Chapter - 7

Ag-Based Cluster in diverse Organic Transformations

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Abstract—*A brief discussion has been entailed around the synthesis and applications of several Ag-based materials. Major focus has been diverted towards some of the most advanced reaction in the field of catalysis.*

Introduction

Brief Description of Cluster

In chemistry, the word cluster refers to an ensemble of bound atoms with the polyhedral structure to which ligands are attached. Some of them contain small atom inside the cavity of the polyhedra, but most of them comprise of nothing.[1] In the case of metallic clusters, the metal atoms (same or different) are directly linked with each other leading to polyatomic metallic nucleus. These are found to be either isolated or associated with a definite number of ligands.[2]

The term 'Cluster' was first introduced by F.A. Cotton in the early 1960s to describe compounds containing metal-metal bonds. Later, the term

'Cluster' was evolved to introduce compounds containing element-element bond as well as any molecule containing metal-metal bond.[3] These clusters may contain a different number of metal atoms varying from two or three to several dozens, and also there is no limit on their size as well as in their variety. Moreover, the metal atoms in the cluster may be bonded with each other by a single or double or triple and sometimes by quadruple bonds. In some cases, it may be observed that the metal atoms are linked with each other by bridging ligands including organic polydentate ligands.[4]

Although the term 'cluster' contains any compound containing polyhedral structure and having an element-element bond, the compounds containing metal-metal bonds are of more interest, and they are specifically known as 'metal atom clusters compounds.[5] The chemistry of low-valent transition metal atom clusters has been a most focussed subject of interest for the scientist throughout the 1970s and 1980s. During these two decades, a wide range of new cluster core frameworks was discovered and found to bind a variety of main group and hydrocarbon fragments, many of them displaying different coordination modes. The main reasons for the strong interest in the investigation of clusters were because of their potential and unique applications. In recent times, it has been observed that there is a considerable development in metal clusters as homogeneous catalysts and also possesses hydrogen uptake and storage systems, along with fundamental discoveries related to novel transformations that can take place inside the cluster framework. Along

with the synthesis, analysis and their applications, the development of theoretical models are also available in the literature that might provide a deeper understanding of these metal clusters and, most importantly, delivers the framework for a clear rationalization of the combinations of metals and ligands encountered.[6] From the structural point of view, one of the most important appeals of clusters is that they bridge the interface between ''conventional" organometallic and colloidal chemistry. In Figure 1, the growth particle size from a single atom to the bulk metal is illustrated.[7]
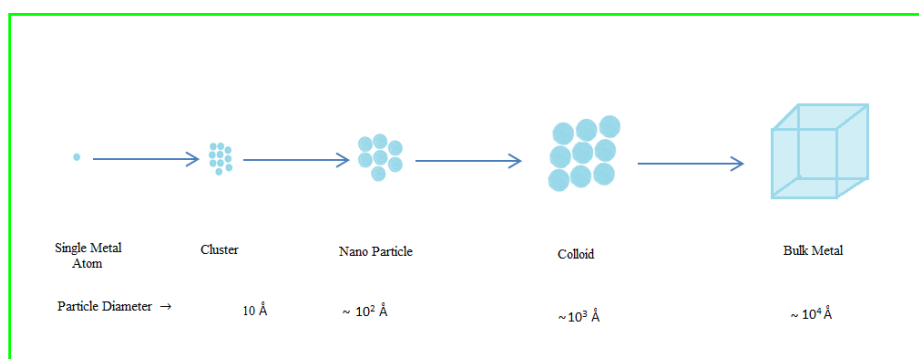

Figure 1. Schematic representation of particle growth size from a single metal atom to bulk metal.

Metal atom clusters play an important role in inorganic as well as in organometallic chemistry, giving us numerous unique structures and reactivity associated with their metal-metal bonds. There are some metal clusters which are sufficiently large to be considered as colloids or nanostructures. These metal nanoclusters show physical properties which are significantly different from their bulk materials. In bulk materials, the metallic properties such as delocalization of electrons gives them some

unique properties such as electrical conductivity, thermal conductivity, and light reflectivity; but in case of the metal nanoclusters, such properties are absent despite of which some unprecedented novel properties like catalysis, magnetic and optical properties provide insights leading to improvements in synthetic methods.[8]

In addition to metal nanoclusters, in the past few decades, sub-nanometer sized metal clusters have also been synthesized with dimensions between metal atoms and nanoparticles. The syntheses of these sub-nanometer sized metal clusters have attracted more attention due to their unique electronic structures as well as their subsequent unusual type of physical and chemical properties. Although a considerably smaller size of these sub-nanometer sized metal clusters brings the difficulty to their synthesis compared with the easier preparation of large nanoparticles. Nowadays, various synthetic techniques and routes have been successfully employed for their preparation.[9]

Classification of Cluster[2]

Clusters can be broadly classified into two classes.

