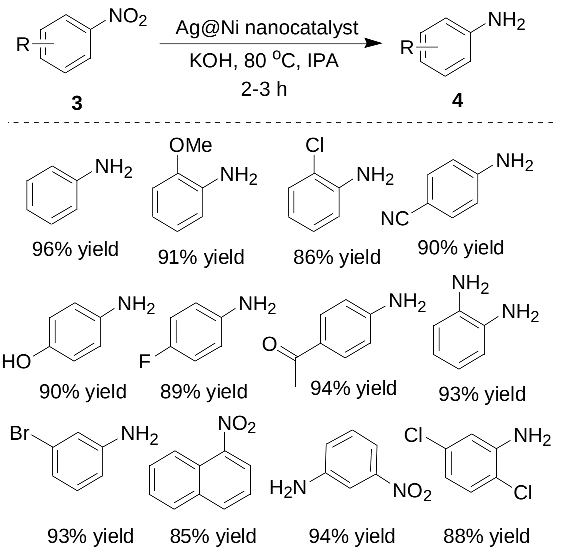
Scheme 2. Nano Ag/Al_2O_3-catalyzed reduction of nitroaromatic compounds

Early in 2010, Kaneda and coworkers have found the hydrotalcite-supported silver nanoparticles (Ag/HT) exhibited high activity for the reduction of nitroaromatic compounds when CO/H_2O was used as a reducing reagent.[27] The nanosilver catalyst system showed complete chemoselectivity for nitro groups in the presence of inter- and intra-molecular olefinic functionalities, for example, the desired product **4b** was obtained with >99% selectivity. In addition, this nanosilver catalyst could be reusable without any loss of its activity or selectivity. In 2012, Kaneda and coworkers designed a silver-cerium dioxide core-shell nanocomposite catalyst for the reduction of nitroaromatic compounds, in which the AgNPs@CeO_2 was synthesized by the combination of the reverse micelle technique and the redox reaction between silver(I) and cerium(III).[28] The novel nanosilver was proved to a highly efficient catalyst in the selective reduction of nitroaromatic compounds (Scheme 3). The nitroaromatic compounds containing alkene functionality resulted in selective reduction of nitro group but the carbon-carbon double bond was reserved under the reaction conditions. The nitro-substituted indole was also suitable substrate in this reductive transformation of nitro-functionality to amine moiety. Notably, the nitrobenzene was efficiently converted to aniline (96% yield) while styrene was almost not reduced at all (<1 % yield).

Recently, Gawande et al. investigated the application of core-shell Ag@Ni magnetic nanocatalyst for transfer hydrogenation of nitroaromatic compounds.[29] The catalytic performance was supported by the reaction results showed in Scheme 4. We can see that the general reaction proved to widely applicable as the corresponding aromatic amines were obtained in excellent yields. And notably, no dehalogenation product was obtained in this reduction reaction nitroaromatic compounds containing chloride or bromide moiety. Notably, the stability of the Ag@Ni magnetic nanocatalyst was tested by recycling and it was found to be a recoverable catalyst because of reusing the catalyst 8 times without any significant decreasing yield. In the field of nanosilver-catalyzed reduction of nitroaromatic compounds, Venkatesan and Rajesh have ever prepared a graphite-grafted-hyperbranched polyamidoamine (PAMAM) dendrimer supported silver nanoparticles for reduction of nitroaromatic compounds.[30] The nanosilver catalyst system also exhibited moderate to excellent yields for various nitroaromatic compounds (61-100% yields).

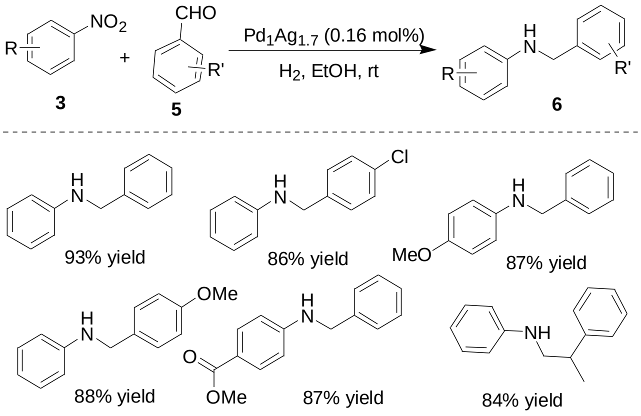


Scheme 3. Reduction of nitroaromatic compounds containing alkene group.



Scheme 4. Reduction of nitroaromatic compounds.

One-pot transformation of nitroaromatic compounds to synthetically useful molecules via reduction and subsequent reaction is expected to be an interesting topic in organic synthesis. In 2013, Li and coworkers identified an optimal bimetallic $Pd_1Ag_{1.7}$ nanocatalyst for the tandem reductive amination of nitroaromatic compounds with aldehydes.[31] The desired secondary amine products were obtained in good to excellent under mild reaction conditions (Scheme 5). Various substituted aldehydes as well as nitroaromatic compounds bearing either electron withdrawing group or electron donating group were capable of giving the substituted secondary amines in good results including high selectivities. Thus the bimetallic $Pd_1Ag_{1.7}$ nanocatalyst has excellent functional compatibility in this reductive transformation of nitroaromatic compounds. Unfortunately, the role of silver in the bimetallic nanocatalyst is not clear in this work.

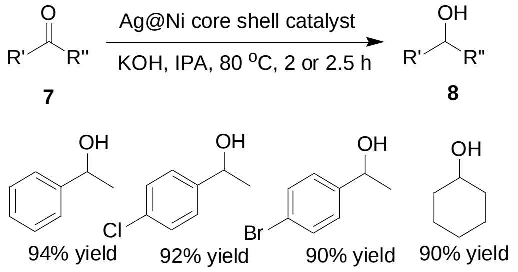


Scheme 5. Reductive amination of nitroaromatic compounds with aldehydes.

In some cases, the reduction of nitroaromatic compounds led to the formation of intermediate because of partial hydrogenation, in which the azobenzene was a major product.[32] However, it is not an easy task for the selective and high-yield synthesis of azobenzene with nanosilver catalyst.

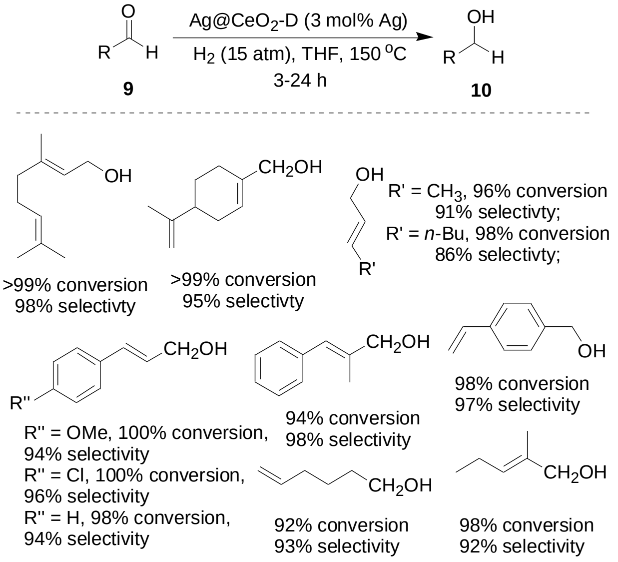
2.2 Reduction of carbonyl compounds

The reduction of carbonyl compounds to alcohols is one of the most important and fundamental reactions organic chemistry. In this regard, the hydrogenation of carbonyl compounds using silver nanoparticles as a catalyst revealed the emerging potential of silver catalyst in reduction reaction. In general, the catalytic activity of silver nanoparticles has been found to be quite low for alkene or carbonyl functionality during the reduction of nitroaromatic compounds as described in the previous section. However, recent work with the utilization of the core-shell Ag@Ni magnetic nanocatalyst in reduction reaction that reported by Gawande et al.[29], further supported the powerful activity in the reduction of carbonyl compounds. In this reduction reaction of carbonyl compounds, the corresponding alcohols were obtained in excellent yields (90-94% yields) under the hydrogen transfer hydrogenation reaction conditions (Scheme 6). Interestingly, the halide-containing substrates led to only selective reduction of ketone moiety without dehalogenation.



Scheme 6. Reduction of ketones to secondary alcohols

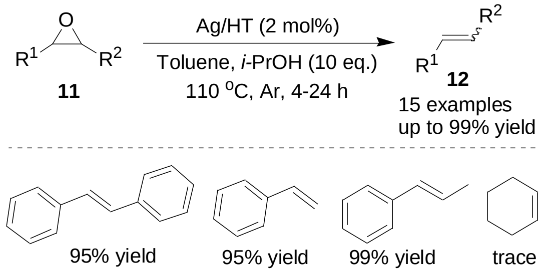
Very recently, Kaneda and coworkers reported that the core-shell nanocomposite acted as catalyst for reduction of unsaturated aldehydes in the presence of H_2 to the corresponding unsaturated alcohols.[33] With the AgNP@CeO_2-D catalyst (core-shell AgNP@CeO_2 dispersed on CeO_2) in hand, the authors evaluated the reduction of unsaturated aldehydes and various alkyl aldehydes containing olefin functionality (Scheme 7). Various aldehydes, such as terpenes and aromatic α,β-unsaturated aldehydes as well as unconjugated aldehydes were efficiently converted to corresponding alcohols with high selectivity. Notably, the AgNP@CeO_2-D catalyst was easily recovered by simple filtration and no leaching of silver species was found. In addition, the catalyst was reusable without any loss of its high efficiency, which supported the high durability of AgNP@CeO_2-D catalyst in this reaction.



Scheme 7. Reduction of aldehydes to primary alcohols.

