



A REVIEW ON THE APPLICATIONS OF NANOPARTICLES OF FERRITES AS CATALYST

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ABSTRACT

Silver nanoparticles are extensively used for biomedical applications due to the antibacterial and antiviral properties. In addition, silver nanoparticles can excite resonance effect of light trapping when pairing with dielectric materials, such as polymer. Comparing to the traditional fabrics, polymer Nano fibers can provide larger number of reaction sites and higher permeability contributed to their high surface-to-volume ratio and high porosity. By embedding the silver nanoparticles into polymer nanofiber matrix, the composite is promising candidates for biomaterials, photovoltaic materials and

catalysts.

KEYWORDS: Biomedical, light trapping, Nano fibers, nano fiber matrix, catalysts.

INTRODUCTION

Due to their antibacterial^[1], fungicidal^[2] and antiviral^[3] properties, silver particles have drawn tremendous academic and industrial interests. Besides of the benefits of their biomedical applications, when the size of silver particles decreases to nanoscale, the high surface area and surface energy make silver nanoparticles one of the best candidates for catalysis and optical absorption. The silver nanoparticles enable surface plasmon resonances when being placed in dielectric environment, leading to higher optical absorption efficiency.^[4] Therefore, the applications of silver nanoparticles expand from biology, electronics, textile industries and catalysis material to optical and photovoltaic materials, such as solar cells. Fibers with nanostructures have also been intensively investigated because of its high surface-to-volume ratio. Compared to traditional materials, membranes and films composed of nanofibers have extremely high surface area and nanometer grade micropores, which can provide both larger number of reactive sites for chemicals and excellent filtration

property and breathability when being used as insulating fabrics and biomaterials such as wound dressing and protective textiles.

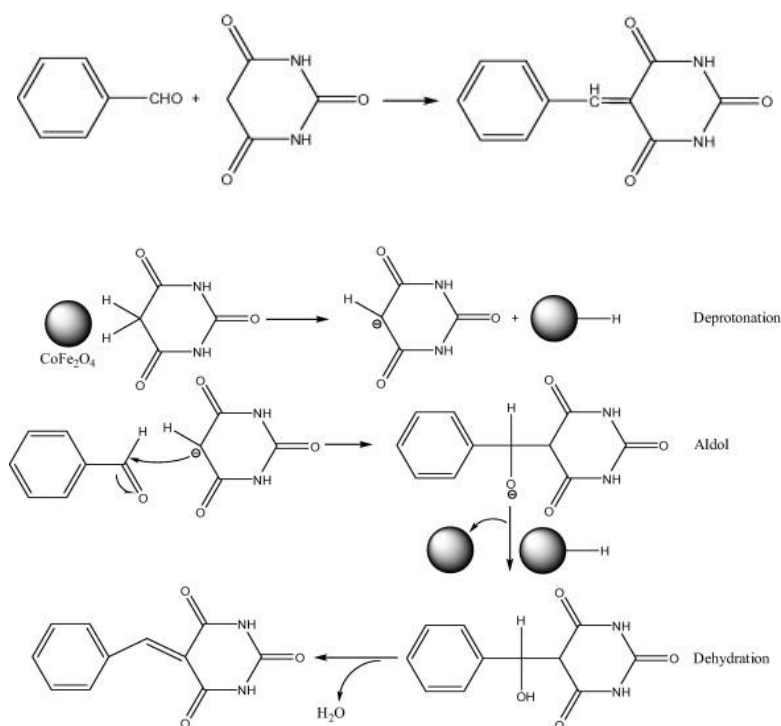
Catalyst for Hydrolysis/Electrolysis of Polymer Matrix

