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Recent Advances in Nano Silver Catalysis for Organic Transformations

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Abstract. This account explains three types of reactions to form homogeneous or heterogeneous nanocatalysts; coupling reaction, reduction reaction, and cascade reaction. Catalyst is an important technology and has various advantages. Metal oxides, or metals, placed on a support or carrier in a different state, are the catalytically active part of a solid catalyst. Particles that range in size from 1 to 100 nm are referred to as metal nanoparticles, and they are frequently used in synthetic organic chemistry. Based on their characteristics, nanocatalysts have several benefits, including increased chemical reaction selectivity and efficiency. Furthermore, this report shows different example that scientists exploring nanocatalysts through coupling reactions, reduction reactions, and cascade reactions, and different ways, such as experiments or filter paper to produce catalysts. Discovering that nanocatalysts not only have the function of accelerating but also help the treatment of tumors. In the future, nanocatalysts will find more applications in other industries. It will enable people to succeed more highly in a variety of industries.

Keywords: Organic Reactions, nanoparticles, catalyst.

1. Introduction

A key technology that allows the functionalization and use of a wide range of raw materials for the creation of valuable goods is catalysis. Homogeneous catalysis is when the catalyst and the reactants are in the same phase. Homogeneous catalysts are soluble, which can increase the phase of reactants [1]. Heterogeneous catalysis refers to catalysis at an interface in which the reactants and catalyst are in various phases. In heterogeneous catalysis, the reactants are in gases or liquid state, catalysts are powders or solids which are recyclable after simple filtration. The catalytically active component of a solid catalyst is metal oxides or metals, which are fixed on a support or carrier in a separate state. Metal nanoparticles are known as particles with a size between 1 to 100 nm and have been commonly utilized in synthetic organic chemistry. Nanocatalysts have several advantages based on their properties, such as enhanced efficiency and selectivity of chemical reactions. This review summarizes the recent advances in the application of Ag nanoparticles as efficient catalysts in organic transformations, including reductions, coupling reactions, and cascade reactions.

2. Coupling reactions

An organic reaction known as a coupling reaction involves two chemical species, a bond between the molecules of the reactants, and a left-to-right flow of energy [2]. Scientists have shown that catalysts can be created by coupling processes. Palladium, for instance, has a high coupling reaction efficiency, making it a potential catalyst.

Suzuki cross-coupling reactions will be significantly impacted by the size and form of nanocatalysts, and this will have an impact on future advances of cross-coupling reactions, according to a 2011 review by Aziz Fihri and colleagues. As seen in **Figure 1** [3], the example formula for the Suzuki coupling reaction is Br coupled with $B(OH)_2$ to produce biphenyl.

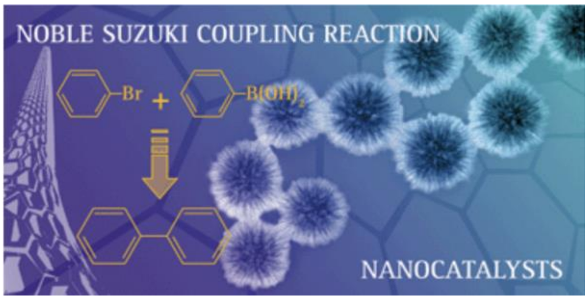

Figure 1. Suzuki coupling reaction [3]

Ag nanoparticles are commonly stabilized by applying capping agents or distributing them on supports, as Dr. Jian Cao found out in 2018. They stated that the novel nanocatalyst has excellent activity with remarkable durability and reusability in the three components of the reaction involving haloalkanes, alkynes, and amines (**Fig. 2**). Thus, Ag loadings of up to 8% and particle sizes of 11.0±3.2 nm were achieved. Eight successful recycling cycles of this catalyst have resulted in activity loss or AgNP aggregation. Consequently, they are able to demonstrate that the Ag nanoparticle can be used as a catalyst by means of a coupling process [4].