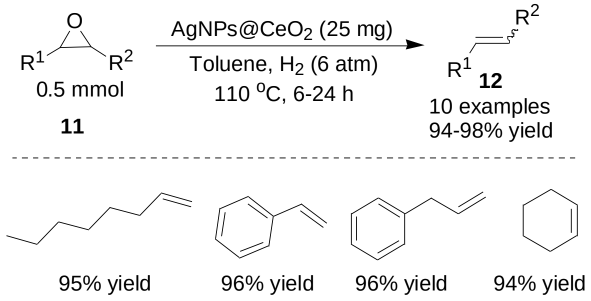
2.3 Other reductive transformations

Reductive deoxygenation of epoxides into alkenes is very interesting and important reaction in both organic synthesis and biological chemistry.[34] In 2010, Kaneda and coworkers discovered the intrinsic ability of silver nanoparticles in catalyzing deoxygenation of epoxides, in which the silver nanoparticles supported on an inorganic material of hydrotalcite[35] (Ag/HT) allowed highly efficient catalytic deoxygenation of epoxides into alkenes using alcohols as reductant (Scheme 8).[36] It was found that the Ag/HT catalyst was effective for the deoxygenation of epoxides having phenyl groups, such as styrene oxide, stilbene oxide, and 1-phenylpropylene oxide. However, cis-stilbene oxide gave a mixture of the *Z/E*-alkene isomers. And unfortunately, the nanosilver catalyst was not suitable for the deoxygenation of aliphatic epoxides. Notably, under the similar reaction conditions, the gold nanoparticles supported on hydrotalcite (Au/HT) gave more higher activity in this reaction than that of Ag/HT catalyst.[37] Slightly different from the alcohol-promoted deoxygenation of epoxides, Kaneda et al. also reported the deoxygenation of aromatic epoxides into alkenes could be efficiently catalyzed by the Ag/HT using CO/H_2O as a reductant.[38]



Scheme 8. Catalytic deoxygenation of epoxides to alkenes.

On the basis of previous findings and the silver-cerium dioxide core-shell nanocomposite ($AgNPs@CeO_2$) catalyst for reduction of nitroaromatic compounds,[28] Kaneda and coworkers[28] found that the $AgNPs@CeO_2$ exhibited unique reduction ability in the deoxygenation of epoxides to the corresponding alkenes (Scheme 9). Various epoxides including aromatic, aliphatic, and alicyclic epoxides were smoothly converted into the corresponding alkenes in excellent yields (94-98%) and selectivities (>99). It should be noted that the $AgNPs@CeO_2$ could be recovered by simple filtration from the reaction mixtures and reused without any loss of activity and selectivity.



Scheme 9. Catalytic deoxygenation of epoxides to alkenes.

Although research on palladium nanoparticles-catalyzed reduction and related reductive transformations have been realized in the past years,[39] the introduction of silver to palladium nanoparticles to the construction of Pd-Ag nano alloys for reductive transformation was also reported recently.[40] The Pd-Ag nanoparticles exhibited the highest TOF of all nanoparticles (such as various alkylamine- and alkanethiolate-stabilized palladium and bimetallic PdAg nanoparticles) evaluated in this work, in which the high stability of $Pd_{91}Ag_9$ alloy was responsible for the catalytic activity. Similarly to Scott's findings,[41] the presence of silver on Pd-Ag nanoparticle catalysts dramatically improved the selectivity for hydrogenation over the isomerization product, and the overall rate of hydrogenation was enhanced. However, it is still not a practical procedure for organic synthesis because the Pd-Ag nanoparticles-promoted hydrogenation and isomerization of allyl alcohol led to the formation of mixtures.

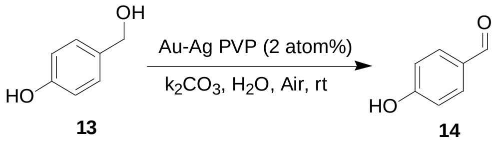
The reductive transformation of glycerol to 1,2-propanediol is value-added reaction because of the wide application of the corresponding product in antifreeze, coolant, humectant in the pharmaceuticals, foods and tobacco industries, and other fields. In 2012, Yadav et al. descried a catalytic hydrogenolysis procedure of glycerol to 1,2-propanediol (1,2-PDO) by silver-based nanocatalyst.[42] The 30% w/w Ag-OMS-2 (silver incorporated octahedral molecular sieve) was found successfully to effective catalyst for the selective hydrogenolysis of glycerol. It is a very efficient catalyst for the hydrogenolysis of glycerol to 1,2-PDO at 200 °C and 50 atm, in which the high conversion of glycerol (about 65-70%) with about 90% selectivity toward 1,2-propanediol was obtained within 8 h.

3. Oxidation of Alcohols, Silanes, Olefins, and other Oxidative transformations

Similarly to reduction, oxidation reaction is a fundamental process in nature and one of the most important transformations in organic chemistry. In the past decades, the metal nanoparticles –catalyzed oxidation reaction has attracted a considerable degree of research interest as a result of the social requirement to develop environmentally friendly and highly efficient catalytic processes.[43] In this reaction, various nanosilver catalyst systems have been determined as a type of powerful heterogeneous catalyst in oxidation of alcohols, silanes, and related oxidative transformations.

3.1 Oxidation of alcohols

The selective oxidation of alcohols to carbonyl compounds or its derivatives is one of the most important and fundamental reactions in organic chemistry and modern catalysis.[44] In the past decade, a number of heterogeneous metal catalysts including supported copper, gold, platinum, and rhenium nanoparticles, have been developed for the oxidation of alcohols.[45,46] In fact, the catalytic activity of silver-based alloys or heterogeneous silver-based catalyst systems in general oxidation of alcohols had been realized in the past decades.[47] For example, Yamamura, Kaneda, and Imanaka have ever reported the oxidation of allylic alcohols to α,β-unsaturated carbonyl compounds using a Pd-Ag catalyst (Pd_7Ag_{93}).[47a]



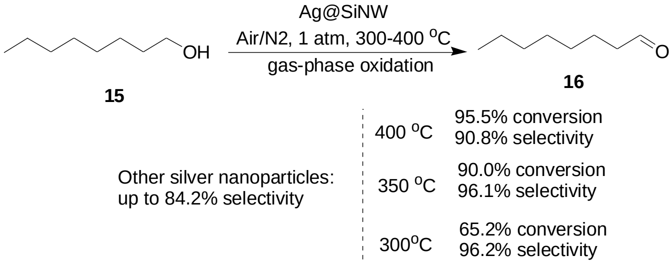
Scheme 10. Aerobic oxidation of 4-(hydroxymethyl)phenol catalyzed by nanosilver system.

Table 2. The catalytic activity of various Au-Ag alloy clusters in the aerobic oxidation of *p*-hydrobenzyl alcohol (**13**).[48]

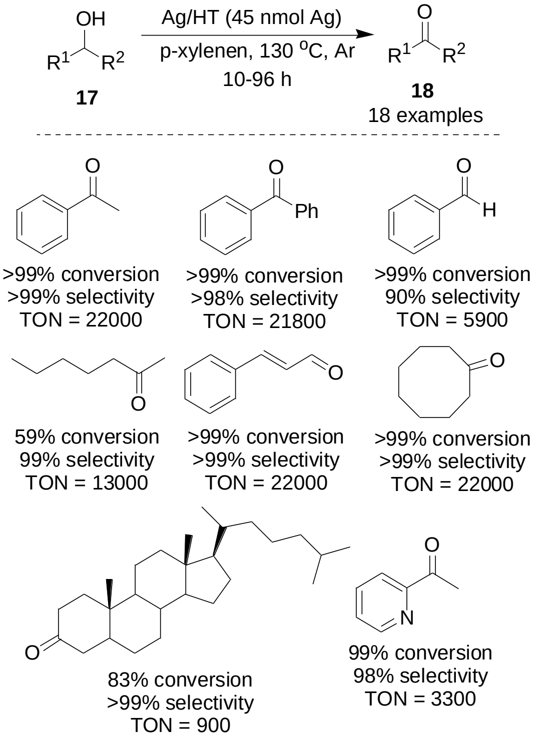
Catalyst	Au/Ag ratio	Particle size (nm)	Yield of 14 (%)
1	100/0	1.3±0.2	5
2	95/5	1.6±0.3	3
3	90/10	1.9±0.5	6
4	85/15	2.0±0.4	17
5	80/20	2.2±0.6	28
6	70/30	2.2±0.4	68

In recent years, the oxidation of alcohols catalysed by nanosilver was also realized by several groups.[48-50] In this context, Tsukuda and coworkers prepared a set of nearly monodispersed Au-Ag alloy clusters (size range 1.6-2.2 nm) with various silver content (5-30%) for catalytic oxidation of *p*-hydroxybenzyl alcohol (Table 2 and Scheme 10).[48] It was found that the presence of <10% silver on the gold-silver nanoparticles enhances the catalytic activity of this catalyst (82-87% yield of **14**).

Subsequently in 2008, Tang and Xu reported a novel catalyst of silver nanoparticles embedded in a silicon nanowire array support (Ag@SiNW) for the gas-phase oxidation of high alcohol to corresponding aliphatic aldehyde.[49] The target product of this reaction, 1-octanal (**16**), is a synthetically useful intermediate of organic synthesis and a food flavor. In addition, Scheme 11 showed the relationship between the conversion/selectivity of 1-octanol (**15**) oxidation and reaction temperature over this silver nanocatalyst. It is worthy noticing that the Ag@SiNW presents a much higher selectivity to the desired product than other silver catalysts, such as commercial available electrolytic silver and the mixed electrolytic silver and silicon powder (47.6-84.2% selectivity).



Scheme 11. Gas-phase oxidation of octan-1-ol catalyzed by silver nanoparticles.

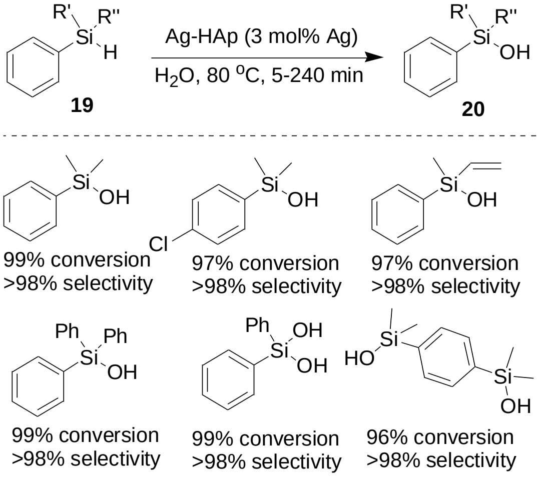


Scheme 12. Oxidation of alcohols to aldehydes or ketones

In 2008, Kaneda and coworkers found that the hydrotalcites (HTs)-supported silver nanoparticles (Ag/HT, 3.3 nm, 0.005wt% for silver) showed remarkably high catalytic for dehydrogenated oxidation of a wide range of alcohols (Scheme 12).[50] Moreover, when 1-phenylethanol was oxidized by the Ag/HT nanocatalyst in the presence of styrene, only acetophenone was obtained in 99% yield and no ethylbenzene derived from styrene was detected. The authors also claimed that nanosilver leached into the filtrate and the Ag/HT nanocatalyst could be reused with four subsequent reactions with no reduction in the reaction rate, thus the total TON based on the silver catalyst could be greater than 100000. Notably, the authors compared the Ag/HT, Ru/HT, and Pd/HT for the oxidation of cinnamyl alcohol to cinnamaldehyde under the similar conditions. Interestingly, the Ag/HT nanocatalyst exhibited the best activity and selectivity in this reaction, while other two catalysts resulted in low yield of desired product (<50%) and poor selectivity.

