Heterogeneous magnetic catalyst for S-arylation reactions

Niranjan Panda*, Ashis Kumar Jena, Sasmita Mohapatra**

Department of Chemistry, National Institute of Technology, Rourkela-769008, Odisha, India

Abstract

A convenient method for the synthesis of monodisperse, superparamagnetic copper ferrite (CuFe2O4) nanoparticles with high surface area has been described. The synthesized material was characterized by various techniques. XRD showed the nanocrystalline nature of CuFe2O4 with a crystallite size of 6 nm. TEM analysis showed that uniform spherical CuFe2O4 particles are formed with a size of 55 ± 5 nm. N2 adsorption/desorption measurements confirmed the mesoporous nature of the sample with surface area >216 m² g⁻¹. The field dependent magnetization, illustrated by VSM and saturation magnetization was found to be 44 emu g⁻¹. The catalytic applications of the synthesized CuFe2O4 nanoparticles were explored for the cross-coupling of thiols with diverse range of aryl halides. Aryl iodides and bromides result in biarylsulfides in good to excellent yields (62–98%) whereas aryl chlorides gave significant amount of diaryldisulfide. Scope of this catalytic protocol further extended to one-pot synthesis of biologically important tricyclic dibenzothiazepines. The superparamagnetic nature of CuFe2O4 nanoparticles was found to be advantageous for their easy, quick and quantitative separation from the reaction mixture. Negligible leaching of Cu and Fe in consecutive cycles makes the catalyst economical and environmentally benign.

Keywords: Superparamagnetic nanoparticles, Heterogeneous catalyst, Cross-coupling, S-arylation, Dibenzo[b,d]thiazepines, Dibenzo[b,d]thiazepinones, Aryl halides

1. Introduction

Transition-metal-catalyzed cross-coupling reaction presents one of the robust methods for the formation of carbon–carbon and/or carbon–heteroatom bonds [1–3]. Among the various cross-coupling reactions, metal-catalyzed S-arylation has received less attention as compared with N- or O-arylation reactions until very recent times. This is because (i) thiols are prone to undergo oxidative S–S coupling reactions to undesired disulfides, and (ii) strong coordinating properties of organic sulfur compounds, often make the catalyst ineffective (catalyst poison) [4]. Usually, palladium, copper and nickel-based catalysts are extensively used for various C–S cross-coupling reactions [5–9]. In spite of having wide scope and excellent compatibility with many functional groups, these protocols, often suffer from the disadvantages resulting from (i) the high cost of the palladium precursors, (ii) the need for ancillary ligands rendering the catalysts sufficiently reactive, (iii) concerns about the toxicity of these metal salts, and (iv) the extended reaction times, which are necessary in many cases. Considering the cost and environmental factor, the use of Cu catalysts for various cross-coupling reactions is attractive one from industrial perspectives. Moreover, ligands such as phosphazene, ethylene glycol, neocuproine, N-methylglycine, oxime-phosphine oxide ligand, tripod ligand, benzo triazole, 1,2-diaminocyclohexane, β-ketoester, L-proline, BINAM, polyethylene glycol, and ethylene diamine, are used as chelating agents in the copper-catalyzed cross-coupling reactions [10]. On the other hand, the simple separation and regeneration of the catalyst from the reaction mixture are in strong demand for the cost-effective process of molecular synthesis. In pharmaceutical industries, it is also essential to remove all traces of metal residues, which frequently interfere with the subsequent reactions and contaminate the final products. In contrast, developments of reusable heterogeneous catalytic systems for cross-coupling reactions have been received less attention although the situation is changing in recent years [11]. Evidently, certain heterogeneous catalytic system for the cross coupling of arylthiols with aryl halides have been reported. For instance, Cul-catalyzed cross coupling of arylthiols with aryl iodide was reported by van Koten [12] and Li [13] individually. Luque and co-workers developed a microwave-assisted, Fe-Cu co-catalyzed heterogeneous catalytic system for the cross-coupling of thiols with aryl iodides [14]. More importantly, Punniyamurthy and co-workers exploited the high surface area and reactive morphology of the CuO nanoparticles for successful C–S cross-coupling reactions under ligand free conditions [15]. Ranu and co-workers also employed copper nanoparticles for the cross-coupling of aryl iodides and bromides with thiophenols at 110 °C [16,17]. Although these results are promising, the small size of nanoparticles often makes their separation and recycling difficult, which impedes their use in industrial processes [18,19]. In order to circumvent such problems, we...