1. cluster containing no stabilizing ligands, known as 'naked cluster.'

2. cluster containing stabilizing ligands.

For metal clusters, the stabilizing ligands are commonly halides, carbonyls, linear and cyclic dienes, cyclic tetraenes, isocyanides, hydrides, etc.

Among the two classes of clusters, the first class is exemplified by the anions such as Pb_5^{2-} or Sn_5^{2-} in Figure 2(a) and the second class of cluster is represented by the compounds such as $[Mo_6X_8]^{4+}$ shown in Figure 2(b)

Figure 2(a)   Figure. 2(b)
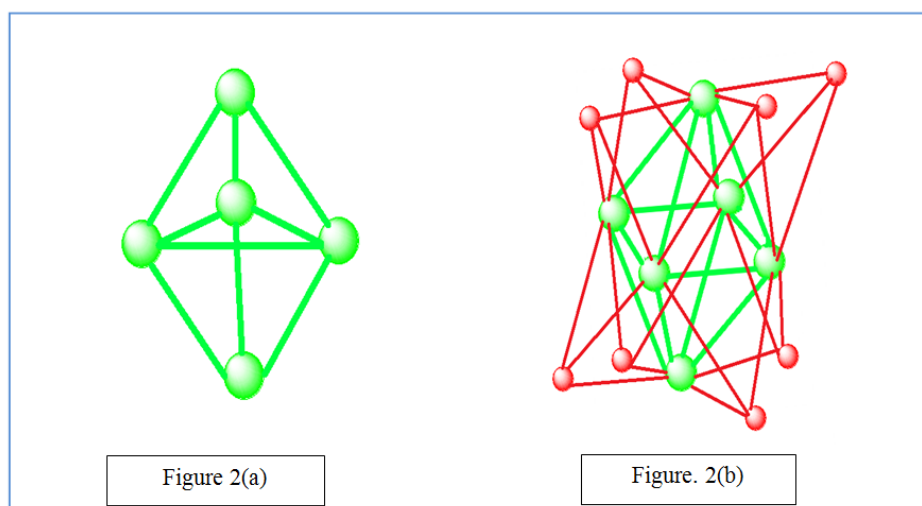
However, depending upon the stabilizing ligand present, molecular clusters can be broadly classified into two classes

I.   Halide type cluster

II.   Carbonyl cluster or in general organometallic cluster.

Metal Clusters in Catalysis

The uses of metal clusters in chemical reaction as a catalyst are well known from the late 1970s. The use of Co-ordinately unsaturated per (phosphite) rhodium clusters as a homogeneous catalyst for the hydrogenation of arenes has been discovered in 1977.[10] The potential of metal clusters as homogeneous catalysts is one of the important driving force that has permitted the surprising development of cluster chemistry. Nowadays, supported metal clusters are also developed, which are important as industrial catalysts. The typically supported catalysts that are commonly used for industrial purpose consists of

(a) Porous support; for example, metal-oxide, carbon, mesoporous materials like aluminosilicate, or a microporous material like zeolite.

(b) The catalytic species dispersed on the support, usually clusters, nanoparticles of metal and sometimes metal oxide or metal sulfide.

Porous metal-oxide supports have internal surface areas up to hundreds of square meters per gram, and the microporous materials have even higher internal surface areas. Supported metals typically have high dispersions ability, so that a large fraction of the atoms are present at a surface and accessible to reactants. Due to these reasons, these supports are commonly used as an industrial catalysts.[8]

