The Uses of Various Nanoparticles in Organic Synthesis: A Review

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ABSTRACT
Nanoparticles have been widely applied in different areas including, medicine, sensor and catalysis. In our study we have concentrated our work towards the application of the metal nanoparticles in the field of catalysis. Several reports has been found on wide range of application of various supported metal nanoparticles in catalysis including Au, Ag, Pt, Cu, Cd, Ni etc. metals in the form of reduced metals and in compounds forms as heterogeneous catalysis. Nanoparticles have potential for improving the efficiency, selectivity and yield of catalytic processes. Higher selectivity of the nanoparticles towards reaction proceeds through less waste and fewer impurities which could lead to safer technique and reduced environmental impact. In this review we have focused on the developments in new types of green nanocatalysts as well as developments in green catalytic reactions.

Keywords: Nanoparticles; Nanocatalysts; Organic synthesis; Green Nanocatalysts; Green reactions; Nanotechnology.

INTRODUCTION
The last decade has witnessed enormous development in the field of nanoscience and nanotechnology. Several reports show the amazing level of the performance of nanoparticles as catalysts in terms of selectivity, reactivity and improved yields of products. In addition, the high surface-to-volume ratio of nanoparticles provides a larger number of active sites per unit area, in comparison with their heterogeneous counter sites [1,2]. In this review, we focus on green nanocatalysts as well as industrially important green reactions. This article has two parts. The first part involves green nanocatalysts and the second part involves green reactions.

SYNTHESIS OF VARIOUS NANOPARTICLES
Various nanoparticles are shown in Figure 1 and Schemes 1-53 in Tables 1-15.

Calcium oxide nanoparticles

Among various nanoparticles, calcium oxide nanoparticles have
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Table 1: Reduction Reactions.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reference No.</th>
<th>Reaction</th>
<th>Nano particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td></td>
<td>[Scheme 1: Synthesis of Amine-Substituted MCR Scaffolds and Dihydroquinolizine Derivatives]</td>
<td>Ag</td>
</tr>
<tr>
<td>86</td>
<td></td>
<td>[Scheme 2: Reduction of Methylene Blue dye]</td>
<td>Ag</td>
</tr>
<tr>
<td>87</td>
<td></td>
<td>[Scheme 3: Oxygen Reduction Reaction at Gold Nanoparticles]</td>
<td>Au</td>
</tr>
<tr>
<td>88</td>
<td></td>
<td>[Scheme 4: (i) Synthesis of styrene from 2-phenyl oxirane (ii) Synthesis of cyclohexanol from cyclohexanone]</td>
<td>AuNP/CeO2</td>
</tr>
<tr>
<td>89</td>
<td></td>
<td>[Scheme 5: Selective reduction of nitrobenzene]</td>
<td>Au/CeO2</td>
</tr>
<tr>
<td>90</td>
<td></td>
<td>[Scheme 6: Synthesis of 1,2-diphenyldiazene from nitrobenzene]</td>
<td>Au/ZrO2</td>
</tr>
<tr>
<td>91</td>
<td></td>
<td>[Scheme 7: Synthesis of substituted ketone by substituted alcohol]</td>
<td>Pt-Cu alloy</td>
</tr>
</tbody>
</table>

received considerable attention because of their unusual properties and potential applications in diverse fields [3]. Calcium oxide (CaO) itself as cost effective, highly basic, non-corrosive, environment friendly, and economically benign, that can be regenerate and reused. Also, they require only mild reaction conditions to produce high yields of products in short reaction times, in comparison with traditional catalysts [4-6]. Many researchers reported that calcium oxide nanoparticles as an active catalyst in many chemical transformations such as adsorption of Cr (VI) from aqueous solutions [7], biodiesel trans-esterification [8-19], removal of toxic heavy metal ions in water [20] and artificial photosynthesis [21] and the degradation of bromocresol green [22], purification of vehicle gas exhaust [23]. In accordance with the above mentioned consequence of nanoparticles in catalysis, and the significance of...
Calcium oxide nanoparticles, as an efficient, non-explosive, eco-friendly, non-volatile, recyclable and easy to handle catalyst, can be used in the catalysis of many organic transformations.