Another application to include silver nanoparticles in polymer nanofibers is to speed up the hydrolysis of the bulk material. Silver nanoparticles exhibit strong catalytic properties for hydrolysis and electrolysis of organic materials when being fabricated into silver nanoparticle/polymer composites.^[5-6] In addition, the catalytic activity can be tailored by controlling the size of silver particles and polymer matrix. Generally, the smaller particle size presents higher catalytic activity^[7] with larger number of reaction sites, kink sites per surface area.^[8] This size dependence becomes even more significant when the particle size shrinks to nanoscale. Studies have synthesized silver nanoparticles using a chemical reduction method, followed by embedding them into the polyvinyl acetate (PVAc) polymer matrix^[9], to prepare silver nanoparticle PVAc nanocomposite. By introducing silver nanoparticles into polymer matrix, the hydrolysis of this hybrid material can be accelerated. The silver nanoparticles demonstrate a strong connection with the PVAc polymer chain, meaning that they can be remained in the matrix and continuously act as catalyst even when the backbone of polymer chains is broken down during hydrolysis. With the presence of silver nanoparticles, the hydrophobic PVAc polymer become hydrophilic and is subsequently dissolved in selective solvents, resulting in accelerated hydrolysis.

Cobalt ferrites

Cobalt ferrites having different sizes, from ultrasmall 2 nm to 50 nm, can be fabricated by distinct techniques mainly the co-precipitation method (CPM), sometimes without using any capping agents/surfactants. Thus, the CPM was used to synthesize ultrasmall CoFe_2O_4 superparamagnetic nanoparticles (SPMNPs, 2–8 nm of an average size and high surface area of $140.9 \text{ m}^2/\text{g}$) without any surfactant. Their catalytic activity was verified in the synthesis of arylidene barbituric acid derivatives using CoFe_2O_4 SPMNPs as a magnetically separable and reusable catalyst in aqueous ethanol. The advantages of this protocol were very short reaction time, high yields, high turnover frequency, simple work-up procedure, economy, a clean reaction methodology, and chemoselectivity, as well as provision of an ecofriendly and green synthesis. More large-size CoFe_2O_4 magnetic nanoparticles (25 nm) were used as a catalyst for the oxidation of various alkenes in the presence of *tert*-butylhydroperoxide (*t*-BuOOH) with almost quantitative yields.^[10-11] It seemed that this

heterogeneous catalysis system proceeds by coordination of *t*-BuOOH to the metal (Fe^{3+} cations) on the surface of the catalyst. The separation of the catalyst from the reaction media was easily achieved with the aid of an external magnet, and the catalyst can be reused several times with no loss of activity. As an example, effect of solvent on oxidation of styrene catalyzed by CoFe_2O_4 . In addition, combination of synthesis techniques can also be used for cobalt ferrite preparation. Thus, synthesis of spinel CoFe_2O_4 MNPs (average sizes 40–50 nm) was achieved by the combined sonochemical and co-precipitation technique in aqueous medium, also without any surfactant or organic capping agent. These uncapped NPs (nanoparticles) were utilized directly for aldol reaction in ethanol. After the reaction was over, the nanoparticles were compartmented by using an external magnet.