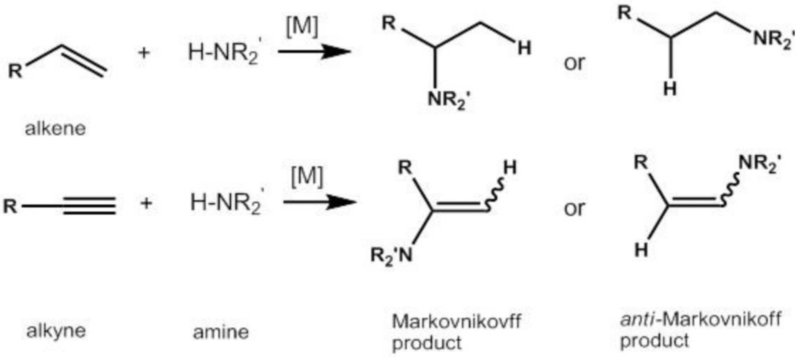

Figure 2. Haloalkanes, alkynes, and amine reaction [4]

In 2020, Mario Pagliaro and colleagues demonstrated that silver nanoparticles have a rich and varied chemistry and can transform catalysts through coupling reactions. In the field of catalysis, molecularly doped metals were first used in 2002. **Figure 3** illustrates the extraordinary performance of the catalyst produced by the polyacid Nafion trapped in silver after three years of research by Avnir and colleagues in the acid-catalyzed pinacol–pinacolone rearrangement and the dehydration of 2-phenylethanol to styrene. They stated that silver nanoparticles can be used in additional fields in the future, based on the main benefits of silver catalysts. [6]

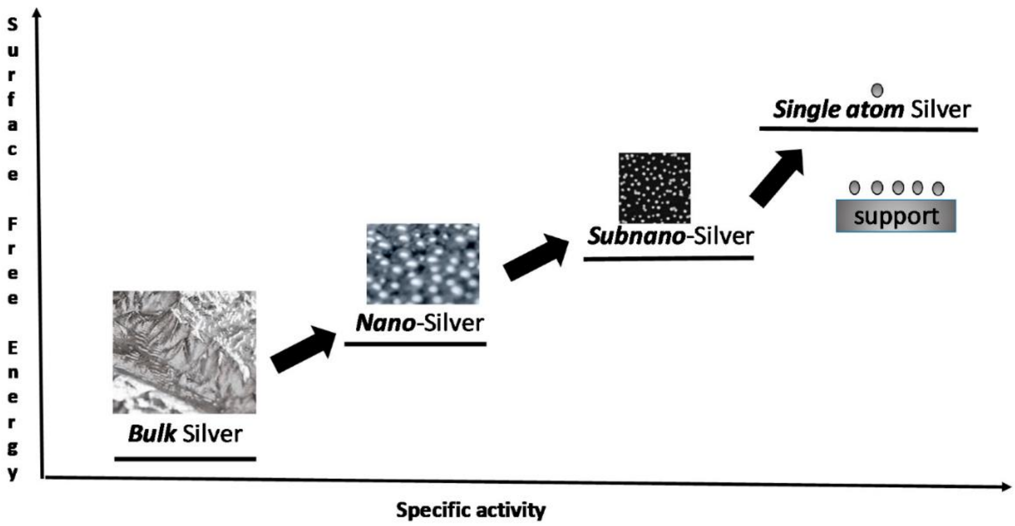

Figure 3. Reduced Ag particle size has an impact on catalytic specific activity [6]

Wang Xie and associates conducted metal nanoparticle research in 2024. They stated that the Cu (II)-Based Framework may accommodate the assembling of metal NPs. Using H3TPA, BIBT, and DMF, a Cu (II)-based MOF $\{[Cu_{1.5}(TPA)(BIBT)]_4DMF\cdot6H_2O]\}n$ (1) was created under solvothermal conditions. Cu-MOF 1 has interpenetrated 3D coordination frameworks and 1D channels along the a-axis, according to the structural analysis. Various analytical techniques confirmed that Ag NPs were encapsulated within the pores of Cu-MOF 1 to create MOF composites and Ag NPs. These composites can operate as coupling reaction catalysts because of their strong resistance to aggregation. With the use of Cu (II)-based MOFs loaded with Ag NPs, our work offers a workable strategy for heterogeneous catalysts in A3-coupling processes (**Figure 4**.) [7].