**Preparation of CaO nanoparticles**

NaOH (1 g) was added to a mixture of ethylene glycol (12 ml) and Ca(NO₃)₂·4H₂O (6 g) and the solution stirred vigorously at room temperature for 10 min; the gel solution was kept about 5 h at

---

**Table 2: Oxidation reactions.**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reference No.</th>
<th>Reaction</th>
<th>Nano particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>92</td>
<td><img src="image" alt="Scheme 8" /></td>
<td>phenylmethanol → benzaldehyde</td>
</tr>
<tr>
<td>2.</td>
<td>93</td>
<td><img src="image" alt="Scheme 9" /></td>
<td>phenylmethanol → AuNP phenylmethanol</td>
</tr>
<tr>
<td>3.</td>
<td>94</td>
<td><img src="image" alt="Scheme 10" /></td>
<td>2-hydroxymalonic acid</td>
</tr>
<tr>
<td>4.</td>
<td>95</td>
<td><img src="image" alt="Scheme 11" /></td>
<td>cyclohexane → cyclohexanol + cyclohexanone</td>
</tr>
<tr>
<td>5.</td>
<td>96</td>
<td><img src="image" alt="Scheme 12" /></td>
<td>p-tolylmethanol → 4-methylbenzaldehyde</td>
</tr>
</tbody>
</table>
| 6.     | 97            | ![Scheme 13](image) | methanol → formaldehyde }
Table 3: Conversion of organosilanes to silanols.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reference No.</th>
<th>Reaction</th>
<th>Nano particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>98</td>
<td></td>
<td>Pt Nano cluster</td>
<td>Pt</td>
</tr>
<tr>
<td>99</td>
<td></td>
<td>Pd/AuNp's</td>
<td>Pd</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>AuNPs</td>
<td>Au</td>
</tr>
</tbody>
</table>

**SCHEME 14:** Synthesis of Silanols from organosilanes

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reference No.</th>
<th>Reaction</th>
<th>Nano particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>101</td>
<td></td>
<td>PdNPs</td>
<td>Pd</td>
</tr>
</tbody>
</table>

**SCHEME 15:** Synthesis of Silanols

**SCHEME 16:** Synthesis of Silanols

Table 4: Suzuki cross-coupling Reactions and Sonagashira Reaction.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reference No.</th>
<th>Reaction</th>
<th>Nano particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>102, 103, 104, 105</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>106</td>
<td></td>
<td>Pd NPs</td>
<td>Pd</td>
</tr>
</tbody>
</table>

**SCHEME 17:** Synthesis of methyl cinnamate

**SCHEME 18:** Synthesis of biaryls

**SCHEME 19:** Synthesis of substituted biaryls

**SCHEME 20:** Synthesis of substituted biaryls by Phenyl boronic acid
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**SCHEME 21:** Synthesis of substituted Alkyne

\[
\text{Ar-X} + R \xrightarrow{\text{PdNPs}} \text{Ar} - R \xrightarrow{\text{Pd}}
\]

**Table 5: Hydrogenations.**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reference No.</th>
<th>Reaction</th>
<th>Nano particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>109, 110</td>
<td>Rh@TiO2/RhNPs/Rh@SiO2</td>
<td>Rh</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R = H, CH3, OCH3</td>
<td></td>
</tr>
</tbody>
</table>

**SCHEME 22: Synthesis of substituted cyclohexanes**

**SCHEME 23: Synthesis of substituted anilines**

**SCHEME 24: Synthesis of substituted alkenes**

**SCHEME 25: Synthesis of Aniline and 1-phenylethanol**

**SCHEME 26: Synthesis of Aniline**

**SCHEME 27: Synthesis of cyclohexanecarboxylic acid**
SCHEME 28: Synthesis of Alkene derivatives

\[
\begin{align*}
1-\text{Hexene} & \xrightarrow{\text{Pd-Ru NPs}} n-\text{Hexane} + \text{cis-2-Hexene} + \text{trans-2-Hexene} \\
\end{align*}
\]