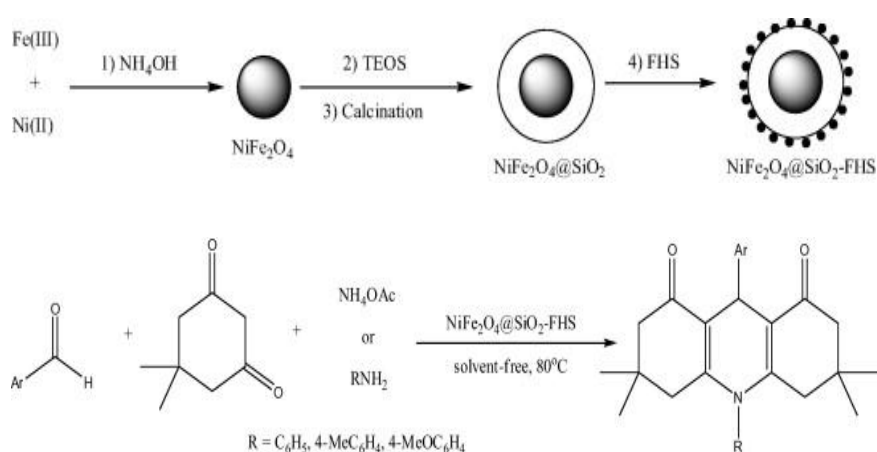


Nickel ferrites

Pure or doped nickel ferrites out of the nano-range size are common and frequently used in several catalytic processes. For instance, high reactivity of NiFe_2O_4 (1 1 1) surfaces (higher than in Fe_3O_4) is well-known; NiFe_2O_4 is an effective metal-doped ferrite catalyst in a typical industrial process such as the water–gas shift (WGS) reaction.^[12] Similarly, NiFe_2O_4 was examined as a catalyst in photocatalytic water oxidation using $[\text{Ru}(\text{bpy})_3]^{2+}$ as a photosensitizer and $\text{S}_2\text{O}_8^{2-}$ as a sacrificial oxidant. The catalytic activity of NiFe_2O_4 is comparable to that of a catalyst containing Ir, Ru, or Co in terms of O_2 yield and O_2 evolution rate under ambient reaction conditions. As an example of non-nano-sized doped ferrites, their

catalysts (granules of ~ 1 mm diameter) of nickel, cobalt and copper, prepared by co-precipitation hydrothermal route and impregnated with palladium, cerium and lanthanum as promoters were tested for carbon monoxide oxidation activities.^[13]

At the same time, nanosize-range pure nickel ferrites are not yet widely applied for catalytic purposes.^[14] As a unique example, ultrasmall spinel oxide NiFe_2O_4 particles (3–8 nm in size) were prepared by the combination of chemical precipitation and subsequent mechanical high-energy ball milling from metal nitrates as precursors. These procedures resulted in the formation of nanocrystalline nickel ferrite, where the particle size can be controlled by the treatment time. Their catalytic behavior in methanol decomposition to CO and methane was tested, showing differences in the phase composition and catalytic behavior depending on the preparation method used. In addition, an interesting observation was made for non-stoichiometric nickel ferrites: the electro catalytic activity of nickel ferrite NPs for hydrogen evolution reaction was found to $\text{Fe}_3\text{O}_4 \leq \text{Ni}_{0.6}\text{Fe}_{2.4}\text{O}_4 < \text{Ni}_{0.2}\text{Fe}_{2.8}\text{O}_4 \leq \text{Ni}_{0.8}\text{Fe}_{2.8}\text{O}_4 < \text{Ni}_{0.4}\text{Fe}_{2.6}\text{O}_4$. Similar to cobalt ferrites, several nickel-containing mixed or core-shell ferrites have been reported as nanocatalysts, but in a more narrow size range (18–50 nm). Thus, a magnetically separable catalyst consisting of ferric hydrogen sulfate (FHS) supported on silica-coated nickel ferrite nanoparticles (50 nm) was prepared. This catalyst was shown to be an efficient heterogeneous catalyst for the synthesis of 1,8-dioxodecahydroacridines (F) under solvent-free conditions. The catalyst can be recycled several times with no significant loss of catalytic activity.



CONCLUSION

Transition metal ferrite nanoparticles, utilized in catalytic reactions, possess different sizes, from ultra-small 2 nm to 100 nm. They are obtained mainly by wet-chemical sol-gel

precipitation methods, sometimes combined with simple calcination at high temperatures the sonochemical technique, mechanical (mechano chemical) high-energy ball milling or spark plasma sintering Microwave heating or hydrothermal route are also frequently used. Sometimes, self-combustion techniques are applied, Due to magnetic properties, ferrite nano catalysts can be easily recovered from reaction systems and reused up to several runs almost without loss of catalytic activity. Standard transition metal salts (usually nitrates) are used as precursors.

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