In recent years, the conversion of carboxylic acid to aldehydes *via* hydrosilylation reaction has attracted the eyes of the scientific community as it involved some mild reaction condition.[11] The hydrosilylation reaction has been performed in the presence of different types of a catalyst such as ruthenium carbonyl clusters and some boron and iron-based catalysts.[12-14] Palladium phosphine complex is also found to catalyze the reduction of carboxylic acids to aldehydes with high selectivity.[15]
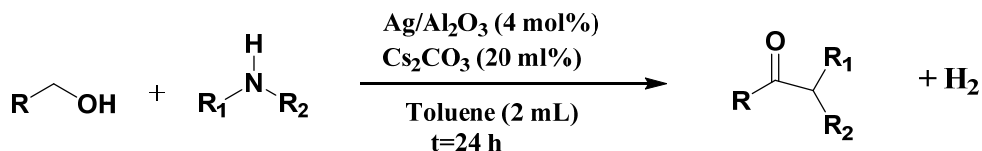
Silver Cluster

However, along with the studies on silver-vanadium clusters, extensive publications are available in the literature on novel applications as well as on the synthesis of silver clusters. Silver clusters are nowadays used as a catalyst in different organic reactions. Ag clusters supported on Al_2O_3 can act as a highly effective heterogeneous catalysts for various reactions such as,

(i) Oxidant-free dehydrogenation of alcohols to carbonyl compounds[16]

(ii) Synthesis of amides via coupling of amines and alcohols[17]

(iii) N-alkylation of anilines with alcohols[18]

(iv) C-C cross-coupling of alcohols[19]

(v) Reduction of nitro-aromatics, and

(vi) Direct synthesis of N-substituted anilines from nitro-aromatics and alcohols.
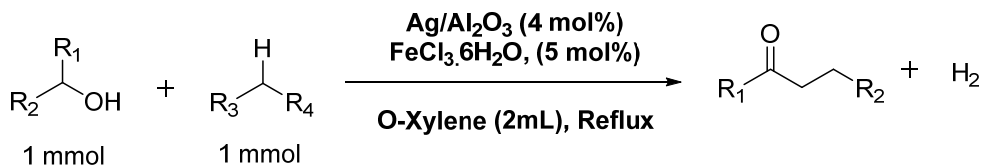
In 2009, Ken-ichi Shimizu *et al.* reported oxidant free dehydrogenation of alcohol catalyzed heterogeneously by alumina supported silver cluster. They reported that alumina supported silver cluster Ag/Al_2O_3 act as an efficient catalyst for oxidant free alcohol dehydration to carbonyl compounds at 373K. This catalyst also shows higher efficiency for dehydration than the conventional heterogeneous catalyst based on the platinum group. Also, another important property of such a catalyst is that it can be recyclable up to many cycles. Both the silver clusters as well as the acid-base sites on the support (Al_2O_3) surface were found to be responsible for the high activity of alumina supported silver clusters. Similarly, the activity of the catalyst also depends strongly on the charge and the size of silver species. Silver clusters, possibly having a slightly cationic nature, show higher activity.
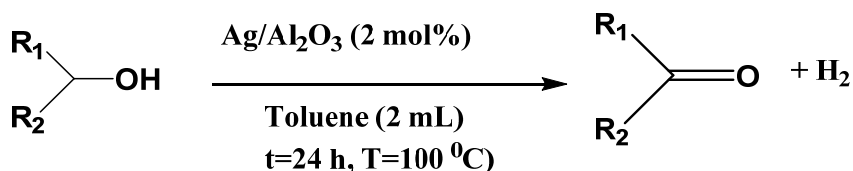
The second application of such a cluster is in the coupling reaction of alcohols with amines that were reported by the same group in the same year. In the presence of alkaline carbonates, Ag/Al_2O_3 acts as an effective heterogeneous catalyst for amidation of amines with alcohols.

$$R\text{—}CH_2OH \ + \ R_1\text{—}NH\text{—}R_2 \ \xrightarrow[\substack{\textbf{Toluene (2 mL)} \\ \textbf{t=24 h}}]{\substack{\textbf{Ag/Al}_2\textbf{O}_3 \textbf{ (4 mol\%)} \\ \textbf{Cs}_2\textbf{CO}_3 \textbf{ (20 ml\%)}}} \ R\text{—}CO\text{—}C(R_1)(R_2) \ + \ \textbf{H}_2$$

