Extended Abstract Journal of Surgery and Emergency Medicine 2020
Vol.4 No.2

Nano Copper Ferrite: A Reusable Catalyst for the Synthesis of Β, Γ -Unsaturated Ketones

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Abstract

Nanoparticles are a highly worthy reactant for the correlation of homogeneous inorganic and organic containing catalysts. This review deals with the very recent main advances in the development of various nano catalytic systems by the immobilization of homogeneous catalysts onto magnetic nanoparticles. Catalytic fields include the use of mainly cobalt, nickel, copper, and zinc ferrites, as well as their mixed-metal combinations with Cr, Cd, Mn and sometimes some lanthanides. The ferrite nanomaterials are obtained mainly by co-precipitation and hydrothermal methods, sometimes by the sonochemical technique, micro emulsion and flame spray synthesis route. Catalytic processes with application of ferrite nanoparticles include degradation (in particular photocatalytic), reactions of dehydrogenation, oxidation, alkylation, C–C coupling, among other processes. Ferrite nano catalysts can be easily recovered from reaction systems and reused up to several runs almost without loss of catalytic activity. Finally, we draw conclusions and present a futurity outlook for the further development of new catalytic systems which are immobilized onto magnetic nanoparticles.

Introduction

Green Chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical product. This encouraged the scientific community to look for efficient ways to separate homogenous catalysts from the reaction media and their subsequent recycling. The use of magnetic nanoparticles (MNPs) as efficient supports for catalysts has become a subject of intense investigation. Magnetic nanoparticles are a class of nanoparticle that can be manipulated using magnetic fields. Such particles commonly contains two components, a magnetic material, often iron, nickel and cobalt, and a chemical component that has functionality. While nanoparticles are smaller than 1 µm in diameter (typically 5–500 nm), the larger micro beads are 0.5–500 µm in diameter. Magnetic nanoparticle groups that are composed of a number of single magnetic nanoparticles are known as magnetic nanobeads with a diameter of 50–200 nm. Magnetic nanoparticle clusters are a basis for their further magnetic assembly into magnetic nanochains (Tadic et al., 2014; Kralj and Makovec, 2015). The magnetic nanoparticles have been attention of much seek recently because they have attractive properties which could see potential use in catalysis including nanomaterial-based catalysts, biomedicine and tissue specific targeting, magnetically tunable colloidal photonic crystals, microfluidics, magnetic resonance imaging, magnetic particle imaging, data storage, environmental remediation, nanofluids, and optical filters, defect sensor and cation sensors (Abu-Dief and Hamdan, 2016, Abu-Dief et al., 2016a, Abu-Dief et al., 2016b, Ibrahim et al., 2017).

This is because MNPs can be well dispersed in reaction mixtures without a magnetic field, providing a large surface area that is readily accessible to substrate molecules. Moreover, after completing the reactions, the MNP-supported catalysts can be isolated efficiently from the product solution through simple magnetic separation, eliminating the need for catalyst filtration and centrifugation. Moreover, they can be reused up to several runs almost without loss of catalytic activity (El-Remaily and Abu-Dief, 2015, Abu-Dief et al., 2016a, Marzouk et al., 2017). Catalysts play a very important role in modern science and technology as they improve reaction yields, reduce temperatures of chemical processes and promote specific enantio selectivity in asymmetric synthesis. There are two main kinds of catalysis, heterogeneous, where the catalyst is in the solid phase with the reaction occurring on the surface and homogeneous, where the catalyst is in the same phase as the reactants (Abdel-Rahman et al., 2016a; Abu-Dief and Mohamed, 2017). Both processes have their benefits. For example heterogeneous catalysts can be readily separated from the reaction mixture but the reaction rate is restricted due to their limited surface area. Meanwhile homogeneous catalysts can react very fast and give a good diversion rate per molecule of the catalyst, but since they are miscible in the reaction medium, it can be a painstaking process to remove them from the reaction medium (Lu et al., 2004, Gupta and Gupta, 2005, Ramaswamy et al., 2015, He et al., 2012, Kavre et al., 2014, Mornet et al., 2006, Gleich and Weizenecker, 2005). The difficulty in removing homogenous catalysts from the reaction medium leads to problems in retaining the catalyst for reuse. The separation and recycling of the catalyst is highly suitable since catalysts are often very expensive. The bridge between heterogeneous and homogeneous catalysts can be achieved through the use of nanoparticles. Nanoparticles of catalytic material provide the benefit of increased surface area which allows for an increased reaction rate. When well dispersed, the nano particulate catalyst forms a stable suspension in the reaction medium allowing an elevated rate of reaction. In addition, nanoparticles can allow additional catalytic missions due to their single properties, for example titania nanoparticles exhibit photo oxidation on their surfaces while other nanoparticles can utilize light energy as a result of their photo physical properties (Hyeon, 2003, Natalie and Shouheng, 2014, Elliott and Zhan, 2001, Philip and Raj, 2006, Philip et al., 2003, Mahendran, 2012, Philip and Felicia, 2013). The physical and chemical properties of magnetic nanoparticles largely depend on the synthesis method and chemical structure. In most cases, the particles range from 1 to 100 nm in size and may show super paramagnetism.

Types of magnetic nanoparticles

Oxides: Ferrites

Ferrite nanoparticles or iron oxide nanoparticles (iron oxides in crystal structure of maghemite or magnetite) are the most explored magnetic nanoparticles up to date. Once the ferrite particles become smaller than 128 nm they turned into superparamagnetic which prevents self-agglomeration since they exhibit their magnetic behavior only when an external magnetic field is applied. The magnetic moment of ferrite nanoparticles can be greatly increased by controlled clustering of a number of individual superparamagnetic nanoparticles into superparamagnetic nanoparticle clusters, namely magnetic nanobeads. With the external magnetic field turned off, the remanence falls back to zero. Just like non-magnetic oxide nanoparticles, the face of ferrite nanoparticles is often modified by surfactants, silica, silicones or phosphoric acid derivatives to increase their stability in solution (Kim and Mikhaylova, 2003).

Ferrites with a shell

The surface of a maghemite or magnetite magnetic nanoparticle is relatively inert and does not usually allow strong covalent bonds with functionalization molecules. However, the reactivity of the magnetic nanoparticles can be improved by coating a layer of silica onto their surface. The silica shell can be easily modified with different surface functional groups via covalent bonds between organo-silane molecules and silica shell. In addition, some fluorescent dye molecules can be covalently bonded to the functionalized silica shell as shown in Fig. 1. Ferrite nanoparticle clusters with narrow size distribution consisting of superparamagnetic oxide nanoparticles (~80 maghemite superparamagnetic nanoparticles per bead) coated with a silica shell have several advantages over metallic nanoparticles (Kralj et al., 2010a, Kralj et al., 2010b, Kralj et al., 2012):

- Higher chemical stability (crucial for biomedical applications)
- Narrow size distribution (crucial for biomedical applications)
- Higher colloidal stability since they do not magnetically agglomerate
- Magnetic moment can be tuned with the nanoparticle cluster size
- Retained superparamagnetic properties (independent of the nanoparticle cluster size)
- Silica surface enables straightforward covalent functionalization.