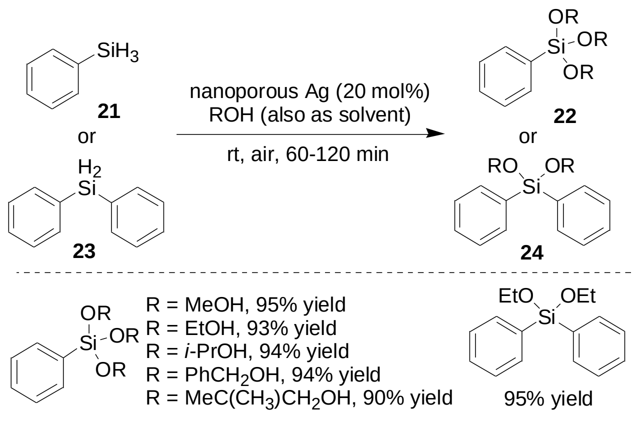
Subsequently, several groups have successfully determined that nanosilver particles supported on different supporters were highly efficient catalysts in the oxidation of alcohols to aldehydes or ketones.[51] These effective silver-based nanoparticles including SiO_2-supported silver nanoparticles (10 wt% of Ag)[51a], γ-alumina-supported silver cluster (Ag/Al_2O_3, 5 wt% of Ag) [51b], dealloyed nanoporous silver that fabricated by the selective leaching of magnesium from a $Ag_{77}Mg_{23}$ alloy foil [51c,52], silver-doped titania [51d], and CuO@Ag nanowires that fabricated through the reduction of $Cu(OAc)_2$ on the surface of Ag nanowires in ethylene glycol solution[51e]. Thus, as expected, the appearance of novel silver-based nanomaterials would be beneficial to the development of highly efficient oxidation of alcohols for the practical preparation of carbonyl compounds.

3.2 Oxidation of silanes



Scheme 13. Oxidation of silanes to silanols

Both silanes and silanols are useful building blocks for the construction of organosilicon-based polymeric materials and important synthons in organic synthesis, such as cross-coupling partners or reductive agents in reduction and hydrosilylation reactions.[53] Interestingly, although the synthesis of silanols from hydrosilanes have been reported using water as an oxidant,[54] the development of environmentally benign, highly selective, and practical processes for synthesizing silanols is still highly desirable.[55] In this context, Kaneda and coworkers reported a highly efficient method for the green synthesis of silanols from hydrosilanes in 2008.[56] They found that the silver nanoparticles supported on hydroxyapatite (Ag-HAp) exhibited high catalytic activities for the selective oxidation of hydrosilanes using water as a green oxidant without the use of organic solvents (Scheme 13). Notably, the solid Ag-HAp catalyst could be easily retrieved from the reaction mixture by simple filtration and was found to be reusing for four times without loss of its activity and selectivity. And larger amount of hydrosilanes **19** (for example, 100 mmol) could be used in the synthesis of silanols and led to high yield and selectivity, which superior to that of previous reports with Ru or Ir-based homogenous catalyst system.[55]



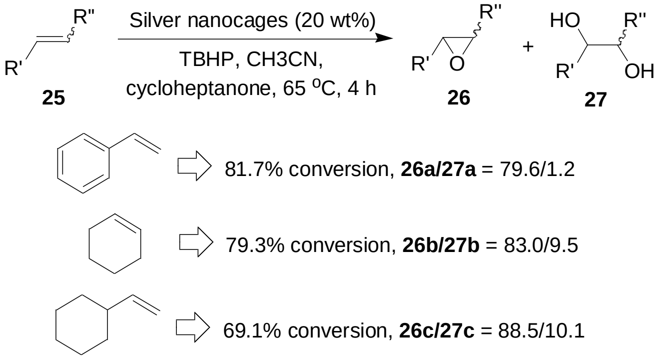
Scheme 14. Oxidation of silanes with alcohols to silyl ethers

Recently, Mizuno,[57] Park,[58] and Zhang,[59] also determined the powerful catalytic activity of silver-based nanomaterials in this reaction. In these reports, both aromatic silanes and aliphatic silanes can be effectively converted into the corresponding silanols or silyl ethers by using water or alcohols as oxidants (Scheme 14). The reduction of hydrosilanes with multi Si-H moiety to silanols or silyl ethers without polymeric products is quite useful for organic synthesis. In the oxidation reaction of organosilanes, the first key point is the adsorption of water onto the nanostructured silver surface, which led to the O-H cleavage of H_2O. And then the resulted nucleophilic group (OH) attacked Si-H bond to generate corresponding intermediate. In the meantime, the silver promoted the liberation of H_2 gas from the intermediate.[59]

Very recently, Li and Wang[60] found that the halloysite nanotube supported silver nanoparticles could serve as active catalyst for the polymerization of an alkylsilane $C_{18}H_{37}SiH_3$ with water to form silanol/siloxane composite microspheres, in which the reductive transformation of hydrosilane might find an utilization in polymer chemistry.

3.3 Oxidation of olefins

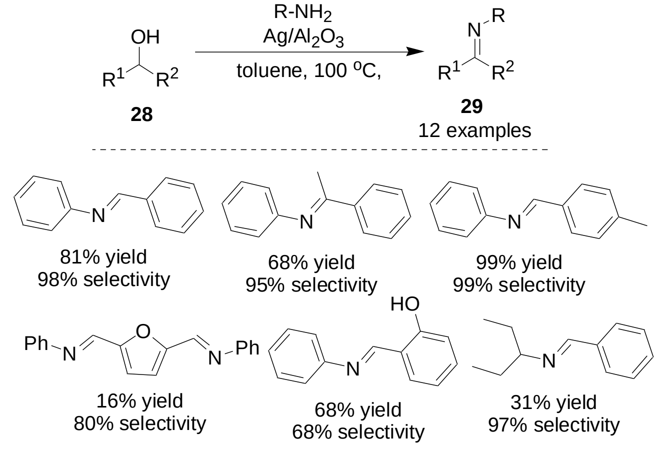
First of all, the olefin substrates can be regarded probably as one of the most important synthetic organic intermediates because of their ready availability and widely transformations into functional compounds. Accordingly, selective oxidation of olefins to produce epoxides or oxygen-containing molecules is of great importance in the fine chemical and pharmaceutical industries.[61] As the need for environmentally benign and practical processes was increasing in the modern green chemistry, the utilization of silver nanoparticles in oxidation of olefins and aromatics has been attracted promising attentions in the past ten years.[62] In 2006, Li and coworkers have ever reported their findings on shape-dependent catalytic activity of silver nanoparticles for the oxidation of styrene.[63] However, the reaction results were not good for practical synthesis of corresponding epoxide. Subsequently in 2009, Purcar and coworkers[64] prepared a novel nanosilver catalyst with different loadings of silver nanoparticles supported on hybrid films containing methyltrimethoxysilane (Ag-MeTMS) for oxidation of styrene. Under microwave irradiation, with 1 % of Ag-MeTMS (0.91 wt% of Ag), excellent selectivity (>99%) and promising conversion (60%) to the desired styrene oxide was achieved at 96 °C. Although recent investigation revealed that silver nanoparticles supported on layered double hydroxide[65] and hollow silver nanoparticles cages assembled with silver nanoparticles[66] exhibited good catalytic activity in the oxidation of styrene, the selectivity was not perfect for such silver-based nanocatalysts.[51e] Anandhakumar and coworkers[66] have also reported the application of such silver nanocages in the oxidation of various olefins (Scheme 15). Acyclic and cyclic olefins allowed to the formation of corresponding epoxides with high selectivities and good conversions.



Scheme 15. Oxidation of alkenes catalyzed by nanosilver catalyst systems

3.4 Other oxidative transformations

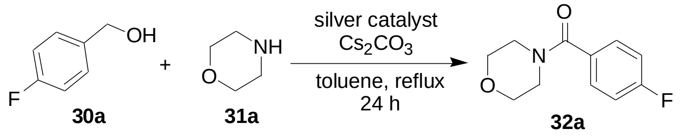
As described in previous reports, since the early investigation of nanosilver-catalyzed oxidation of alcohol reported in 2004,[67] the silver nanoparticles have exhibited good catalytic ability for the oxidation of alcohols to carbonyl compounds. Meanwhile, the formation of aldehydes or ketone to imines was not a difficult task. Very recently, on the basis of oxidative dehydrogenation of alcohols to aldehydes catalyzed by Ag/Al_2O_3 (5 wt% Ag), Kegnæs and coworkers demonstrated the one-pot synthesis of imines from alcohols in the presence of primary amines.[68] The silver supported on Al_2O_3 was found to be an active and highly selective catalyst for the formation of imine (Scheme 16), in which the reaction was performed under oxidant-free conditions.



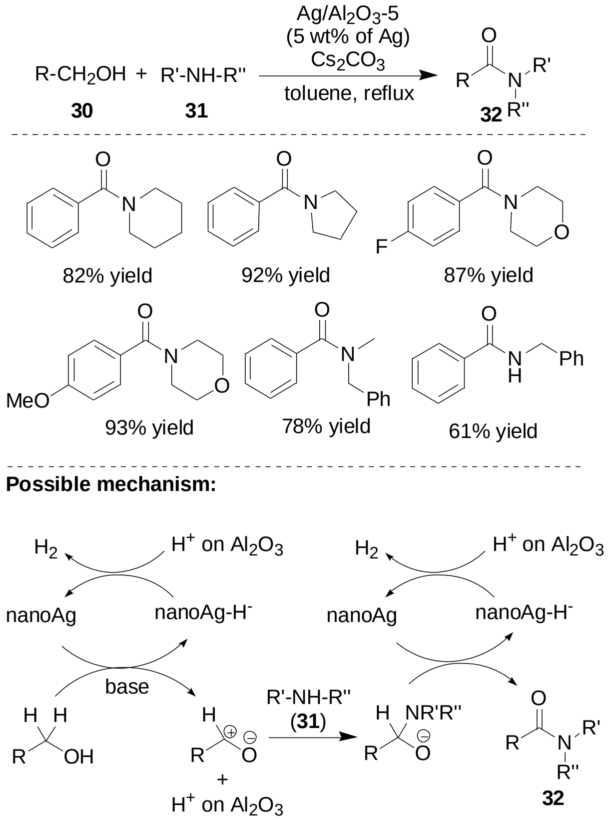
Scheme 16. Oxidative Imidization of alcohols with primary amines.

