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Synthesis of magnetically separable catalyst Cu-ACP-Am-Fe_3O_4@SiO_2 for Huisgen 1,3-dipolar cycloaddition

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Abstract: The present manuscript elicits the use of novel magnetically separable silica coated copper (Cu-ACP-Am-Fe_3O_4@SiO_2) as a heterogeneous nanocatalyst for the Huisgen 1,3-dipolar cycloaddition reaction of alkyl or aryl halide, sodium azide and terminal alkyne, which provide a series of 1,4-disubstituted-1,2,3-triazoles. The catalyst was characterized by various physicochemical techniques such as Powder X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Energy Dispersive X-Ray Spectroscopy(EDS), Thermogravimetric analysis (TGA-DSC), X-ray Photoelectron spectroscopy (XPS) and Vibrational sampling magnetometer (VSM). The acquisition of this nanocatalyst is also exemplified by employing reusability test and recycling of synthesized catalyst was achieved multiple times just by sequestering with an external magnet. It is noteworthy that the key-features like mild reaction conditions, simple work-up, High turnover number (TON), high turnover frequency (TOF), no use of hazardous organic solvents, easy recovery and reusability of the catalyst makes the present protocol more fascinating from an environmental and economic point of view.

Keywords: Magnetic Nanoparticles, Acetyl Pyridine, Heterogeneous catalyst, Reusability, Cycloaddition.

Introduction:

In current scenario due to environmental legislation, the society's driving force is to search for an ecofriendly catalyst which can be utilized in eco-benign solvents (e.g., water, ethanol). Nano metal catalysts are being widely used for promoting organic reactions owing to their superior catalytic activity over bulk metal catalysts. In spite of having advantages such as enhanced activity and cost effectiveness, most of the times the separation of nano catalyst becomes expensive due to need of filtration, solvent extraction or centrifugation of the final reaction mixture. Sometimes, product and catalyst are insoluble in common solvents lead to difficulty in work-up. Scientific community put forward remedy to overcome the isolation issues of nano materials by discovery of highly paramagnetic nano materials[1]. Magnetic separation is an attractive alternative to filtration or centrifugation as it prevents loss of the catalyst results in remarkable catalyst recovery and increases reusability. Their insoluble and paramagnetic nature enables easy and efficient separation of the catalysts from the reaction mixture with an external magnet. This makes the catalyst cost-effective and promising for industrial applications.[2] The use of magnetic nano particles has been studied extensively for various biological applications such as magnetic resonance imaging, drug delivery, and bio molecular sensors.[3] Recently, research in the super paramagnetic nanoparticles have been boosted to a large extent owing to their extraordinary physicochemical properties and wide range applications in various fields such as biomedicine/biotechnology,[4-7] catalysis,[8] magnetic sensors,[9] magnetic fluids,[10] data storage devices,[11] magneto-optical devices[12] and magnetic refrigeration.[13] Thus, in last decade magnetically separable nano material as a heterogeneous catalyst became a choice of catalyst from the organic synthetic viewpoint.

In this context, iron oxides and relevant iron containing nanoparticles have gained considerable attention and several chemical methods have been reported in the literature for their synthesis.[14-19] However, a major demerit for most of the methods is the instability of the nanoparticles rooted from their high tendency for aggregation and possible degradation on exposure to harsh environments. The best way to improve their dispersibility and to overcome these limitations is coating them with protective layers, forming core-shell type nanocomposites, organic (surfactants or polymers) or inorganic (silica, carbon, precious metals or oxides).[1,4a,8,12] Remarkably, silica coating has been proved as a promising tool to shield the magnetic dipolar interactions between magnetic nanoparticles. Furthermore, chemical stability of silica coating offers additional advantages *viz.* biocompatibility and easy surface alteration which allows grafting of new functionalities onto the surface of nanoparticles. [1,4,8] Herein, we report a simple and efficient synthesis of a nano-ferrite-supported, magnetically recyclable, and inexpensive Cu catalyst and its application in Huisgen 1,3-dipolar cycloaddition reaction to synthesize 1,2,3-triazoles *via* one of the most powerful click reaction.

Over the past few years click reaction for synthesis of 1,2,3-Triazoles have dragged immense attention of synthetic chemists due to their multifarious applications in pharmaceuticals, agro chemicals, dyes, photographic materials, corrosion inhibition[20], etc. They are found to exhibit wide range of bioactivities such as antiviral[21], antiallergic[22], anticancer[23], anti HIV[24] and antimicrobial activities[25] against gram positive bacteria which reflects their versatility and significance in drug chemistry. In this context, the researchers are in