

Acid Functionalized Silica Coated Magnetic Nanoparticle Catalysts

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Introduction

Magnetic nanoparticles have received increasing attention in recent years due to their potential use as catalyst supports. This use has arisen from several advantageous characteristics of the magnetic nanoparticles (MNPs) including high surface area to volume ratios, the ability to be easily dispersed into and recovered from solution, high thermal stability, and the capacity for surface modifications. [1] Current literature describes MNP supported enzymes, transition metal complexes, and organics. The supported organo-catalysts include several reports of basic amines. However, no report of MNP supported sulfonic acids exists currently.

This work examines four potential methods for immobilization of sulfonic acids to create a hybrid organic/inorganic catalyst. The inorganic support was developed in two steps: synthesis of cobalt spinel ferrite nanoparticles followed by application of a silica shell to the nanoparticle core. Sulfonic acid functionalities were immobilized on the inorganic support using post-grafting methods.

Materials and Methods

Superparamagnetic CoFe_2O_4 nanoparticles were prepared [2] and silica coated (SiMNP) via modified literature procedures [3]. Sulfonic acid functionalities were supported on the SiMNP in several ways. These include the oxidation of thiols (SiMNP- SO_3H) [4], hydrolysis of arene sulfonic acids [5], ring opening of fluorinated sulfonic acid sultones (SiMNP- FSO_3H) [6], and via perfluorosulfonic acid silanes [7]. The supported acid catalysts were characterized by thermogravimetric analysis (TGA), FT-IR spectroscopy, titrations, and transmission electron microscopy (TEM) and evaluated in the deprotection reaction of benzaldehyde dimethylacetal (BADMA) to benzaldehyde.

Results and Discussion

Attempts to immobilize sulfonic acid sites on non-silica coated MNP via the oxidation of supported thiols were thwarted for various reasons. Thiols have been shown to bond to nanoparticles, and the MNP were found to be excellent catalysts for the decomposition of hydrogen peroxide, preventing the oxidation of non-surface bound thiols to sulfonic acids. Consequently, the MNP were silica coated to provide an inert barrier preventing any adverse reactions caused by the MNP core. Upon coating, transmission electron microscopy (TEM) images displayed silica coated aggregates ranging in size from 100 nm to 1 μm instead of the desired core-shell architecture observed by Abu-Reziq and coworkers [3]. Despite the heterogeneity in particle size, the SiMNP were still suitable for surface modification. Thermogravimetric analyses (TGA) and titrations indicated acid loadings ranging from 0.11 – 1.00 mmol/g.

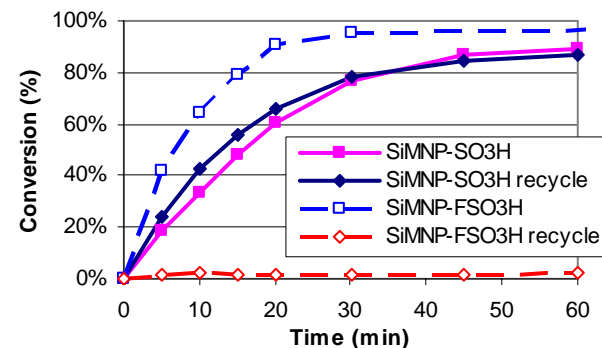


Figure 1. Kinetic data for the acid catalyzed deprotection of benzaldehyde.

The deprotection of benzaldehyde was chosen as a simple benchmark reaction for evaluation and comparison of the synthesized acid catalysts (Figure 1). The SiMNP- SO_3H catalyst reached >86% in 60 minutes. Similar initial and recycle kinetics indicated the catalyst was recyclable. All catalysts were easily recovered magnetically. However, the SiMNP- FSO_3H catalyst was found to be inactive upon reuse. This presumably occurred from leaching of the fluorinated sulfonic acid into solution resulting from cleavage of the Si-O-C bond by water present in the reaction mixture. The potential and limitations of the various methods of creating magnetic acid catalysts will be discussed.

Significance

This work illustrates the first use of a hybrid organic/inorganic acid functionalized nanoparticle catalyst. Additionally, the advantage of silica coating the magnetic nanoparticles has been shown to prevent adverse reactions. Since nanoparticles can be dispersed into solution, similar acidic nanoparticle catalysts could potentially be utilized in a variety of organic transformations where diffusion limitations of traditional heterogeneous catalyst supports slow reaction kinetics. Additionally, the magnetic catalyst can be recovered quickly and cheaply for reuse.

References

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