Journal of Organometallic Chemistry 870 (2018) 58–67

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Supported 4-carboxybenzyl sulfamic acid on magnetic nanoparticles as a recoverable and recyclable catalyst for synthesis of 3,4,5-trisubstituted furan-2(5H)-one derivatives

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ARTICLE INFO

Article history:
Received 10 December 2017
Received in revised form
3 June 2018
Accepted 15 June 2018
Available online 20 June 2018

Keywords:
Magnetic nanocatalyst
Aryl aldehydes
Anilines
Dimethyl acetylenedicarboxylate
4-Carboxybenzyl sulfamic acid on magnetic nanoparticles

ABSTRACT

4-Carboxybenzyl sulfamic acid functionalized Fe_3O_4 nanoparticles as a novel catalyst was manufactured. This catalyst was characterized and evaluated in the one-pot synthesis of furan-2(5*H*)-one derivatives from dimethyl acetylenedicarboxylate, aryl aldehydes, and various anilines in terms of activity and reusability. The catalyst showed high catalytic activity, good recoverability and reusability, thermal stability and provides clean production of fine furan-2(5*H*)-one derivatives in short reaction times. The heterogeneous catalyst could be used at least five times without significant loss of its activity.

1. Introduction

Nanostructure catalysts have played important roles in synthesis of organic materials because of their highly small size and large surface to volume ratio, that lead to change in both their chemical and physical properties compared to bulk materials with similar chemical composition such as mechanical and biological properties, superior catalytic activity, thermal and electrical conductivity, optical absorption and melting point [1–3]. Recently, surface functionalized iron oxide magnetic nanoparticles (MNPs) have been greatly applied in biotechnology science and catalytic process [3–8]. Nanocatalysts based on magnetic materials can be easily separated from obtained products using an external magnetic field and reused. Excellent bio-environmentally and biodegradability, as well as basic magnetic properties, could be considered for all of the functionalized organic materials grafted to magnetic nanoparticles [9–12].

Multi-component reactions (MCRs) are one-pot sequential reactions which are quite different from the regular multi-step reactions in which the reactants were added step by step and proved to be less efficient than MCRs. These reactions are highly selective, efficient, cost-effective, time-saving, easy to perform and reduce waste products [13–15].

Heterocyclic compounds were found to be an area of importance in synthetic chemistry. A large number of compounds both natural and target drug compounds contains a heterocyclic core. Synthesis of these kinds of compounds was found to be challenging. These heterocyclic systems have enhanced pharmacological efficiency in a variety of biological activity including antiviral, antitumor, antibacterial and anti-inflammatory activities [16–19].

Furans were used as synthetic intermediate materials and as final products. An efficient and impressive reason for their preparation is their applications in the synthesis of a lot of pharmaceuticals. Compounds containing 2(5*H*)-furanones are usable synthetic modules in organic synthesis and are principal structural elements present in several pharmaceutical active products [20]. Narayana et al. reported the synthesis of 2(5*H*)-furanones in the presence of β-cyclodextrin [21]. Literature survey revealed reporting many methods for synthesis of 2(5*H*)-furanones. However, some of the

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https://doi.org/10.1016/j.jorganchem.2018.06.012
0022-328X/

reported procedures have disadvantages including the use of reagents in stoichiometric amounts, long reaction times, and low yields of the products [22–26].

In continuation of our efforts in designing heterogeneous hybrid catalysts [27], herein we describe the preparation of 4-carboxybenzyl sulfamic acid functionalized Fe_3O_4 nanoparticles (SA- AMBA-MNPs) as a novel green and magnetically easy separable catalyst for the synthesis of 3,4,5-trisubstituted-2(5*H*)-furanone derivatives **4** from aryl aldehydes **1**, various anilines **2** and dimethyl acetylenedicarboxylate (DMAD) **3** (Scheme 1).

2. General procedure

2.1. Materials and methods

Melting points were measured on an Electrothermal 9100 apparatus. X-ray powder diffraction (XRD) patterns were recorded on a Phillips X'Pert X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å) in a range of Bragg's angle (10–80°) at room temperature. The morphology of AMBA-MNPs and SA- AMBA-MNPs was characterized by scanning electron microscopy (VEGA//TESCAN KYKY-EM 3200). Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were obtained from a Philips EM 208 electron microscope. The thermal stability was investigated with a thermogravimetric analysis (STA-780, London, UK). The TGA was conducted on SA-AMBA-MNPs in the temperature range of 0–700 °C. NMR spectra were recorded with a Bruker DRX-400 AVANCE instrument (400.1 MHz for ^1H, 100.6 MHz for ^{13}C). The spectra were measured in DMSO-d_6 as a solvent. Fourier transform infrared spectra (FT-IR) characterization of the nanocatalyst was obtained on an FT-IR spectrometer coupled with an ATR accessory (Bruker Inc. Vector 22). The magnetic properties tests were carried out at room temperature using vibration sample magnetometer (VSM, MDK, and Model 7400) analysis. Inductively coupled plasma (ICP) analysis was provided on a Shimadzu ICPS-7000.