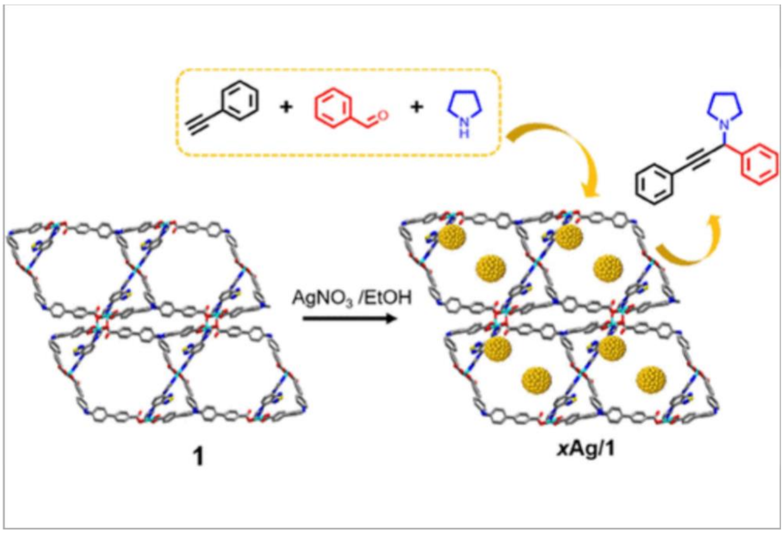

Figure 4. Cu(II)-Based Metal–Organic Framework with silver nanoparticles[7]

Overall, the coupling reaction is an important way for nanoparticles to transfer to nanocatalysts, and the nanocatalyst has a strong potential for utilization in different areas.

3. Reduction reaction

The primary process in the creation of nanocatalysts, besides coupling reactions, is the reduction reaction. A reduction reaction occurs when electrons move from reactants to products via simultaneous reduction and oxidation [8]. Reduction reactions have several applications and are crucial to biological reactions nanoparticles can be created using a reduction reaction at a highly effective catalyst, according to a 2018 Hannaneh Heidari paper. Nano fibrillated cellulose (NFC) hydrogel was prepared in two different ways to serve as a support, stabilizer, and reducing agent during the in situ green production of silver nanoparticles (Ag NPs). It was examined whether these composites could catalyze the change of 4-nitrophenol (4-NP) into 4-aminophenol (4-AP). A range of characterization methods were used to examine the structure of the produced composites at various concentrations of AgNO3. All of the nanocomposites had good catalytic activity, according to the data. Of them, the Ag@NFC-2 sample with a 0.25 M $AgNO_3$ concentration, prepared by the second technique, had the highest catalytic efficiency. Ag NPs were uniformly dispersed and spherical throughout the nanofiber [9].

Scientists Mohini Mourya and colleagues reported in 2018 that a highly efficient catalyst may be produced using a certain technology. Researchers dispersed silver nanoparticles on filter paper and discovered that recycling silver nanoparticles on filter paper is simple. Whatman-40 filter sheets were submerged in suspensions of previously manufactured monodispersed Ag nanoparticles in toluene to create the dip catalyst. The produced Ag NPs based dip catalyst was evaluated in a range of model reactions, including the degradation of methyl orange, the reduction of nitro to amine, and intramolecular cascade reduction. As seen in **Figure 5**., extracting the catalyst from the reaction media is as simple as withdrawing the catalyst strip. It showed exceptional efficiency and reusability [10].

