

New Strategies for the Oxidation of Some Industrial Materials under Microwave Irradiation Using Ag and Cu Metal Ions and Their Nanoparticles

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Abstract:

Over the several past decades, catalysts and catalytic reactions have attracted considerable attention with the aim of finding meaningful applications in the Physics and fine chemical industries. The nanocatalysts are highly selective, reactive, and stable; thereby it supersedes the conventional catalyst.

Introduction:

The new era of Physics is shifting towards the path of innovative techniques which mainly concentrates on environmental aspects [1, 2]. Each and every component of the reaction is investigated on the basis of eco friendly concepts such as use of nonhazardous solvent (water) and solvent-free synthesis or inexpensive catalyst, without affecting the yield and quality of the reaction. Synthesis of heterocyclic core constitutes the important portion of organic

synthesis because it has wide variety of pharmacological actions [3–6].

Various methods have been adopted for the synthesis which includes the use of catalyst [7, 8], ultrasound irradiation [9–11], and microwave irradiation [12, 13]. Although these methods have their own advantages, it also possesses certain disadvantages like expensive instruments, inaccessible materials, non-recyclable and non-selectivity, and so forth. To overcome these, the role of nanocatalyst holds its application [14]. Nanoscience is the cram of phenomenon on a nanometer range. Atoms are a few tenths of a nanometer in diameter, and molecules are typically a few nanometers in size. The smallest structures humans have been made have dimension of a few nanometers and the smallest structures we will ever make will have the dimensions of a few nanometers. This is because as soon as a few atoms are placed next to each other,

the resulting structure is a few nanometers in size.

Classical Physics and Chemistry is the study of molecules and their reactions with each other. Since molecules typically have dimensions of a few nanometers, almost all of nanoscience can be reduced to Physics. Physics research in nanotechnology concerns carbon nanotubes, self-assembly, C-60 molecules, and structures built using DNA. Sometimes the chemical description of a nanostructure is insufficient to describe its function. Owing to the hasty progress of nanoscience and nanotechnology, the primeval colloid science is given a new life. Because of their great differences from single molecules and bulk materials, nanoscale materials, including colloids, have

attracted much attention since the last decade, especially in the field of catalysis.

Dimensional aspects of Nanoparticles:

Nanoparticles with a diameter of less than 10 nm have generated intense interest over the past decade due to their high potential applications in areas such as sensors, nanoscale electronics, catalysis, and optics. The catalytic activity of nanoparticles is affected by size; therefore, the relative ratio of surface atom types changes dramatically with varying particle size. In many cases, the activity increases as the particle size decreases due to favorable changes in the electronic properties of surface atoms, which are located mainly on edges and corners in small particles.

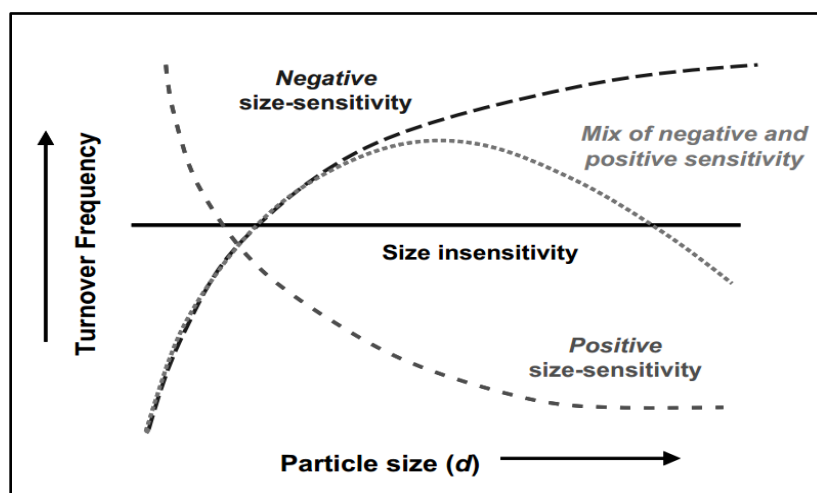


Fig 1: Catalytic activity of nanoparticles size

Aside from considerations of NP size, a second major area of inquiry is that of the effect of nanoparticle shape on reaction rate, selectivity, and deactivation. This work is derived from the abundance of research done on single crystal surfaces, which has demonstrated what is known as structure sensitivity in catalysis. Experiments on a wide variety of catalysts have determined that the atomic arrangement of atoms on a surface has a significant effect on catalyst behavior.