In general, synthesis of amides is mostly based on acids and amines. Alternatively, the direct synthesis of amides from alcohols and amines through oxidative amidation has attracted much attention in the past years.[69] In 2009, Shimizu et al. reported firstly a direct dehydrogenative amidation of alcohols with γ-alumina-supported silver cluster (Table 3).[70] As shown in Table 3, it is clear that the silver catalyst with Ag loading of 5wt% (average particle size of supported silver is 0.84 nm) showed the highest yield and rate formation of for **32a**. With the optimal nanosilver catalyst and reaction conditions, the scope and limitation of the direct nanosilver-catalyzed amidation of alcohols were showed in Scheme 17. As described by the authors, the oxidative reactions of alcohols and amines with various electron-withdrawing and electron-donating groups proceeded successfully in moderate to good yields. Notably, this reaction did not proceed through an ester intermediate or aldehyde intermediate but through aldehyde-like species adsorbed on the γ-alumina-supported silver cluster (Scheme 17, down). The Experimental results suggested the nanosilver-mediated C-H cleavage of the alkoxide or hemiaminal could be the rate-determined step in the present reaction.

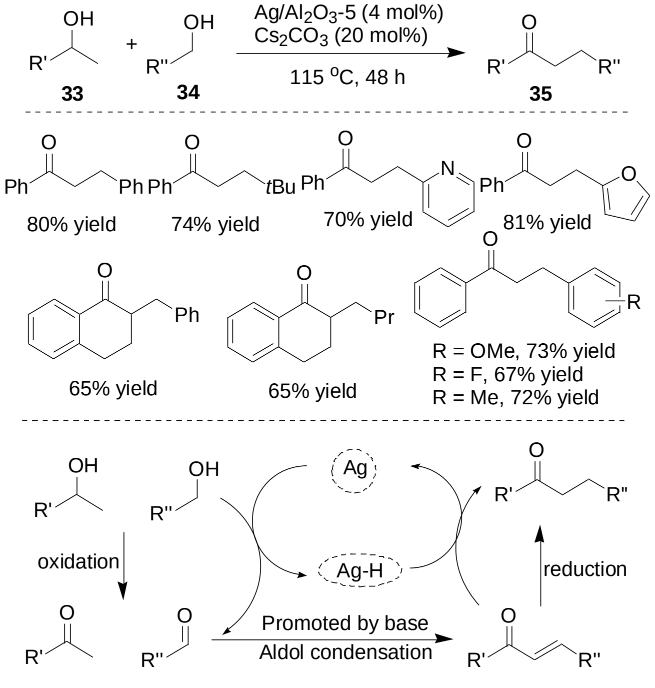
Table 3. Direct dehydrogenative amide synthesis from (4-fluoro-phenyl)-methanol (**30a**) and morpholine (**31a**) by various silver catalysts.[70]



Catalyst	Ag loading (wt%)	Particle size of Ag (nm)	Yield (%)
Ag/Al$_2$O$_3$	1	0.73	61
Ag/Al$_2$O$_3$	3	0.78	82
Ag/Al$_2$O$_3$	5	0.84	87
Ag/Al$_2$O$_3$	10	1.2	82
Ag/Al$_2$O$_3$	50	30	31
Ag/SiO$_2$	5	1.2	8.1
Ag/ZrO$_2$	5	1.6	43
Ag/CeO$_2$	5	0.9	0
Ag/MgO	5	3.0	8.0
Ag powder	-	-	1.6
AgNO$_3$	-	-	1.1



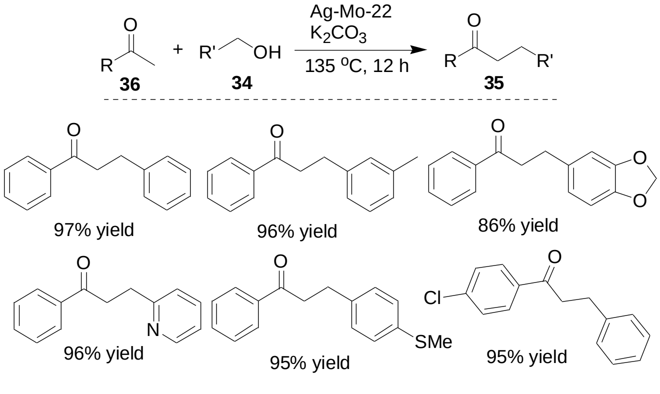
Scheme 17. Oxidative amidation of alcohols with amines catalyzed by nanosilver catalyst system: Substrate scope and mechanism



Scheme 18. Oxidative cross-coupling reaction of secondary alcohols and primary alcohols: Substrate scope and mechanism

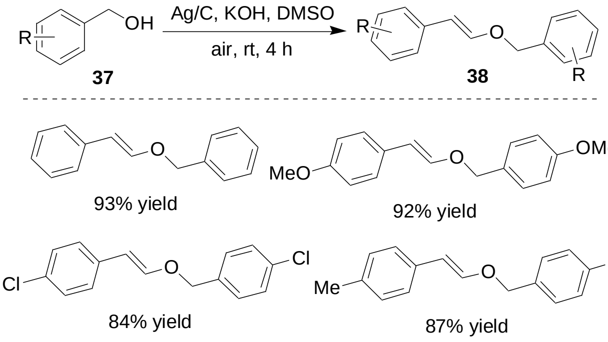
Shimizu and coworkers have also found that the γ-alumina-supported silver cluster was effective in the oxidative cross-coupling reaction of secondary alcohols and primary alcohols.[71] With suitable reactions established by the authors, the direct oxidative cross-coupling reaction of various secondary alcohols and primary alcohols resulted in moderate to good yields of corresponding products in the presence of γ-alumina-supported silver subnanoclusters (Scheme 18). This reaction further supported the privileged role of nanosilver catalyst in the oxidative transformation of alcohols. On the basis of experimental results, the authors proposed the nanosilver-catalyzed cross coupling of two alcohols begins with the oxidation of the alcohols to the corresponding aldehyde and ketone as well as the generation of silver hydride (Ag-H) species.[51a] And then the base (Cs_2CO_3) -promoted cross-aldol condensation occurs between aldehyde and ketone. At last the selective transfer hydrogenation of the C=C bond of α,β-unsaturated ketone with the silver hydride species generated in the dehydrogenation of alcohol to give the desired product (Scheme 18, down).

In 2011, Shi and coworkers[72] also found that the heterogeneous Ag/Mo hybrid materials ($Ag_6Mo_{10}O_{33}$) is a highly effective catalyst with excellent yields (86-97% yields) in similar cross-coupling reaction of alcohols and ketones (Scheme 19).



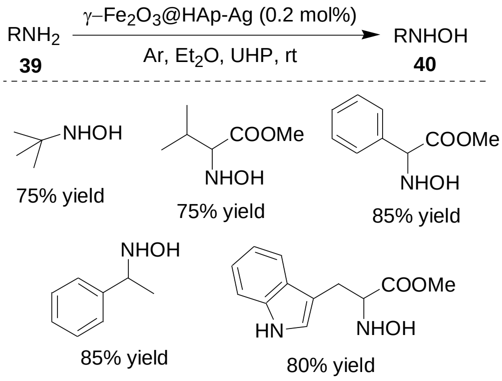
Scheme 19. Cross-coupling reaction of alcohols and ketones

Different from that of Shimizu's cross-coupling reaction of secondary alcohols with primary alcohols, Li and coworkers[73] found that the silver nanoparticles exhibited high activity for the oxidation of benzyl alcohols in basic DMSO, in which styryl ethers was obtained in excellent yields (Scheme 20). Scheme 20 supported that several substituted benzyl alcohol are compatible with reaction conditions in the presence of nanosilver catalyst, giving the corresponding homo-coupling products, styryl ethers, in excellent yields. This work demonstrated that applying nanosilver catalysts to organic reactions could lead to the facile synthesis of complex compounds. More interestingly, the experimental results and EPR study suggested that the super oxide anion radical was rapidly consumed in the Ag/C-catalyzed cross coupling reaction. In addition, it was confirmed that the Ag/C nanocatalyst plays an important role in the activation of molecular oxygen (O_2) as well as in the oxidation of benzyl alcohol.



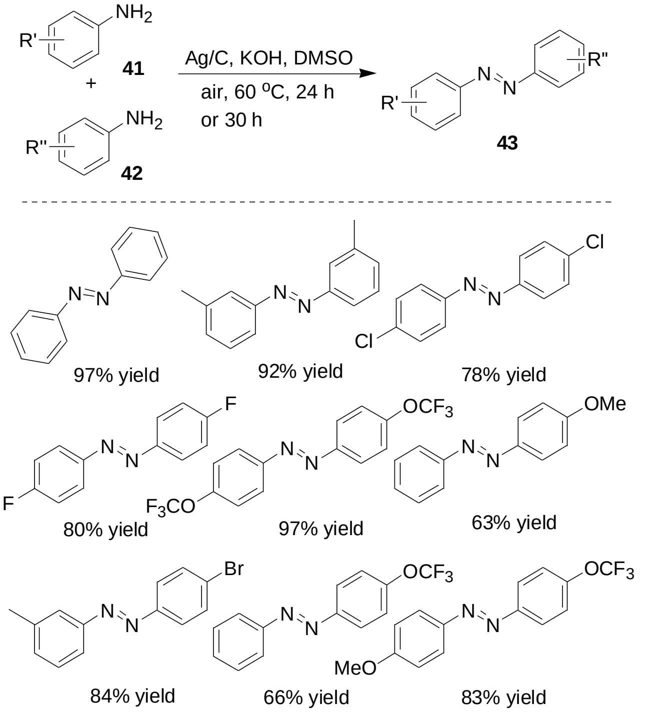
Scheme 20. Oxidation of benzyl alcohols to styryl ethers

Beside the nanosilver-catalyzed transformation of alcohols, the oxidation of amines has also been investigated with nanosilver catalysis in the past years.[74] For example, in 2011, Heydari et al. [74a] reported the magnetically recoverable silver nanoparticles could be applied in the chemoselective oxidation of primary amines to N-monoalkylated hydroxyamines (Scheme 21). In this reaction, it was found that under the optimal reaction conditions, 0.2 mol% of γ-Al_2O_3@HAp-Ag nanoparticles (about 10 nm) and 1.2 mmol UHP (hydrogen peroxide/urea complex) in diethyl ether as solvent under an inert atmosphere, various primary amines, including amino acid-derived substrates, led to the formation of *N*-monoalkylated hydroxyamines in good yields (75-85%).