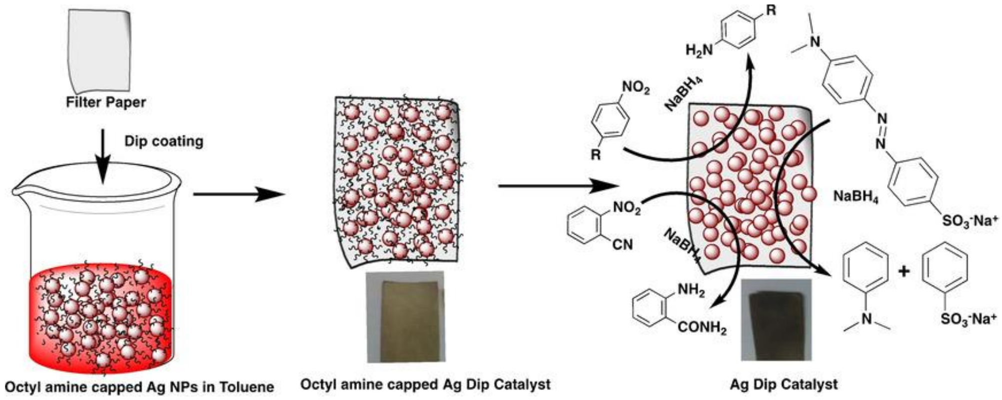

Figure 5. Processes of producing catalyst using filter paper[10]

In general, a reduction reaction is a way to produce a highly efficient catalyst, and it has fewer limitations and can be applied to different methods.

4. Cascade reactions

Cascade reaction is the most complex process among these three reactions and can also be used to manufacture catalyst, in addition to reduction and coupling reactions. A tandem or domino reaction is the same as a cascade reaction. At least two single reactions make up a cascade reaction, and the subsequent reaction occurs after the preceding reaction is finished [11]. According to a 2018 study by Mohini Mourya, filter paper can be coated with silver nanoparticles to create catalysts. In order for the catalyst to fully develop, a cascade reaction is also required [10].

According to J Mater Sci in 2020, M-NPs' surface electrons aid in the facilitation of reduction processes. The conversion of 4NIP is aided by this electron transport from the NP surface to the support and vice versa. The adsorption of reactants on the surface and the electron relay process utilizing NPs supported on a substrate are depicted in **Figure 6.** This phenomenon is not exclusive to 4NIP; rather, it lays the groundwork for investigating further nitro phenol reduction processes that are heterogeneously NP-catalyzed. The rate constants for 4NIP reduction by $NaBH_4$, supported transition M-NPs-catalyzed, at 25°C have been reported in another research [12].

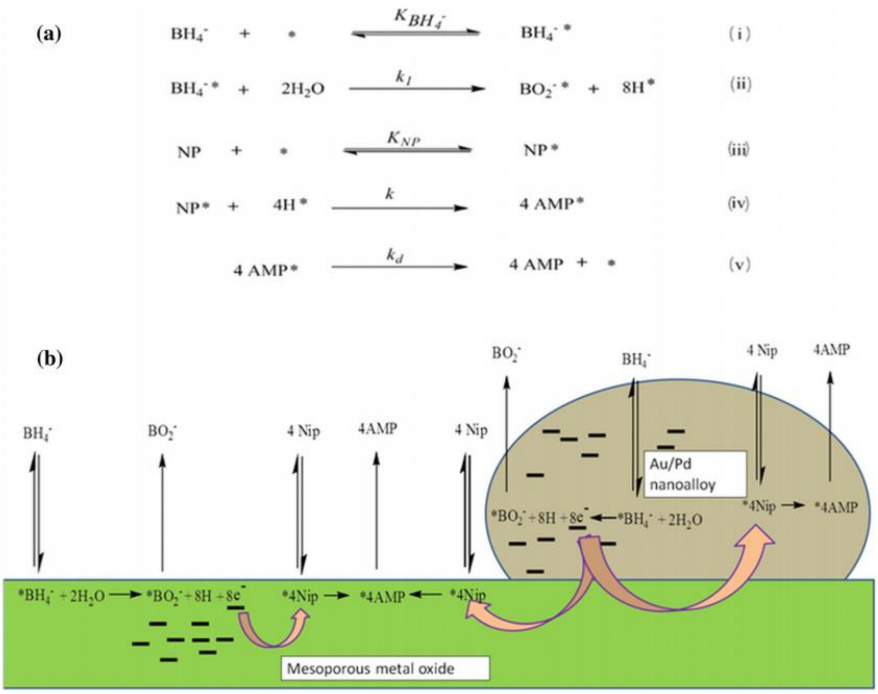

Figure 6. (a) Development of hydrogen from borohydride and surface adsorption and reduction of four NPs. **(b)** Adsorption onto the support's surface, NPs, and the electron relay system[12]