Metallic Nanoparticles:

About two-thirds of chemical elements are metals. Using the molecular orbital description, as is usual for covalently bonded atoms in molecules, the generation of a metallic material can simply be understood as the formation of an infinitely extended molecular orbital, leading to energy bands. The development of a metallic band structure requires a minimum number of electronic levels, which have to be very similar in energy so that electrons can move by only thermal activation. All the properties that we know for a bulk metal derive from the existence of such a band.

The most important property of a metal is its ability to transport electrons, namely the property of conductivity. To understand what conductivity is based on, it is necessary to consider the relation between occupied and unoccupied electronic bands, as electrons can become mobile only if the energy band of which they are part is not fully occupied. Most of the d-type transition metals are characterized by only partially filled d-orbitals so that incompletely filled bands result in any case. d10 elements such as palladium, platinum or gold have nearby s-bands that can be used for electron transport. Another important property of metals, at least for some of them, is magnetism, for example the well-known ferromagnetism of iron, cobalt and nickel. The existence of unpaired electrons is a condition for magnetism; however, only the uniform orientation of free spins over a large area results in ferromagnetism while non-oriented free spins produce paramagnetic materials. Copper and gold are the only colored metals, the others looking 'silvery' when they have smooth surfaces. Finely dispersed metals are all dark brown or black. The silvery luster and the dark appearance

are caused by the total reflection of light in the first case, and by the total absorption of light in the latter. Color is caused by the partial absorption of light by electrons in matter, resulting in the visibility of the complementary part of the light. On smooth metal surfaces, light is totally reflected by the high density of electrons and no color results; instead a mirror-like effect is observed [15].

The description of bulk materials is made by means of the laws of classical physics. A metal particle will present properties different from those of metal bulks, because of the reduction in the size (quantum size effect). Indeed, if a size range is attained where the band structure begins to disappear and discrete energy levels become dominant, quantum mechanical rules, which are well-established for describing electronic situations in molecules and atoms, have to replace those of classical physics suitable for bulk materials. Nevertheless, small particles are parts of a material and not atoms nor molecules, and are thus considered as intermediate species.

Metallic NPs, also called nanoclusters, are pieces of metal at the nanometer scale, of one to a few nanometers in size. They can be

noncrystalline, aggregates of crystallites or single crystallites (nanocrystals). Due to the number of bound metal atoms they contain, metallic nanoparticles display intermediate electronic energy levels in comparison with molecules and metal bulks [16]. As a result, particular physical and chemical properties are expected for metallic nanoparticles that can lead to applications in various areas such as in catalysis [17]. In this latter domain, metallic nanoparticles are generally considered as intermediate species between metal complexes and metal surfaces, and the term ‘nanocatalysts’ is now commonly used to describe them.

Metal colloids are very efficient catalysts because a large number of atoms are present on the surface of the nanoparticles. The method that is used in synthesizing transition metal nanoparticles in colloidal solutions is very important for catalytic applications. The reduction method employed controls the size and the shape of the transition metal nanoparticles that are formed, which are very important in catalytic applications.

Experimental Material:

Numerous gold, silver and copper is understood to be the “noblest of all the metals” with the well-established nobility of gold, silver and copper as catalyst, several workers have studied the catalytic activity of transition metals ions.[18]

Gold as an active material for oxidation catalysis has received a great deal of attention in the recent years. My thesis will focus on silver and copper, covering all coinage metals. Both metals also have shown a considerable potential as homogeneous catalysts for different selective oxidation reactions in the liquid phase. Cu and Ag can profit from the extensive knowledge on Au catalysts due to similarities between the coinage metals. As an example, alcohol oxidation which was first studied over gold catalysts can also be efficiently catalyzed by silver.[19] Synthesis techniques from gold catalysts can be adapted for copper and silver but their complex chemistry requires specialized routes for catalyst synthesis. The strengths and opportunities of the two metals will be discussed and compared stressing out the chances of Cu and Ag thereby showing that the two metals are not necessarily

competitors of gold but often complementary.

Only few examples where gold is industrially competitive.[20] On the other hand, the smaller siblings of gold – silver and copper – have long been applied for important catalytic processes in industry, silver being used in methanol oxidation as well as ethylene epoxidation [21] and copper being used in methanol synthesis. However in academics, both silver and copper received far less attention and thus have not made it to step out of the shadow of gold especially in selective liquid-phase oxidations.