The same catalyst was also used in the N-alkylation of amines by primary as well as secondary alcohols by a Japanese group K. Shimizu, R. Sato, & A. Satsuma in 2009. They have reported that in the absence of additives, the reaction of anilines with benzyl alcohols by Ag/Al_2O_3 give imine but in the presence of Lewis acids (like $FeCl_3.6H_2O$) co-catalyst Ag/Al_2O_3 catalyzed the direct *N*-alkylation of aniline with benzyl alcohol The reaction of aniline derivatives or *N*-methylaniline with benzyl alcohol proceeded efficiently but the reactions of aniline and benzyl alcohols with an electron-donating or an electron-withdrawing substituent and with secondary alcohols provided good to moderate yields.

$$R_2\text{—}CH(R_1)\text{—}OH \ + \ R_3\text{—}CH(H)\text{—}R_4 \ \xrightarrow[\textbf{O-Xylene (2mL), Reflux}]{\substack{\textbf{Ag/Al}_2\textbf{O}_3 \textbf{ (4 mol\%)} \\ \textbf{FeCl}_{3.}\textbf{6H}_2\textbf{O, (5 mol\%)}}} \ R_1\text{—}CO\text{—}CH_2\text{—}R_2 \ + \ H_2$$

1 mmol   1 mmol

Alumina supported silver cluster can also be used in the C-C cross-coupling reaction of alcohols. This application was reported by the same group in which N-alkylation of amines by alcohol in the presence of Ag-cluster was reported.

Generally, alcohols are not used as starting materials for C-C coupling due to the poor leaving group ability of hydroxide. However, the authors have carried out a one-pot cross-coupling reaction of different primary and secondary alcohols to give coupled ketones.
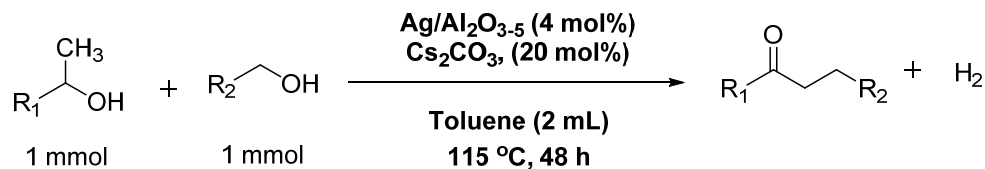

Selective reduction of the nitro group in the presence of other reducible functional groups (such as olefinic bond) is an important reaction to produce functionalized anilines. Stoichiometric amounts of reducing agents such as iron, tin, or zinc in ammonium hydroxide have been used to reduce aromatic nitro compounds containing C=C double bonds. However, these processes produce a large number of by-products along with the desired product, which ultimately reduces the yield of the reaction. Several catalytic systems for selective hydrogenation of nitro benzenes have been reported. In 2009, K. Shimizu *et al.* reported for the conversion of functionalized nitrobenzenes to functionalized aminobenzenes by reacting with H_2 gas in the presence of alumina supported silver cluster as catalyst.
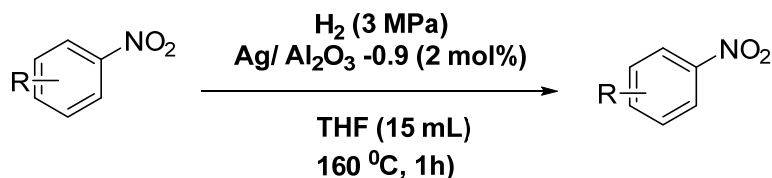
In 2010, K. Shimizu *et al.* used the Ag cluster supported on Al_2O_3-10 for the N-alkylation of nitrobenzenes with benzyl alcohol using H_2 as a

reductant. It is a much cheaper method for the synthesis of N-substituted anilines from nitroaromatics and alcohol.
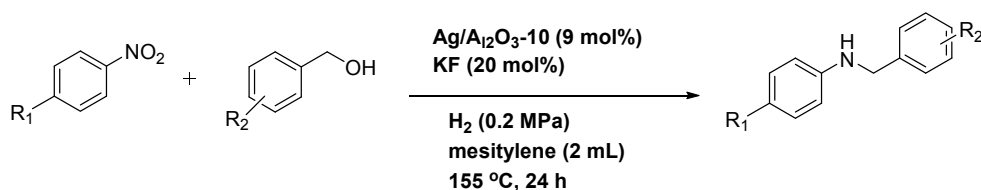
Conclusion

In conclusion, silver clusters were found to be applicable in different organic transformation with high efficiency. The cluster reported in this chapter showed high stability and can withstand up to a number of cycles.

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