Journal of Catalysis 361 (2018) 339–346

Contents lists available at ScienceDirect

Journal of Catalysis

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

Synthesis and characterization of Ag@Carbon core-shell spheres as a novel catalyst for room temperature N-arylation reaction

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ARTICLE INFO

Article history:
Received 29 November 2017
Revised 21 February 2018
Accepted 26 February 2018

Keywords:
Ag-catalyst
Carbon sphere
Core-shell
Hydrothermal method
N-Arylation
Trichloro-1-nitroprop-1-en-2-amine

ABSTRACT

The Ag@Carbon core-shell spheres were synthesized using a green, cheap, and easy process. The products were characterized by XRD, FESEM, TEM, MAP, EDX, Raman, and FT-IR analysis. The synthesis of a novel class of trichloro-1-nitroprop-1-en-2-amine via our Ag@Carbon spheres as a new Ag-catalyzed multicomponent reaction of nitroalkane-trichloroacetonitrile adduct and aryl halides in good yields under mild reaction conditions is reported. The catalytic activity of core-shell spheres was determined by changing the solvent and catalyst. The effect of solvent was investigated by performing the model reaction in the presence of catalyst in various conditions with DMF, DMSO, Toluene, THF, acetone and acetonitrile solvents. Among them, acetonitrile was found to be the best solvent in terms of the reaction time and yield of desired product. A comprehensive catalytic analysis of Ag@Carbon with Ag nanoparticles and carbon spheres as references and commercial AgI, AgBr, $AgNO_3$, and Ag_2SO_4 as Ag based catalysts has been performed.

1. Introduction

The part of materials science and solid state physics related to the carbon materials is a highly interesting topic, due to their unique chemical and physical properties [1–8]. Among these carbon forms, spherical particles such as carbon spheres and core-shell spheres have received more and more attention owing to their unique structure and physical properties such as encapsulation ability, controllable permeability, surface functionality, high surface to volume ratios, and excellent chemical stabilities [9–15]. These properties make core-shell structures attractive for various applications ranging from optical sensors, colloidal catalysts, and hard templates to drug carriers, adsorbents, gas storage, fuel cells, super capacitors and lithium-based batteries [16–19].

Recently, various articles have been published about carbon spheres preparation and their applications [13,15]. In the same time, various articles have discussed advancement in synthesis of noble metal@carbon core-shell particles and their applications [20–22]. However, there exists no special study about catalytic activity of these core-shell structures. Herein, efforts were made to successfully test the sub-micron size Ag@Carbon particles as catalyst. In this procedure, carbon shell protects the silver nano particles from light and moisture and retains the surface functional groups for loading other functional groups onto them. In an attempt to find out the effect of carbon shell on the catalytic activity of Ag@Carbon, the test was performed on carbon spheres as a reference. The results exhibited that the carbon sphere did not show any catalytic activity response. Therefore, the catalytic activity of Ag@Carbon core-shell structures is related to the encapsulated Ag inside the carbon shells. To the best of our knowledge, this is the first time to use encapsulated Ag ions inside carbon spheres as catalysts.

In the current work, we reported the synthesis of two core-shell spheres by using sucrose for a novel catalysis application that both of them have a carbon shell, but with different types of core (Fig. 1). In the first step, the Ag-catalyzed core-shell spheres were synthesized using simple hydrothermal method. In the second step, they were characterized by several methods and the results were compared to those of carbon spheres as the reference sample. At the end, the catalytic performance of our Ag@Carbon catalyst in the N-arylation reaction was compared to the results belonging to the other Ag-based catalysts.

The formation of aryl-N bond plays an important role in the synthesis of organic compounds that are of biological, pharmaceutical, and materials interests[23–27]. In the absence of a catalysts, no C—N coupling occurs at room temperature. Despite significant improvements in various catalysts such as CuI, palladium, nickel,

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https://doi.org/10.1016/j.jcat.2018.02.029

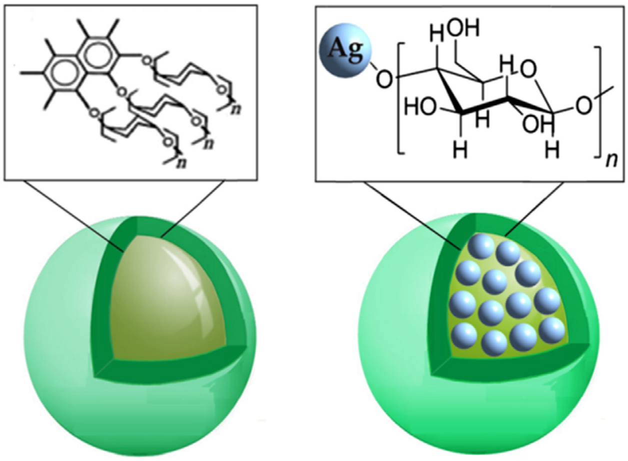

Fig. 1. Schematic representation of core–shell nanoparticles.

Copper and copper ferrite and ZnO during the past years [28–37]. Their usage has some limitations in many cases such as high temperatures, the air and moisture sensitivity, sensitivity to functional groups on the aryl halide, long reaction times, strongly acidic conditions, as well as the high cost of catalysts and the relative ligands. Our interest in this area stems from an experimentally development of a ligand-free catalytic system for C—N formation protocol by Ag-catalyst.