Scheme 21. Oxidation of primary amines to N-monoalkylated hydroxyamines

In their effort to probe the advantages of silver-based nanoparticles in catalysis, Li and coworkers[74b] discovered that the Ag/C nanoparticles (average 12.4 nm) could efficiently activate molecular oxygen in air at room temperature, leading to the synthesis of azo compounds via oxidative coupling of anilines in high yields (Scheme 22). As shown in Scheme 22, various aromatic amines could be smoothly converted into the corresponding symmetric azobenzenes. More importantly, the cross-coupling of more reactive (electron-rich) anilines with less reactive (electron-poor) anilines led to the formation of unsymmetric azobenzenes in good yields, in which the powerful activity of nanosilver catalyst in this reaction provides a synthetically useful strategy for the green synthesis of azobenzenes and opens a new chapter of research on nanocatalysis.

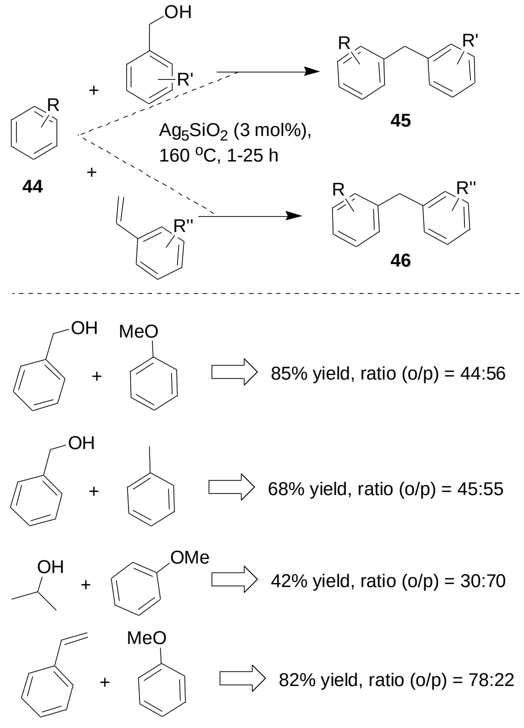


Scheme 22. Oxidation of aromatic amines catalyzed by nanosilver catalyst system

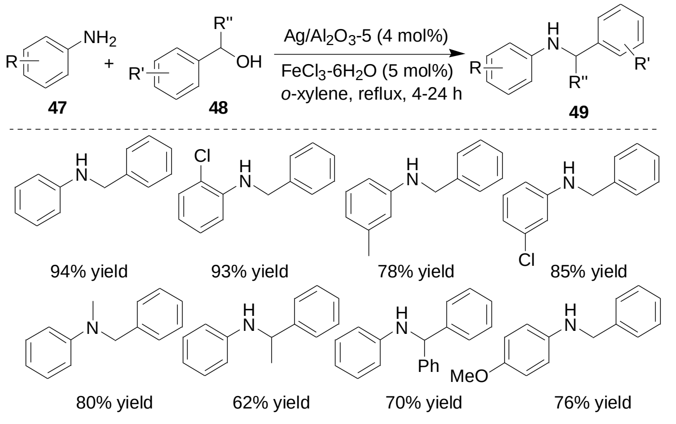
4. Alkylation of Amines and Arenes

Alkylation has long been of great interest to synthetic chemists owing to it ubiquity in a large number of fine chemicals and biologically active molecules. In this context, the catalytic Friedel-Crafts alkylation of arenes that promoted by silica-supported silver nanoparticles (Ag_5SiO_2) has also been reported by Shimizu and coworkers.[75] With the silver nanoparticles (Ag_5SiO_2) as a standard catalyst, the authors examined its catalytic properties in the Friedel-Crafts alkylation of arenes (Scheme 23). Fortunately as described in this work, the desired products were formed in good yields. In particular, the catalyst was applicable to the reaction of arenes with less reactive aliphatic alcohols, styrene, and indene. The silver nanoparticles could be easily separated from the reaction mixture by simple filtration; therefore the recovered catalyst could be reused in the next run. However, the chemoselectivity of the corresponding products was not good, in which *ortho*- and *para*-substituted aromatics were obtained as a mixture (The ratio of *o*/*p*-product varied from 45:55 to 86:14). Notably, in the reaction mechanism of nanosilver-catalyzed alkylation of arenes, the strong interaction of surface $Ag^{\delta+}$-$O^{\delta-}$ species and the α-C-H bond of benzyl alcohol play important role for the key step of hydride abstraction by the $Ag^{\delta+}$ site to form an active intermediate. The primary kinetic isotopic effect revealed that the C-H cleavage is the rate-determining step.

Nitrogen-containing compounds such as amines and amides constitute an important functional group of compounds that are of key and fundamental importance in organic synthesis and industrial chemical synthesis.[76] Among the various synthetic procedures to substituted amines or amides, *N*-alkylation of nitrogen-containing compounds is of particular value. A well-known N-alkylated method for the preparation of *N*-alkylamines is the reaction of amines with alkyl halides or similar alkylating agents.[77] An attractive alternative to these classic methods employs alcohols instead of carbonyl compounds as inexpensive and readily available starting materials is quite interesting and useful in green organic synthesis.[78] In 2009, Shimizu et al.[79] reported their γ-alumina-supported silver nanocluster (Ag/Al_2O_3-5, classified as 5 wt% of Ag), as catalyst in the N-alkylation of anilines with alcohols by the borrowing hydrogen mechanism. In this reaction, a series of Ag/Al_2O_3 catalysts with different silver loading was evaluated firstly and found the 5 wt% Ag-containing silver nanoparticles showed the highest activity in the presence of catalytic amount of $FeCl_3$ $6H_2O$. The scope and limitation of the nanocatalytic method with Ag/Al_2O_3-5 showed in Scheme 24 supported the superior role of bimetallic catalysis in this reaction. Most of substrates evaluated in this work led to the formation of *N*-alkylated amines in good yields. The mechanistic studies showed that the high catalytic performance of this catalyst system originated from cooperative of coordinately unsaturated silver atoms on the silver cluster, acid/base sites on alumina, and a Lewis acidic iron cation. Except the key step of deprotonation of alcohol and subsequent hydrogenative oxidation, the support oxide with higher acidity enables faster proton transfer to the hemiaminal, and additives with higher Lewis acidity enables faster hydride transfer to immonium cation, which would be beneficial to the formation of *N*-alkylated amines. Inspired by this work reported by Shimizu and coworkers, the same authors[80] and Jænicke's group[81] have also reported that the alumina-supported silver nanoparticles could be applied in the *N*-alkylation of amines to the synthesis of *N*-alkylated amines.

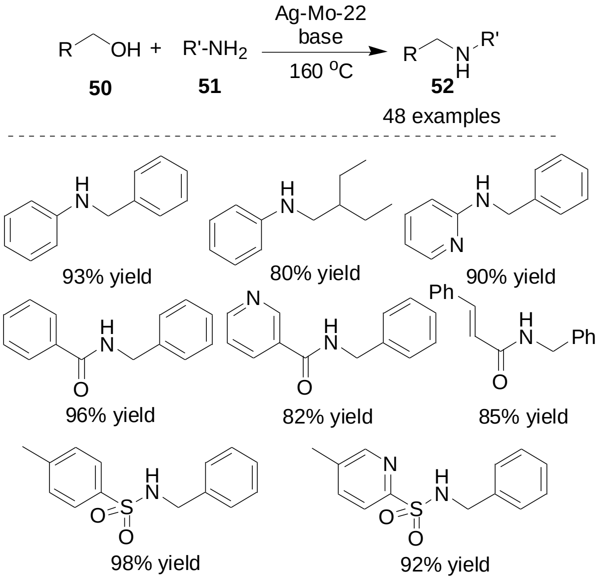


Scheme 23. Catalytic Friedel-Crafts alkylation of arenes



Scheme 24. N-alkylation of amines with alcohols

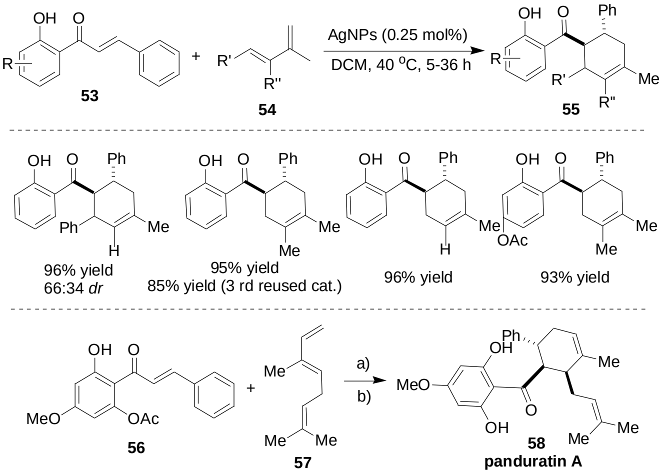
Notably in this field, Shi and coworkers determined a highly effective silver-based nanocatalyst for the alkylation of amines and amides in 2011.[72] The achieved Ag/Mo hybrid materials ($Ag_6Mo_{10}O_{33}$) in this work has been successfully applied in the N-alkylation of aromatic amines, carboxamides, and sulfonamides with simple alcohols through a borrow-hydrogen mechanism. The yields of the corresponding N-alkylated products are normally above 90% without addition of organic ligands (Scheme 25). Thus the catalytic process promoted by heterogeneous silver catalyst shows promise for the economic and green synthesis of substituted amines and amides from commercially available compounds.