According to research done in 2022 by Janne M. Naapuri and colleagues, when silver or gold nanoparticles are combined with aqueous media and an enzyme at room temperature, inorganic silver or gold species can be created. The factors that influence the creation of silver nanoparticles are protein, bioconjugate, and PH. Candida antarctica lipase (CALB) solution was used to create nanobiohybrids, which contained Ag_2O nanoparticles with an average diameter of 9 nm. With the use of specifically created bioconjugates, such as the CALB modified with dextran-aspartic acid polymer (Dext6kDa), a nanobiohybrid containing smaller Ag (0)/Ag_2O nanoparticles was created. Au (0) species were found in all cases employing gold-based nanobiohybrids. Thermomyces lanuginosus lipase (TLL) was utilized to produce nanoflowers with a diameter range of 100–200 nm in addition to nanoparticles. Each nanobiohybrid continued to function in both enzymatic and metallic processes. As seen in **Figure 7**., these nanobiohybrids exhibited remarkable dual activity, for instance in hydrolysis/cycloisomerization cascades that started with allenic acetates. by making use of the characteristics of enzymes and catalysts, which open up new possibilities for cascade reactions. [13].

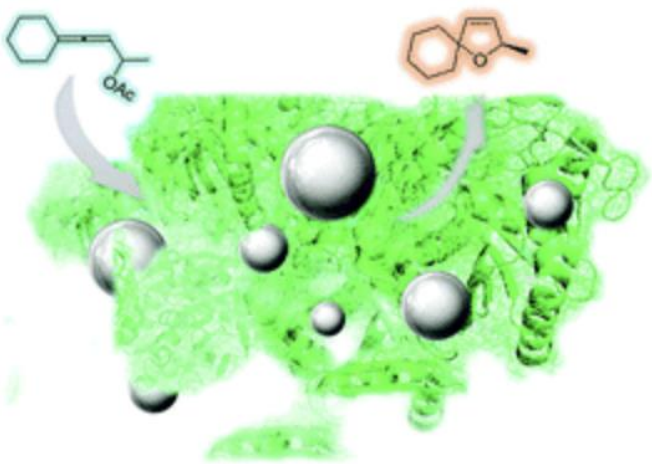

Figure 7. New hybrids with gold or silver nanoparticles [13]

Sangeeta Meena and colleagues employed a cascade reaction in 2023 to investigate the distinctions between Ag-S Type Quantum Dots and superstorm nano catalysts. In 92% of the cases, the moderate reaction involving a decarboxylative radical cascade reaction between α-monocarboxylic acid and clinolamide is made possible by the catalyst $Ag_{62}S_{13}$, allowing for the direct production of pharmaceutically valuable 3,4-dihydroquinolinone. $Ag_{62}S_{12}$ is a more prolific and efficient catalyst than $Ag_{62}S_{13}$.$Ag_{62}S_{12}$-S was created using a range of analytical techniques, including Thermogravimetric Analysis, Brunauer-Emmett-Teller (BET) analysis, X-ray photoelectron spectroscopy, energy dispersive X-ray spectroscopy, electrospray ionization mass spectrometry, single-crystal X-ray diffraction, nuclear magnetic resonance (1H and 31P spectroscopy), and BET analysis. The whole surface area favorable to a one-electron transfer reaction mechanism is revealed by the BET results. Density functional theory states that removing the core S atom of $Ag_{62}S_{12}$-S accelerates the decarboxylation process, increases the amount of charge transferred from $Ag_{62}S_{12}$ to the reactant, and creates a correlation between the catalytic and nano catalyst structures, as seen in **Figure 8**.[14]