RuPd

SCHEME 29: Synthesis of hexanes

\[
\begin{align*}
\text{NO}_2 & \xrightarrow{\text{Fe-Pt CD}} \text{NH}_2 \\
\text{OH} & \xrightarrow{\text{FePt}} \text{OH} \\
4-\text{nitrophenol} & \xrightarrow{\text{FePt}} 4-\text{aminophenol} \\
\end{align*}
\]

SCHEME 29: Synthesis of 4-aminophenol

Table 6: Ullmann Reaction.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reference No.</th>
<th>Reaction</th>
<th>Nano particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>119, 120, 121</td>
<td></td>
<td></td>
<td>Pd</td>
</tr>
</tbody>
</table>

SCHEME 30: Synthesis of biaryl derivatives

\[
\begin{align*}
\text{Cu} & \xrightarrow{200^\circ C} \text{Cu} \\
\end{align*}
\]

SCHEME 31: Synthesis of biaryls

\[
\begin{align*}
\text{Au} & \xrightarrow{\text{mesoporous organo silica}} \text{Au} \\
\end{align*}
\]

SCHEME 32: Synthesis of biaryls

Table 7: Heck cross-coupling Reaction.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reference No.</th>
<th>Reaction</th>
<th>Nano particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>124</td>
<td></td>
<td></td>
<td>Ni</td>
</tr>
</tbody>
</table>

1-((E)-prop-1-enyl)benzene

SCHEME 33: Synthesis of 1-((E)-prop-1-enyl)benzene

\[
\begin{align*}
\text{Co} & \xrightarrow{\text{CoNPs}} \text{1,2-diphenylethene} \\
\end{align*}
\]

SCHEME 34: Synthesis of 1-((E)-prop-1-enyl)benzene and 1,2-diphenylethene
Scheme 35: Synthesis of butyl cinnamate

\[
\text{Ar} - X + \text{CO}_2\text{Bu} \xrightarrow{\text{PdNPs}} (E)\text{-butyl cinnamate}
\]

Scheme 36: 1-methyl-4-(2-methylprop-1-enyl)benzene

Scheme 37: Synthesis of 1,1-diphenyl ethane and 1,2-diphenylethane

Scheme 38: Synthesis of 4-(3,5-dimethoxystyryl)phenol

Table 8: Deoxygenation Reaction.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reference No.</th>
<th>Reaction</th>
<th>Nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td>131</td>
<td></td>
<td>Au Catalyst CO \rightarrow \text{Ph} \xrightarrow{\text{Ph}} \text{styrene}</td>
<td>Au</td>
</tr>
</tbody>
</table>

Scheme 39: Synthesis of Styrene

Scheme 40: Synthesis of Spirooxindoles
**Scheme 40:** Synthesis of substituted but-2-ene

**Table 9:** Alkynylation of Aryl Halides.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reference No.</th>
<th>Reaction</th>
<th>Nano particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>134</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Scheme 41:** Synthesis of \(N,N\)-dialkyl-3-p-tolyprop-2-yn-1-amine

**Table 10:** Arylations and Diarylations.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reference No.</th>
<th>Reaction</th>
<th>Nano particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>135</td>
<td></td>
<td></td>
<td>FeCu</td>
</tr>
</tbody>
</table>

**Scheme 42:** Synthesis of diaryl Sulfane

**Scheme 43:** Synthesis of 2-phenylbenzo[d]thiazole, 2-phenylbenzo[d]oxazole and 1-methyl-2-phenyl-1H-benzo[d]imidazoles derivatives

**Scheme 44:** alkyl 3,3-diphenylacrylate

**Table 11:** Deoxygenation of Epoxides.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reference No.</th>
<th>Reaction</th>
<th>Nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>138</td>
<td></td>
<td>Au, Ag &amp; Cu</td>
</tr>
</tbody>
</table>