Scheme 25. N-alkylation of aromatic amines, carboxamides, and sulfonamides with alcohols

5. Catalytic Cycloaddition and Cyclization to Complex Products

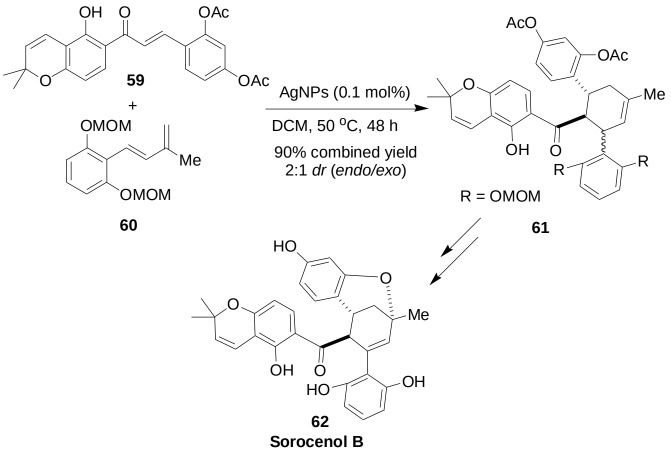
Interestingly, the application of nanocatalysts in the synthesis of complex natural products did not receive enough attention, which is in sharp contrast to transition metal-based catalysts that have been applied extensively in the synthesis of complex molecules.[82] Accordingly, the field of silver nanoparticles should offer opportunities for mining new reactions for the total synthesis. In this regard, Porco's group contributed greatly to the development of nanosilver-promoted natural product synthesis. The first example of catalytic complex compounds with silver nanoparticles was reported by Porco et al. in 2010.[83] As shown in Scheme 26, the cycloadditions catalyzed by the silica-supported silver nanoparticles generally favored the *endo* Diels-Alder cycloadducts with high-yield single regioisomer observed for unsymmetrical dienes. Notably, use of the supported silver nanoparticles at a loading as low as 0.01 mol% Ag also afforded a nearly quantitative yield at slightly higher temperature with prolonged reaction times. More importantly, the silica-supported silver nanoparticles could be applied in the total synthesis of natural product panduratin A via the key step of Diels-Alder reaction (Scheme 26). The mechanistic investigation suggested that the catalytic cycloaddition involved a concerted process mediated by the silver nanoparticles' likely serving as electron shuttle/redox catalyst.



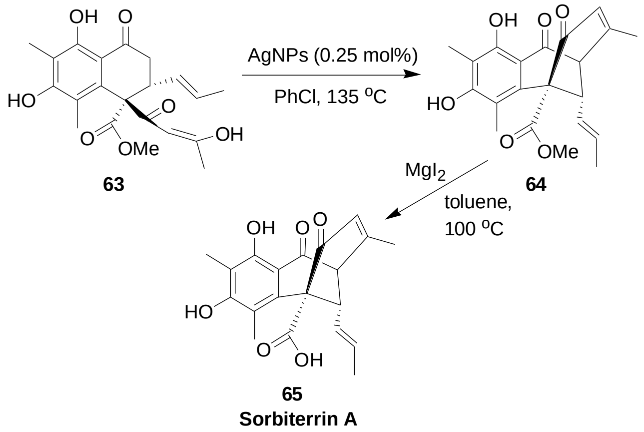
a) Silica-supported silver nanoparticles (0.5 mol% Ag loading), DCM, 50 °C, 48 h, 85% yield;
b) ad. $NaHCO_3$, MeOH, 40 °C, 6 h, 87% yield.

Scheme 26. Nanosilver-catalyzed Diels-Alder reactions

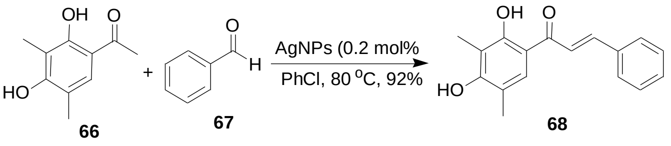
Similarly to Proco's report, Rahaman et al.[84] applied the $AgOTf/Bu_4BH_4$ in 2011 as the precursor of nanosilver catalyst for the catalytic [4+2] cycloaddition of chalcone derivative with diene. The mulberry Diels-Alder adducts, pentamethyl ethers of kuwanon V and dorsterone, could be achived via the key silver-catalyzed cycloaddition. Although the authors did not claim it is example of nanosilver-promoted natural product synthesis, the silver nanoparticles were usually prepared from silver salts in the presence of reductants (such as Bu_4BH_4). Subsequently in 2012, Porco and coworkers[85] continued to report their work on the total synthesis of sorocenol B through nanosilver-catalyzed Diels-Alder cycloaddition. With the chalcone derivative and diene in hand, the authors investigated the key Diels-Alder cycloaddition utilizing silica-supported silver nanoparticles (AgNPs), in which the desired products as 2:1 ratio of separable *endo/exo* diastereoisomers was obtained in 90% total yield. Then *endo* cycloadduct has been used to access the bicycle[3.3.1] framework of serocenol B in that work.



Scheme 27. Total synthesis of Sorocenol B via nanosilver-catalyzed Diels-Alder reaction.

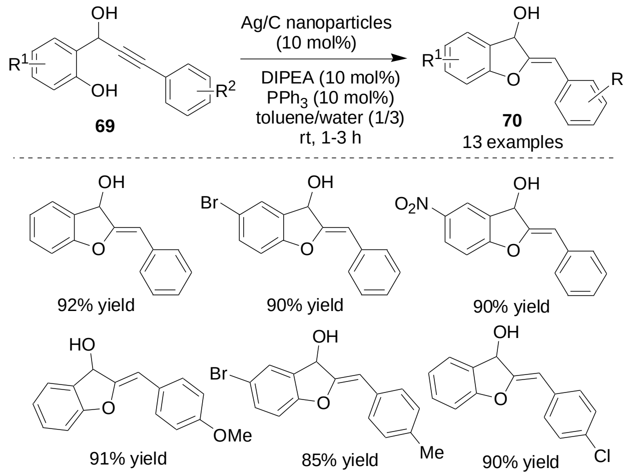


Scheme 28. Total synthesis of Sorbiterrin A via nanosilver-catalyzed cycloaddition



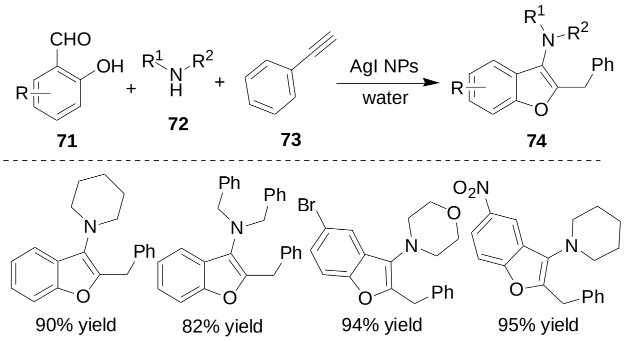
Scheme 29. Model aldol condensation of 2',4'-dihydroxy acetophenone and benzaldehyde

Very recently, Proco and coworkers described a concise approach to sorbiterrin A by silver nanoparticles -catalyzed bridged aldol/dehydriation to access the [3,3,1] framework.[86] Based on their previous studies employing silica-supported silver nanoparticles (AgNPs) as catalyst for the [4+2] cycloaddition of 2'-hydroxychalcone with diene, this nanosilver catalyst system was found to be highly effective in the intramolecular cyclization. 72% yield of the corresponding product was obtained, which led to the successful synthesis of natural product sorbiterrin A by subsequent treatment with MgI_2 in toluene (Scheme 28). As described by the authors, it exhibits the privileged role of nanosilver catalyst in this natural product synthesis because other conditions gave no reactivity or degraded the starting materials. In this work, the silver nanoparticles-mediated aldol condensation was the key transformation in this intramolecular cyclization, thus the authors carried out the model aldol condensation of 2',4'-dihydroxy acetophenone and benzaldehyde in the presence of AgNPs (Scheme 29). Interestingly, silver nanoparticles was quite effective for this reaction, while several silver salts, such as $AgBF_4$, Ag_2O, and AgOTf, did not afford the desired chalcone derivatives. Based on experimental results, including electron paramagnetic resonance (EPR), radical mechanism was involved in the aldol process.



Scheme 30. Nanosilver-catalzyed cyclization

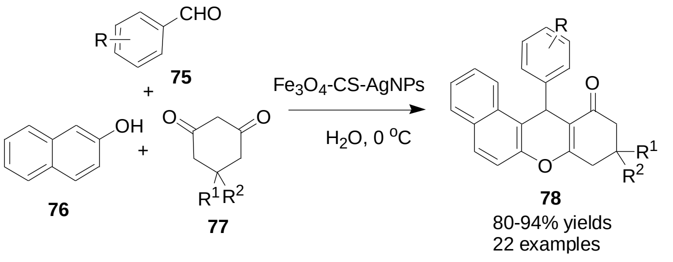
In 2010, Yao and Li et al.[87] prepared a carbon black-supported silver nanoparticles and investigated the annulation of 2-(1-hydroxy-3-arylprop-2-ynyl)phenols to cyclic alcohols. Under the optimized reaction conditions, the catalytic cyclization of various substrates by nanosilver catalyst system led to the corresponding products in good to excellent yields (83-93% yield). It should be noteworthy that phosphine ligand and water proved to be the key factors except nanosilver catalyst.



Scheme 31. Three-component cycloaddition of salicylaldehydes, alkynes, and secondary amines

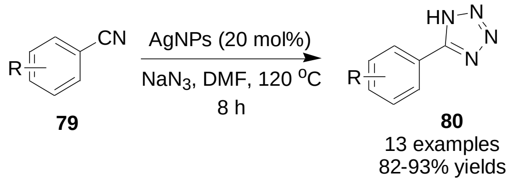
Similarly to Yao's work, Safaei-Ghomi and workers[88] reported easily available AgI nanoparticles -catalyzed three-component cycloaddition of salicylaldehydes, alkynes, and secondary amines to benzofurans under aqueous conditions. It is a quite simple method to the synthesis of substituted benzofurans, which supported the powerful activity of silver nanoparticles in the organic transformations.

Very recently, Kassaee et al. demonstrated a Fe_3O_4-modifed chitosan supported silver nanoparticles as a novel green catalyst in one pot, three-component condensation of aldehydes, 2-napthol, and 1,3-cyclohexadiones to the synthesis of tetrahydrobenzo[α]xanthene-11-ones (Scheme 32).[89] In this case, the desired products **78** were obtained with good to excellent yields (80-94% yields).



