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Bismuth Iron Oxide Nanocomposite Supported on Graphene Oxides as the High Efficient, Stable and Reusable Catalysts for the Reduction of Nitroarenes under Continuous Flow Conditions

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Abstract: An efficient catalyst made of bismuth, iron and graphene oxide composite was developed for the reduction of nitroarenes with hydrazine hydrate to afford corresponding anilines. We found that the bismuth and graphene remarkably promoted the activity of iron oxide catalyst, so that a mixture of ferric chloride, bismuth nitrate and graphene oxide catalysed the complete conversion of 4-nitrophenol into 4-aminophenol. Moreover, a catalyst prepared from the co-precipitation of bismuth, iron and graphene oxide nanocomposite (BFGO) exhibited perfect performance, and it could be recovered magnetically and reused for ten cycles without any activity losing. Furthermore, another heterogeneous catalyst tBFGO was constructed from the bismuth iron oxide nanocomposite with thermal exfoliated graphene. It was a robust and sustainable catalyst and was suitable to be used in the continuous flow microreactor. Applying a catalyst cartridge that filled up with tBFGO, a series of functionalized nitroarenes were successfully converted into corresponding anilines with excellent selectivity, and the work-up procedure was very easy. The catalytic activity of the catalyst did not decline within more than 600 minutes under a flow rate of 1 mL/min.

Keywords: Bismuth Iron Oxide; Graphene; Catalytic Reduction; Continuous flow; Nitroarenes; Anilines

Introduction

Anilines are a kind of important substances as they are key intermediates of a great variety of chemicals such as pharmaceuticals, agrochemicals and dyes [1]. Anilines are usually obtained from the reduction of their corresponding nitroarenes. Iron and other metallic reductants have been employed as the reductant under the acidic catalyst free condition for decades [2-4], however, the catalytic H-transfer procedure is more preferred than stoichiometric metal reduction because of the superiority of less waste, milder conditions and better selectivity [5-7]. Numerous catalytic protocols have been developed to achieve the transformations. The commonly used hydrogen sources include hydrogen gas, $NaBH_4$ and hydrazine hydrate. Although the H_2 is the cleanest hydrogen source, the hydrazine hydrate is considered as a more suitable reductant in the production of anilines. To use the hydrogen gas or $NaBH_4$ as the reductant usually requires the presence of noble metal such as Pd, Pt, Au or Ag[8], and a high pressure vessel is usually necessary for the H_2. Nevertheless, the expensive catalyst is unnecessary when the hydrazine works as the H-source. N_2 is the only by-product means that the hydrazine is also a clean hydrogen source. The hydrazine mediated reduction of nitroarenes fulfils the industrial favourite, because the production of most anilines are still popularly performing in multi-batch way with relatively small scale in today's industry. Thus the hydrazine-mediated reduction of nitroarene takes many advantages: easy to handle, good product quality and less waste.

Although hydrazine-mediated reactions take place even in the absence of a catalyst, harsh conditions are often required [9, 10]. A variety of catalysts have been developed to carry out the reactions in mild and efficient way. These catalysts include the Fe, Co, or Ni based composites [11-14], various carbon materials [15-18], and even the phthalocyanines [19, 20]. What's more, the supported precious metal catalysts such as Au, Pt, Pd and Rh[21] nanoparticles are also efficient in this transformation.

Of these catalysts, the iron based catalysts have attracted the most attention for their low cost and non-toxic nature. The iron based materials had been regarded as a rising star[22], so that a lot of iron oxide composites have been applied in various fields. In 1998 and 1999, Lauwiner, Benz and co-workers reported a series of systematic research work on the iron oxide catalyzed the hydrazine-mediated reduction of nitroarenes [23-26]. Since then, various iron oxide based catalysts have been developed to improve the reactivity and selectivity of the hydrazine mediated reduction of nitro compounds. For example, the in situ generated nano iron oxide from $Fe(acac)_3$ are very efficient [27-29], even the commercially available Fe_3O_4 nanoparticles [30] exhibits good catalytic activity. However, the catalytic reactivity and stability of mono-component iron oxide is not satisfactory enough, so large amounts of catalyst loading or high reaction temperature is usually required. Therefore, the multi-component catalyst have been widely reported, for example, the iron-containing oxide composites in particular with various carbon materials [31-35] exhibit better properties [14,36-42].

A perfect iron based catalyst should take the advantage of exciting activity, wonderful selectivity, good reusability, and easy to prepare. Unfortunately, the diversity of the iron oxide crystal phase and the easiness of phase transformation may cause the loss of the catalytic activity. It is difficult to comprehend accurately how the iron oxide catalyst works on the molecular level, comparing with CeO_2 whose [0,1,0] plane has been demonstrated to be the catalytic active site [43]. Finding some additives to stabilize the crystalline of active iron oxide phase is a promising direction to enhance the activity and stability. We choose the bismuth as the combination because the bismuth iron oxide composite has various crystalline forms, which may help a catalyst to maintain its suitable nano-structure [44-47].