**Scheme 45:** Synthesis of 3-vinylbenzenamine and 3-ethylbenzenamine
Table 12: Oxidative Coupling of Alcohols.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reference No.</th>
<th>Reaction</th>
<th>Nano Particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>139</td>
<td>R1OH + H2N_R3 → Au/TiO2, 1 bar O2, RT</td>
<td>Au/TiO2, 1 bar O2, RT</td>
</tr>
<tr>
<td></td>
<td></td>
<td>98% selectivity</td>
<td>Au/TiO2, 1 bar O2, RT</td>
</tr>
</tbody>
</table>

SCHEME 46: Synthesis of N-(propan-2-ylidene)methanamine

Table 13: Esterification of Alcohols.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reference No.</th>
<th>Reaction</th>
<th>Nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>140</td>
<td>CNAgNPs → O NH2</td>
<td>Ag</td>
</tr>
<tr>
<td>2</td>
<td>141</td>
<td>CNNH2, O Fe3O4 → Fe3O4</td>
<td>Fe3O4</td>
</tr>
</tbody>
</table>

SCHEME 47: Synthesis of benzamide

SCHEME 48: Synthesis of substituted benzamide

Table 14: Hydration of Nitriles.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reference No.</th>
<th>Reaction</th>
<th>Nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>142</td>
<td>Primary alcohols + Molecular O2 → methyl benzoate, methyl butyrate, methyl pentanoate</td>
<td>Au</td>
</tr>
</tbody>
</table>

SCHEME 49: Synthesis of methyl esters

Table 15: Additional Organic Synthesis Reactions.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reference No.</th>
<th>Reaction</th>
<th>Nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>143</td>
<td>R1NH2 + R2NH2 → Nano-Fe3O4, H2O(6.0)</td>
<td>Fe3O4</td>
</tr>
</tbody>
</table>

SCHEME 50: Synthesis of tetraalkylpyrazine
Zinc is the most important component of various enzyme systems, it takes part in body’s metabolism and plays essential roles in proteins and nucleic acid synthesis, hematopoiesis, and neurogenesis [41,42].

Johnson et al. developed a new method for the green synthesis of ZnO nanoparticles. In this method, a new leucine-based diamine amphiphile was synthesized and self-assembled. In the presence of Zn\(^{2+}\) ions, the leucine-based diamine amphiphile assembled into nanofibers that efficiently formed ZnO nanoparticles on heating with Zn(CH\(_3\)COO)\(_2\) [43].

**Platinum nanoparticles**

Platinum nanoparticles (PtNs) possess a wide range of properties that can be used for various applications such as catalysts in organic catalysis, fuel cells, hydrogen storage, electrical conductivity, optics and nonlinear optics, coating, plastics, textile, biosensors and biomedicine [44-50]. Engelbrekt and co-workers demonstrated the synthesis of PtNPs using a variety of green methods such as the hydrogen reduction method in water as solvent, ethanol reduction method in an ethanol-water mixture. Monodisperse green Pt nanoparticles were synthesized by using glucose as the reducing agent and starch as the protective agent [51,52]. This synthesis method is environmentally friendly, highly reproducible, and easy to scale up. These nanocatalysts were tested for reduction and oxidation reactions and were found to have high catalytic activity. Moreover, these Pt nanoparticles are stabilized with ionic liquids and used as catalysts for four-electron reduction of dioxygen to water [53].

**Gold nanoparticles**

In recent years, AuNPs had attracted an immense interests in different fields of science, due to their unique features such as high X-ray absorption coefficient, ease of synthetic strategy, enabling precise control over the particle’s physico-chemical properties, strong binding affinity to thiols, disulfides and amines, unique tunable optical and distinct electronic properties [54-60]. The optical-electronics properties of gold nanoparticles are being explored extensively for high technology applications such as sensory probes, electronic conductors, therapeutic agents, organic photovoltaics, Fuel cells, drug delivery in biological and medical applications, and catalysis [61-65].

Itoh et al. investigated the synthesis and functions of gold nanoparticles with ionic liquids based on the imidazolium cation.
At room temperature green imidazolium-based ionic liquids such as 1-butyl-3-methylimidazolium hexafluorophosphate are used as liquid media for the synthesis of gold nanoparticles which can be used in dyes [66].