Scheme 32. Three-component condensation of aldehydes, 2-napthol, and 1,3-cyclohexadiones

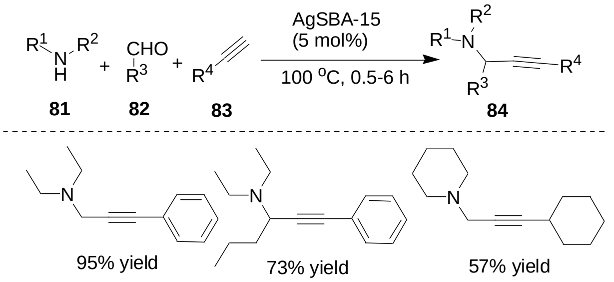
As an important type of nitrogen-containing heterocyclic compounds, tetrazoles have gained wide attention due to its use in the field of material sciences and synthetic organic chemistry as well as pharmaceutical sciences.[90] In this field, Awasthi and coworkers[91] have ever established a synthetic method to substituted 1H-tetrazoles with the aid of silver nanoparticles. With the optimized reaction conditions with 20mol% of silver nanoparticles, the [3+2]-cycloaddition of nitriles **79** with NaN_3 resulted in quite good yields for the corresponding products **80** (Scheme 33). It was suggested that the silver nanoparticles act as a Lewis acid to activate the nitrile groups via complexation and enhancement of electrophilic character of cyanide groups.



Scheme 33. [3+2]-cycloaddition of nitriles with NaN_3

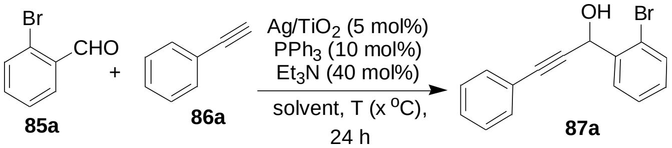
6. Other catalytic reactions to valuable chemicals catalyzed by silver nanoparticles

Three-component coupling reactions of aldehydes, alkynes, and amines (A^3-coupling) have attracted much attention because the corresponding are versatile building blocks for the synthesis of synthetically useful molecules.[92] Heterogeneous catalysis offers the opportunity for green synthesis of such products via A^3-coupling reaction. In this context, the nanosilver catalyst has been found to be effective heterogeneous catalyst in this A^3-coupling reaction of aldehydes, alkynes, and amines.[93] For example, the mesoporous SBA-15 supported silver nanoparticles with a highly ordered hexagonal mesostructure (AgSBA-15, average 8 nm) allowed the A^3-coupling reaction to the desired products with moderate to excellent yields (Scheme 34), (c) that different for the catalytic activity of AgI nanoparticles (Scheme 31).[88] As a result, the nanosilver-catalyzed A3-coupling reaction was found to be affected by the steric hindrance of the aldehydes. The authors suggested that it was possibly ascribed to the unfavorable effect of the SBA-15 channels on the addition of iminium ions to activated alkynes. Similarly, Movahedi and coworkers[94] have also reported a good example of catalytic synthesis of propargylamines through one-pot three-component A^3 condensation of aldehydes, amines, and alkynes, by immobilized silver on surface-modified ZnO nanoparticles.



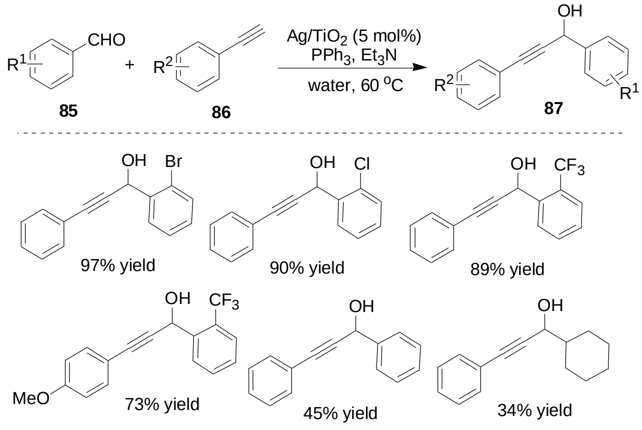
Scheme 34. A^3-coupling reactions of aldehydes, alkynes, and amines

Table 4. The effect of particle size of nanosilver on catalytic addition of alkyne **86a** to aromatic aldehyde **85a**.[95]



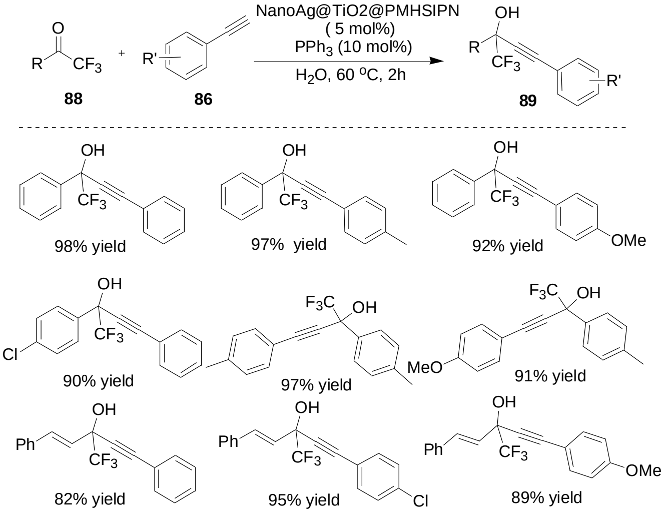
Entry	Particle size of Ag (nm) on TiO_2	Solvent	Temperature (°C)	Yield (%)
1	1	H_2O	100	59
2	5	H_2O	100	85
3	5	H_2O	60	89
4	10	H_2O	100	77
5	20	H_2O	100	81
6	10	H_2O/DCM	40	5
7	10	H_2O/toluene	100	7
8	10	THF	70	0
9	10	Toluene	110	0

Although nanosilver-catalyzed A^3-coupling of aldehydes, alkynes, and amines has been determined in 2010, the first example of 1,2-addition of alkynes to aldehydes that catalyzed by silver nanoparticles was only reported in 2012.[95] In this work, Yao et al. found the titanium oxide-supported silver nanoparticles could be utilized as an efficient catalyst for the direct addition of terminal alkynes to aromatic aldehydes (Table 4 and Scheme 35). Under the optimized reaction conditions (*see* entry 3 of Table 4), a series of aldehydes and alkynes was investigated in this reaction. Interestingly, the *ortho*-substituted aldehydes with halide groups or trifluoromethyl group gave good to excellent yields in every cases. However, general aromatic aldehydes and aliphatic aldehydes led to poor yields.



Scheme 35. Direct addition of terminal alkynes to aromatic aldehydes

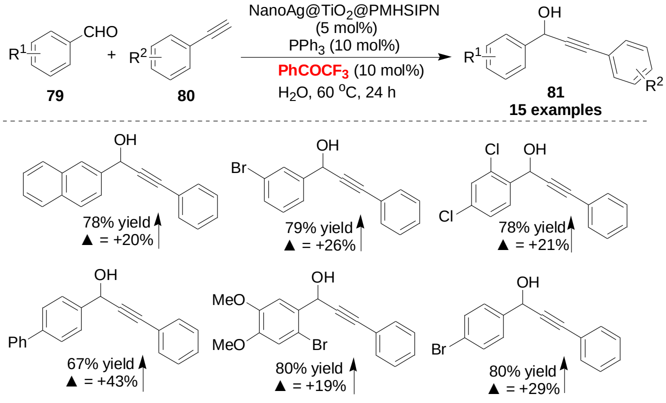
Very recently, we have developed successfully a new strategy to mono-dispersed hybrid Ag@TiO_2 nanocomposites using a novel functional material, polymethylhydrosiloxane (PMHS)-based semi-interpenetrating networks (PMHSIPN).[96] And then the results of catalytic addition of alkynes to carbonyl compounds showed that the nanosilver catalyst (nanoAg@TiO_2@PMHSIPN) had excellent activity in the alkynylation of trifluoromethyl ketones or α,β-unsaturated trifluoromethyl ketones with terminal alkynes. As shown in Scheme 36, the hybrid Ag@TiO_2 nanoparticles showed an extremely high level of catalytic activity for the selective 1,2-alkynylation of various trifluoromethyl ketones and *α,β*-unsaturated trifluoromethyl ketones in water, which led to a wide broad of fluorinated alcohols in high yields (up to 98% yield). Therefore this nanocatalytic protocol offers considerable benefits including environmentally benign aqueous transformation.



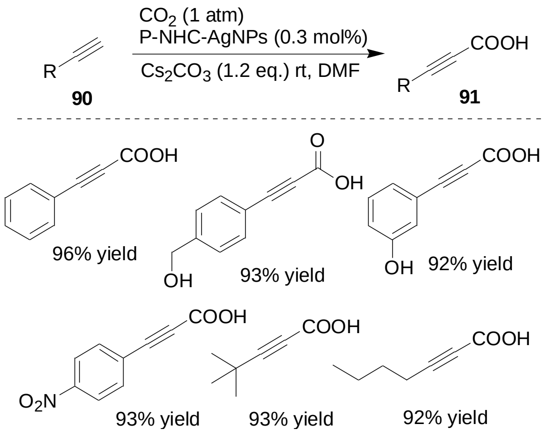
Scheme 36. Nanosilver-catalyzed alkynylation of trifluoromethyl ketones and α,β-unsaturated trifluoromethyl ketones

More importantly, on the basis of the nanoAg@TiO_2@PMHSIPN-catalyzed alkynylation of trifluoromethyl ketones, we developed a new concept that high-reactive substrate as a "reactive tractor" to pull transformation of low-reactive substrates, called as springboard chemistry or HDL catalysis, in which we found trifluoromethyl ketone could be used as a high-reactive additive for the activation of nanosilver-catalyzed alkynylation of aldehydes dramatically.[96] The nanosilver-catalyzed alkynylation of aromatic aldehydes proceeded in good to high yields under optimized reaction conditions (Scheme 37, up to 99% yield).

In the past years, enormous efforts have been made towards the development of efficient incorporation and utilization of carbon dioxide in organic synthesis.[97] In 2012, Zhang et al. reported a poly-(*N*-heterocyclic carbene, NHC) supported silver nanoparticles system that could serve as a reusable heterogeneous catalyst for the carboxylation of terminal alkynes with CO_2 (Scheme 38).[98] The nanosilver catalyst system exhibited very high activity and excellent stability in the carboxylation of various alkynes, including aromatic alkynes and aliphatic alkynes, with carbon dioxide. Notably, except the high yields for such nanosilver-catalyzed transformation, the nanosilver catalyst is stable to air and can be easily recovered and reused. In addition, it was suggested that the unique N-heterocyclic carbene polymer and silver nanoparticles provided a synergistic effect on activation of terminal alkynes and carbon dioxide.