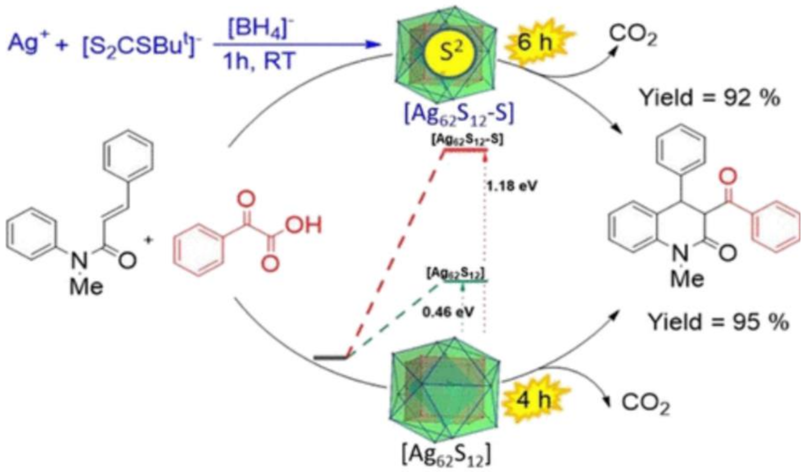

Figure 8. High-nuclearity silver nanoclusters [14]

Furthermore, through cascade reactions, nanocatalysts can be applied in several fields. Au NPs are a unique nanozyme that mimics glucose oxidase and particularly accelerates the β-D-glucose oxidation process into gluconic acid and H_2O_2. Shanshan Gao and colleagues have revealed that Au NPs can promote tumor cell death through a cascade reaction. **Figure 9.** illustrates the results of thorough in vitro and in vivo assessments that these biocompatible composite nanocatalysts underwent, which demonstrated remarkable efficacy of nanocatalytic therapy with an acceptable tumor-suppression rate (69.08%). Nanocatalysts will therefore have a significant impact on tumor treatment [15].

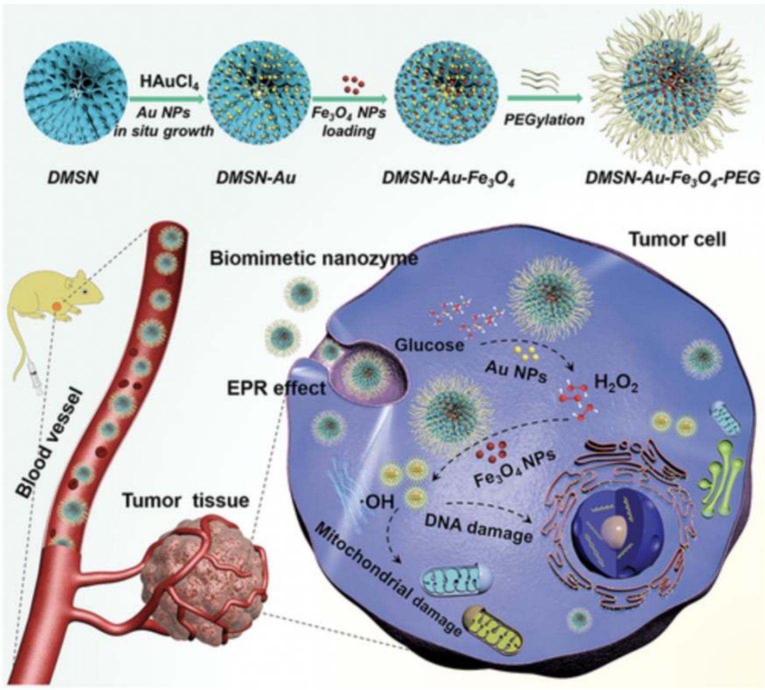

Figure 9. Nanoparticles cause the death of malignant cells [15]

Overall, cascade reaction is a method for producing catalysts and can be applied in various situations. Its unique property helps scientist to solve different problems and further develop the role and function of nanocatalysts.

5. Conclusion

This review of three different types of reactions for silver nanoparticles to produce a catalyst. Coupling reaction, reduction reaction, and cascade reaction, each reaction has different advantages and disadvantages, scientists used this reaction to form highly efficient catalysts, through various ways, such as filter paper or another experiment. There will be more uses for nanocatalysts in different fields in the future. Which will help people to achieve higher levels of success in different fields.

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