The gold nanoparticles were prepared by the addition of HAuCl₄ to green tea leaves extract at room temperature. The synthesis of the Au nanoparticles does not involve any toxic chemicals/organic solvents so it is a green synthetic process. The gold nanoparticles are used as catalysts for the reduction of methylene blue dye [67]. Au nanoparticles have been synthesized by a green photo catalytic method in which the synthesis is conducted in water [68]. Calcium-alginate stabilized gold nanoparticles are prepared using a photochemical green synthetic method [69]. Zhan and co-workers used Au nanoparticles as catalysts for the 4-nitrophenol reduction reaction. They have prepared Gold/TS-1 nanoparticles using two green routes which are sol-immobilization method and adsorption reduction method [70]. This gold nanoparticle catalyst show excellent performance for the propylene oxidation reaction.

Silver nanoparticles
Silver nanoparticles have commercialization applications for instance, sterilizing nanomaterials in consuming and medical products, textiles, food storage bags, refrigerator surfaces, and personal care products [71-74]. Additionally, they show optical, thermal, and catalytic properties and antimicrobial ability [75-79].

Silver nanoparticles have been synthesized using several green methods such as the seed-mediated growth method, in the presence of ionic liquids, and other reduction methods such as hydrazine reduction method, and sodium borohydride reduction method. Ag nanoparticles have been synthesized by a green photo catalytic method in which reaction is conducted in water [68]. Calcium-alginate stabilized silver nanoparticles are prepared using a photochemical green synthetic method [69]. These nanoparticles are used as catalysts for the 4-nitrophenol reduction reaction.

Aluminium nanoparticles
Solvent-free methods as well as methods involving the use of water as solvent have been used to synthesize aluminium oxide nanoparticles. Aluminum oxide nanoparticles are synthesized in water as the solvent which makes it a green nanocatalyst [80].

Bimetallic nanoparticles
Bimetallic nanoparticles (Figure 2) have been prepared by the ethanol reduction method, hydrogen reduction method, and other green methods. These nanoparticles have been used as catalysts in several organic chemistry, including, oxidation of carbon monoxide in aqueous solutions, hydrogenation of alkenes in organic or biphasic solutions and hydrosilylation of olefins in organic solutions [81,82].

Nickel-platinum nanoparticles
Nickel encapsulated by Pt (NiPt) has been synthesized using a green colloidal method [83]. Pt NPs are very expensive as electrocatalysts so the remedy for this is to diminish the cost by the synthesis of Ni-Pt bimetallic nanoparticles.

Gold-palladium nanoparticles
Au-Pd nanoparticles are prepared in the absence of organic ligands and adsorbed onto TiO₂ supports and is found to be stable in oxidative catalysis conditions [84]. It was investigated that 70% gold, 30% Pd composition of the bimetallic nanoparticles show the highest catalytic activity for the oxidative catalysis.

Application of various nanoparticles in green reactions
Applications of different nanoparticles in green reactions are brief in Figure 3 and summarized in Tables 1-15 [85-145].
CONCLUSION

There been many different types of metal nanoparticles that have been used as catalysts for many reactions. In many cases, the metal nanoparticles are synthesized in aqueous solution in which water is the solvent, or is conducted in the presence of ionic liquids. There have also been cases where the nanoparticles are used as catalysts for different types of green reactions. Green reaction conditions include using water as the solvent, using solvent that is organic-free, conducting the reaction using ionic liquids, and running the reaction at atmospheric pressure. While there has been a lot of progress in applying the use of green chemistry to catalysis with nanoparticles, there is lot more room to further expand this field. In this review article, we have focused on the synthesis of various nanoparticles and their use in organic synthesis. Still there is need to explore and to synthesize new nanocatalysts with more properties. This review provides a comprehensive understanding on organic reactions which are catalyzed using environmentally friendly nanoparticles and nanocatalysts.

ACKNOWLEDGEMENTS

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CONFLICT OF INTEREST

No authors have stated any conflicts of interest.

CONTRIBUTIONS

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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