2.2. Synthesis of AMBA–MNPs

A mixture of $FeCl_3.6H_2O$ (2.43 g, 0.09 mol) and $FeCl_2 \cdot 4H_2O$ (0. 89 g, 0.0045 mol) was dissolved in 100 mL distilled water and the solution was sonicated until the salts dissolved completely. Then a 0.3 g of AMBA in 10 mL of NH_4OH solution was added to the above mixture with vigorous stirring under constant nitrogen flow to produce a black suspension. The suspension was refluxed at 100 °C for 12 h, and the obtained AMBA–MNPs were separated from the aqueous solution by an external magnet, washed with distilled water several times and dried in an oven overnight (Scheme 2).

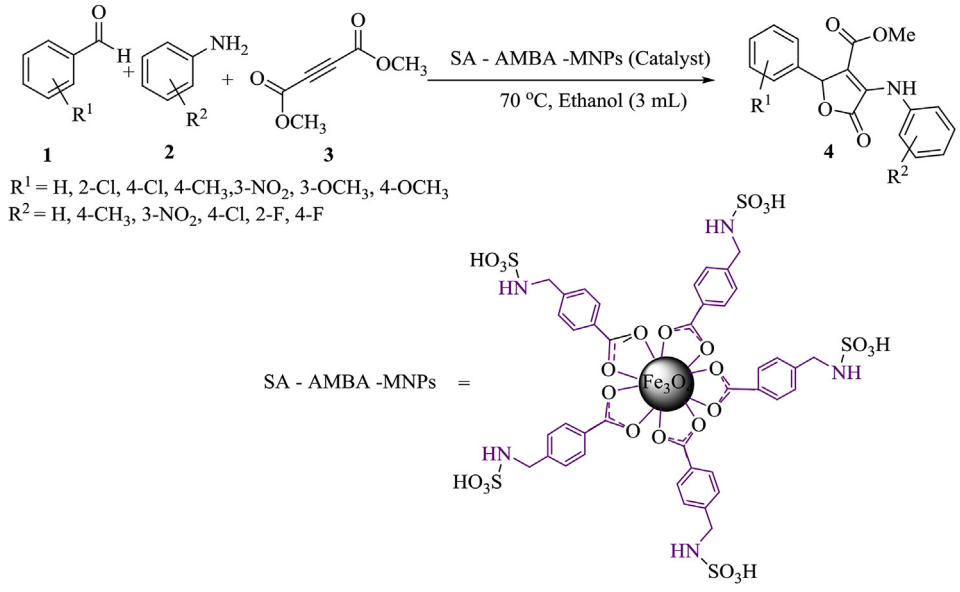
2.3. Synthesis of SA-AMBA-MNPs

The AMBA-MNPs (0.5 g) was dispersed in dry CH_2Cl_2 (10 mL) by the ultrasonic bath for 30 min. Eventually, chlorosulfuric acid (0.7 mL) was added dropwise over a period of 25 min at room temperature and hydrogen chloride gas expelled from the reaction. Then, the prepared functionalized MNPs were separated by the magnetic field and washed with dry CH_2Cl_2 four times to remove the unattached substrates and dried by vacuum (Scheme 3).

2.4. General procedure for synthesis of 3,4,5-trisubstituted furan-2(5H)-ones

In a 10 mL round-bottomed flask, a mixture of aryl aldehyde (1 mmol), aniline (1 mmol) and dimethyl acetylenedicarboxylate, DMAD, (1 mmol, 0.142 mg) were reacted in the presence of SA-AMBA-MNPs (15 mg) in ethanol (3 mL) at 70 °C for the specific time. When the reaction was complete, the reaction mixture was cooled and the solvent removed on a rotary evaporator. Then, the mixture was diluted with dichloromethane and the catalyst was separated by the magnetic field. The solution containing the product was evaporated to give the solid product. This crude product was purified by recrystallization from ethanol to give the pure product. All of the products were characterized by comparison of their physical and spectral data with those reported in the literature. The separated catalyst was recovered simply by washing with dry ethanol and vacuum drying and it is ready to be checked for reusability.

Methyl-2,5-dihydro-5-oxo-2-phenyl-4-(phenylamino)furan-3-carboxylate (Table 2, entry 1): White solid, m. p.: 167–169 °C.; IR (KBr): νmax = 3290, 3220, 1710, 1670 cm^{-1}; ^1H NMR (400.13 MHz,



Scheme 1. Synthesis of 3,4,5-trisubstituted furan-2(5*H*)-one derivatives.