Establishing new processes on the background of the discussion on “Green Science” is certainly important and the price of a catalyst is a crucial factor in making a process sustainable. With respect to CO oxidation, both silver [22-25] and copper [26-29] have proven their ability to catch up with gold. Applications of heterogeneous copper and silver catalysts in the total oxidation of harmful organic compounds in wastewater effluents [30-33] underline their potential in liquid phase oxidations. Recently, the potential of the coinage metals

mainly in gas phase reactions was summarized in two reviews.[34-35]

In the past, efforts were made for the oxidation of alkyl substituted benzene to useful products such as benzylic and allylic ketones by adding stoichiometric amounts of strong oxidants such as chromium (IV) reagents, permanganates, tert-butyl hydroperoxide (TBHP), selenium oxide (SeO₂), ruthenium (VIII) oxide, hydrogen peroxide, nitric acid, and oxygen [36–38]. However, most of these chemicals are either toxic or corrosive to reactor wall, unstable in atmospheric conditions, nonspecific in actions, which produce many undesirable side products, and that increases the purification cost and environment pollutant [36–38]. These traditional transformation schemes are also time consuming and cannot be recycled [39]. The green Science approaches must meet health and environmental safeties and use very little chemicals reducing both cost and time [40]. Catalytic approaches might be considered as green since specific chemical transformation could be achieved within very short time with the addition of very little catalysts, significantly reducing production cost as well as health and environmental risks [41,

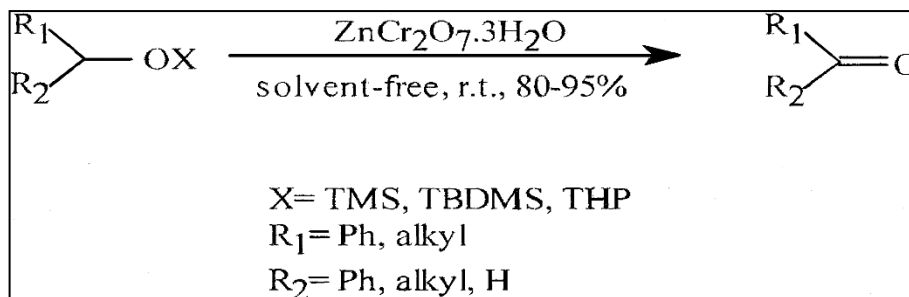
42]. According to the North American Catalysis Society, approximately 35% of global GDP rest on catalysts and the use of catalysts in industry are increasing 5% per year [43]. Currently, more than 60% of chemical synthesis and 90% of chemical transformations in chemical industries are using catalysts [44, 45]. In the recent time, some transition metal ion complexes have shown high selectivity, efficiency and reproducibility to catalyze the reaction under mild conditions. The single catalytic entity in homogeneous catalysts can act as a single active site which can speed up reaction and reduce the reaction time [46]. However, homogeneous catalytic processes produce huge waste materials, significantly disrupting the environmental and ecological stability [47–49].

Result and Discussion:

In our study, we have introduced a new and useful applications of ZnCr₂O₇·3H₂O as oxidant in organic synthesis. Zinc dichromate trihydrate has been developed and recently used as an oxidant by Firouzabadi et al. which has been only used for the oxidative conversion of a few functional groups[50-53]by using this reagent under solvent-free and mild reaction

conditions, immediate and high yielding conversions of TMS, TBDMS and THP ethers into their aldehydes and ketones.[54] Oxidative deprotection of tetrahydropyranyl ethers of various alcohols with zinc dichromate trihydrate under solvent-free condition and at room temperature were also investigated. Primary and secondary aliphatic THP-ethers also were oxidized to

the corresponding aldehydes and ketones in 80–85% yields.[55] A new efficient method for deprotection of various types of silyl and pyranyl ethers into their corresponding carbonyl compounds under solvent-free conditions using zinc dichromate trihydrate (ZDC)[56] as an easily prepared, stable, and inexpensive reagent.



Conclusion:

In the presence of zinc dichromate trihydrate, various sulfides were cleanly converted into the corresponding sulfoxides in excellent yields (80%-90%) phenyl alkyl sulfides were efficiently converted to their corresponding sulfoxide (85%-90%) in very short reaction time. Benzyl phenyl sulfide and dibenzyl sulfide were oxidized to the corresponding sulfoxides in a 90% yield.

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