4TH National Conference of Iran Chemistry, Chemical Engineering and Nano

SYNTHESIS AND CATALYTIC APPLICATION OF 1,1,3,3-TETRAMETHYLGUANIDINE MODIFIED GRAPHENE OXIDE

N. Porahmad, R. Baharfar
Faculty of Chemistry, University of Mazandaran, Babolsar, Iran,
n.porahmad@stu.umz.ac.ir
baharfar@umz.ac.ir

Abstract: Graphene oxide (GO) was synthesized and functionalized with (3-chloropropyl)-trimethoxysilane (CPTMS) and then with 1,1,3,3-tetramethylguanidine (TMG) to produce GO-Si-TMG. The resultant material was characterized by elemental analysis, FT-IR, TGA and FE-SEM spectroscopy and was used in Michael addition of different C-nucleophiles to various substituted nitrostyrenes to explore its catalytic activity. GO-Si-TMG showed very good catalytic activity and gave a conversion of >99.99 % (based on ^{1}H NMR of the crude reaction mixture) under the optimized reaction conditions (r.t., EtOH-H_2O (1:1), 1.5 h). Moreover, it could be easily recovered through filtration and reused for at least seven times without significant decrease in its catalytic performance.

Keywords: Graphene oxide, 1,1,3,3-Tetramethylguanidine, Michael addition, Dimethyl malonate, β-Nitrostyrene.

1. INTRODUCTION

Immobilization of soluble catalysts on solid supports is a way to take advantage of heterogeneous catalysts such as easy handling and reduced waste [1]. Graphene, graphene oxide (GO) is a one-atom-thick sheet generated from exfoliation of graphite oxide in polar solvents. The presence of oxygen-containing functional groups on the basal plane and edge of GO provide it with the capability of being modified through covalent and noncovalent bonding [2].

Different metallic nanoparticles and organic compounds have been supported on GO nanosheets through noncovalent interactions and the resultant composites have been applied as catalyst in various organic reactions [3-9]. There have been some instances of covalently modified GO including sulfonated and amine-functionalized GO nanosheets which have been reported as acidic [10], basic [11] and acid-base bifunctional catalysts [12].

1,1,3,3-Tetramethylguanidine (TMG) catalyzes various organic reactions [13-15]. TMG has been immobilized on different solid supports and the resultant materials were applied in various organic reactions [16-19].

There have been only a few reports of GO functionalization with TMG [20] and this encouraged us to prepare and study this kind of materials. In continuation of our previous studies [21], we have synthesized GO and functionalized it with (3-chloropropyl)-trimethoxysilane (CPTMS) and then with 1,1,3,3-tetramethylguanidine (TMG) to produce GO-Si-TMG and characterized it by elemental analysis, fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA) and field emission scanning electron microscopy (FE-SEM) and examined its performance in Michael addition of different C-nucleophiles to various substituted nitrostyrenes. The catalyst recyclability was also studied at the optimal conditions and the products were successfully isolated by column chromatography and identified by ^{1}H and ^{13}C NMR spectroscopy.

2. EXPERIMENTAL OBSERVATIONS – CATALYST PREPARATION

A catalyst containing GO and TMG (GO-Si-TMG) was synthesized (Scheme 1). In the first step, graphite powder was oxidized using a modified Hummers' method [22] and the oxidation product was exfoliated to GO nanosheets by ultrasonication. The next step was GO functionalization with CPTMS through the hydroxyl and epoxy groups on GO to