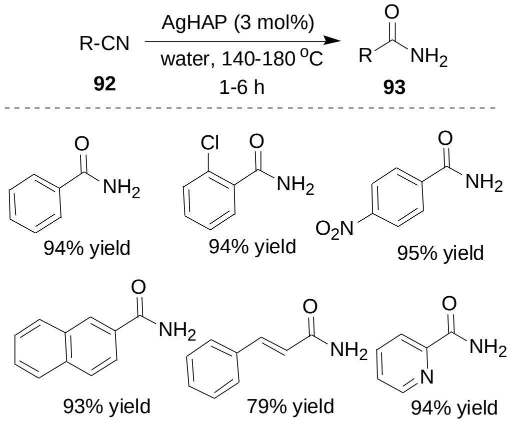
Scheme 37. Trifluoromethyl ketone-promoted nanosilver-catalyzed alkynylation of aromatic aldehydes based on the concept of HDL Catalysis.



Scheme 38. Nanosilver-catalyzed carboxylation of terminal alkynes with CO_2

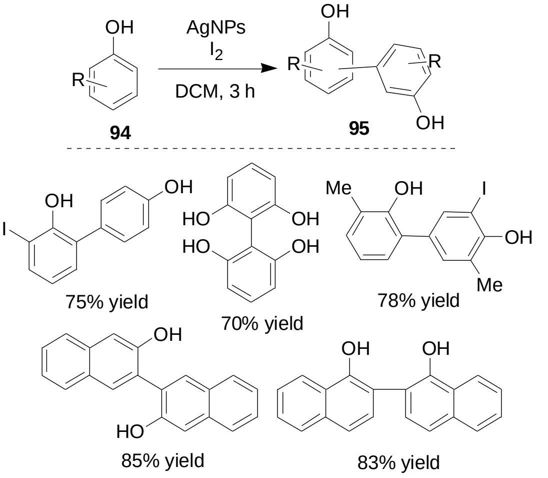
In the topic of nanosilver-catalyzed transformations to the preparation of fine chemicals, selective hydration of nitriles is non-negligible and important reaction in the synthesis of amides.[99] In 2009, Kaneda et al. have ever found that the hydroxyapatite-supported silver nanopartilces (AgHAP) was a highly efficient and reusable heterogeneous catalyst for hydration of nitriles in water (Scheme 39).[99a] In this reaction, the nanosilver catalyst system was quite effective for aromatic nitriles, heteroaromatic nitriles, and cinnamonitrile, which led to good to excellent yields. However, the hydration of aliphatic nitriles was not successful because only trace product was detected in such case. In the hydration of aromatic nitriles, Tyler's Ag-PTA nanoparticles (PTA = 1,3,5-triaza-7-phosphaadamantane) were also effective to give the corresponding products in moderate to high yields (up to 90% yields).[99b] In addition, the Ag-PTA nanoparticles catalyst has also been applied in the hydration of acetone cyanohydrin, in which the 2-hydroxy-2-methylpropanamide was obtained in promising yield (17%) under the optimized reaction conditions.

Except above reactions that supported the distinctive catalytic activity of silver nanoparticles, nanosilver catalyst systems have also been found some application in other simple reactions, such as the amination of β-dicarbonyl compounds to the synthesis of β-enanmino ketones or esters,[100] and acylation of amines and alcohols with acetic acid under solvent-free conditions.[101]

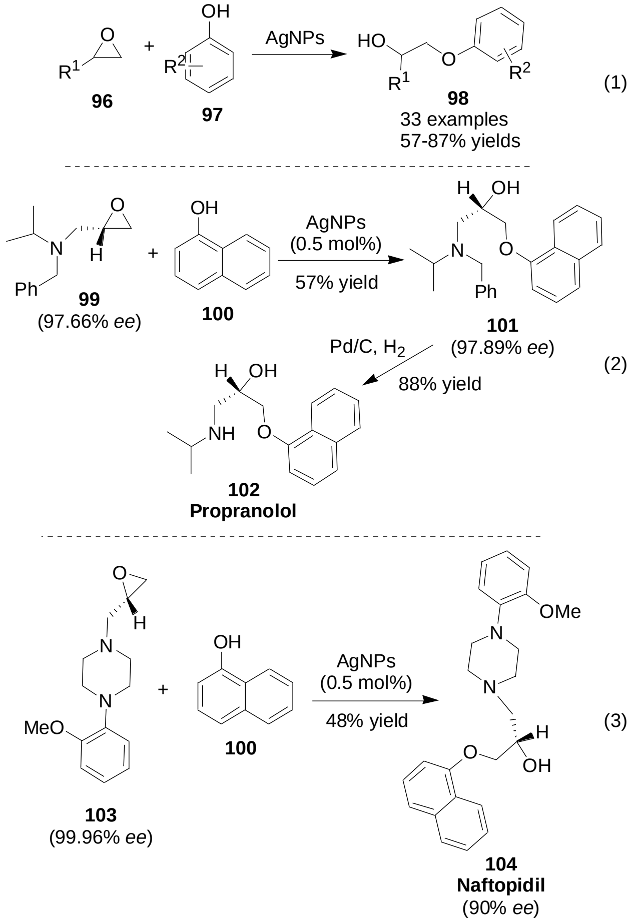


Scheme 39. Nanosilver-catalyzed hydration of aliphatic nitriles

Natural chitosan-supported silver nanoparticles has been determined in 2009 as an efficient catalyst in selective carbon-carbon coupling reaction of phenolic compounds in the presence of molecular iodine.[102] It is a very interesting report on the homo-coupling of phenols with silver nanoparticles as catalyst. The experimental results indicated that the coupling reaction of simple phenols proceeded via the formation of *para*-iodophenol followed by *ortho-para* site coupling, leading to the corresponding products in good yields (Scheme 40). For other phenol substrates, including naphthols, the homo-coupling of such phenols occurred at *ortho*-position.

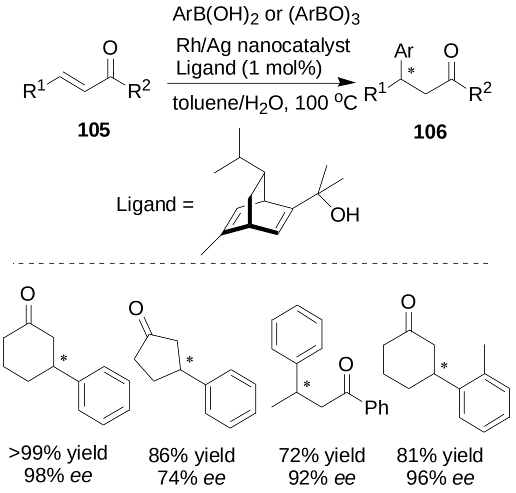


Scheme 40. Cross-coupling of phenols promoted by nanosilver system.



Scheme 41. AgNPs-catalysed epoxide phenolysis

Very recently, Chakraborti et al.[103] reported a chemoselective epoxide phenolysis/ring opening reaction catalyzed by silver nanoparticles, in which the silver nanoparticles exhibited high activity and other metal nanoparticles, such as Au, Pd, Cu, In, and Ru, are less effective in this reaction. The role of the silver nanoparticles was envisaged by the authors as synchronous dual activation of model with epoxide-phenol with the aid of a cooperative network of coordination, anion-π interaction, and hydrogen bond. In the catalytic ring-opening reaction of epoxides with phenols, the corresponding ether products were obtained in good yields with excellent region-selectivity (Scheme 41). Importantly, the AgNPs-catalysed epoxide phenolysis offers a new and practical synthetic strategy for construction of a wide range of ether-containing alcohols and has been exemplified through the synthesis of cardiovascular drugs propranolol (**102**) and naftopidil (**104**) in optically pure forms.



Scheme 42. Enantioselective conjugate addition

At last, it should be noted that the nanosilver particles could be applied as heterogeneous catalyst in asymmetric catalysis. The only one example was reported by Kobayashi and coworkers in 2012.[104] The authors developed successfully a highly active bimetallic nanoparticles, PI/CB (polymer-incarcerated (PI), copolymer and carbon black (CB) as a second support) Rh/Ag, for asymmetric conjugate addition of arylboronic acids (**105**) to enones (**106**) (Scheme 42). In this protocol, the structures of the bimetallic Rh/Ag catalysts and chiral ligands strongly affect their catalytic activity and enantioselctivity as well as the amount of metal leaching. To understand why Ag affects both the Rh leaching and catalytic activity of Rh/Ag nanocatalyst, the authors carried out STEM and energy-dispersive X-ray spectrometry (EDS) analyses. These studies suggested that the size effect and the existence of metal-metal interactions play important role in the formation of bimetallic structure. Silver that formed alloy nanoparticles with Rh can prevent aggregation of the Rh nanoparticles, thus it enhances the catalytic activity and improve the stability of bimetallic nanoparticles to control the metal leaching. Although the authors did not determine the oxidation states of the metals on the surface of Rh/Ag NPs, this is a remarkable example of the positive effects of silver in nanocatalysis, which would also open a new opportunity for the development of asymmetric heterogeneous catalysis in the near future.

Conclusions

In summary, silver nanoparticles catalysis has been of great interest in organic synthesis and has expanded rapidly in the past ten years because of nanosilver catalysts' unique reactivity and selectivity, stability, as well as recyclability in catalytic reactions. Especially, synthetic interest in nanosilver-mediated organic synthesis has increased spectacularly in the last few years as a result of the novelty of the concept of nanocatalysis and several advantages from an atom-economic and environmental benign point of view. As can be seen from the research results reported in this review, the application of heterogeneous silver-based nanoparticles to general organic reactions has proved to be an effective strategy in the development of highly efficient organic transformations in term of efficiency and selectivity. In particular, nanosilver catalysis has been found it is powerful function in total synthesis of natural products and pharmaceutical molecules. Although we did not discuss the synthetic procedures of silver-based nanoparticle and related information on detail impact of support on the catalytic activity of silver in this review, the positive effect of support, including inorganic and polymeric materials, for silver nanoparticles is fascinating since it has enabled unprecedented or low selective transformations to highly reactive and chemoselective catalysis for various nanosilver-catalyzed reactions. Undoubtedly, the future direction is to continue to expand the scope of nanosilver-catalyzed organic reactions with unique nanostructural features through the investigation of the potential method of supported silver nanoparticles. The story of application of nanosilver catalyst systems for organic reactions will continue to expand with rise of new inorganic methodologies in the preparation of heterogeneous and supported silver nanoparticles. Therefore it is envisaged that future developments will include a greater emphasis on 'nanosilver' with excellent activity and selectivity in new reactions and synthetically useful transformations.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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