In this article, a class of one-pot, ligand-free, room temperature, three-component reactions of nitroalkane ($R-CH_2-NO_2$; R = H or Me), trichloroacetonitrile and various aryl halides (ArX; X = I or Br) for the synthesis of trichloro-1-nitroprop-1-en-2-yl aniline has been described. The general protocol of these new reactions in presence of Ag@carbon core-shell spheres as Ag catalyst is illustrated in Fig. 2.

2. Experimental methods

2.1. Materials

All the chemicals were used as received: Silver nitrate ($AgNO_3$; 99.99%), Sucrose ($(C_{12}H_{22}O_{11})_n$) and ethanol were obtained commercially from Merck company of analytical grade. Trichloro acetonitrile (Cl_3CCN: 98%), Acetonitrile (CH_3CN: 98%), Nitromethane (CH_3NO_2: 98%), (Nitroethan: $CH_3CH_2NO_2$: 98%), Iodobenzene (C_6H_5I: 98%), 4-Iodotoluene ($CH_3C_6H_4I$: 99%), 1-Bromo-4-iodobenzene (BrC_6H_4I: 98%), 4-Bromobenzonitrile (BrC_6H_4CN: 99%), 1-Bromo-3-nitrobenzene ($C_6H_4BrNO_2$: 99%), 1-Chloro-4-iodobenzene (ClC_6H_4I: 99%), 4-Iodoanisole ($IC_6H_4OCH_3$: 98%), 4-Bromotoluene ($CH_3C_6H_4Br$: 98%), Sodium hydride dry (NaH: 95%), Potassium carbonate (K_2CO_3: 99%) were purchased from Sigma Aldrich and used without further purification. For all the preparation steps, Deionized (DI) water with pH 6.4–6.5 was used.

2.2. Sample preparation

2.2.1. Synthesis of carbon sphere

Preparation of carbon sphere using hydrothermal methods was described elsewhere [13,21]. In a typical synthesis of colloidal carbon spheres, sucrose was dissolved in deionized water to form a clear solution (85 mL, 0.1 M), which was transferred to a 100 mL Teflon-lined stainless steel autoclave. Then it was sealed and heated at 190 °C for 4 h. When the reaction was completed, the autoclave was cooled to room temperature, and the black or brown precipitate was collected and washed by centrifugation at 6000 rpm for 20 min with deionized water and ethanol for three times, and the final product was dried at 45 °C for 10 h. We did not employ any catalyst or template in the preparation of these particles.

2.2.2. Synthesis of Ag@Carbon

In a typical procedure, both $AgNO_3$ and sucrose were dissolved in deionized water, resulting in a clear and homogeneous solution. 1 mL portion of $AgNO_3$ aqueous solution (0.1 M) was added drop-by-drop into the above-mentioned 0.1 M sucrose solution using a syringe pump at an injection rate of 6 mL h^{-1}. After stirring for more 10 min, the solution was transferred and sealed in a Teflon-sealed autoclave and heated to 190 °C for 4 h before being cooled in air naturally. The resulting products were centrifuged, washed, redispersed in deionized water and ethanol three times. After that, the products were oven dried at 50 °C. The formation of Ag@Carbon core-shell structures involved two primary steps: nucleation of inner silver nanoparticles, and consequent epitaxial growth and thickening of carbonaceous shell on the silver core. The presence of carbonaceous material in the preparation process acts as a barrier and prevents Ag particles from agglomeration leading to the long-term stability. Thus, Ag^+ ions sustained release can be controlled by tunable thickness of carbon shell. Generally, it is very

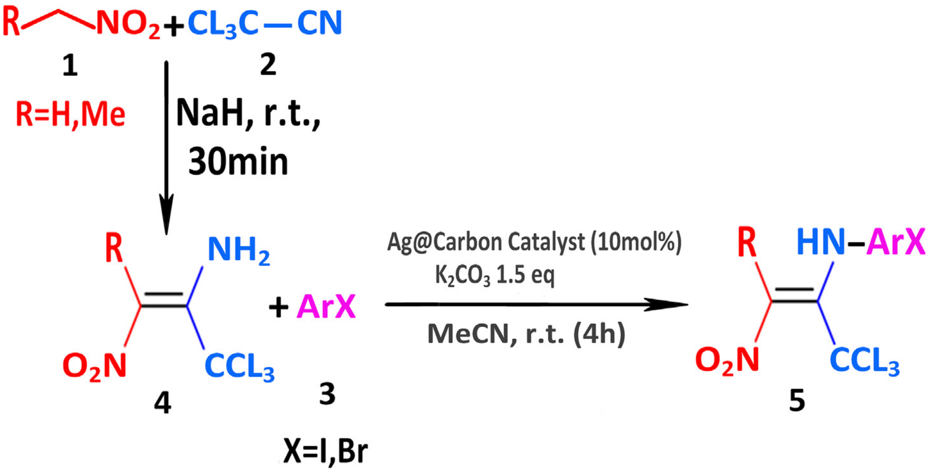

Fig. 2. A general protocol for multicomponent reaction of nitroalkane-trichloroacetonitrile adduct and aryl halides in room temperature by a silver-catalyzed C—N bond formation.