Nitro compound reduction in the presence of robust palladium immobilized on modified magnetic Fe_3O_4 nanoparticles as a recoverable catalyst

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abstract

We report the synthesis of recoverable magnetic nano catalyst Pd@ Fe_3O_4 and its utility as a recyclable catalyst for reduction of nitro group. The catalyst is easily removed from the reaction media by an external magnetic field and can be re-used for at least 10 times without any considerable loss in its activity. The catalyst was characterized by scanning electron microscopy (SEM), thermal gravimetric analysis (TGA), inductively coupled plasma spectroscopy (ICP), Fourier transform infrared spectroscopy (FTIR), CHN analysis, and vibrating sample magnetometery (VSM).

Key Words: Reduction, nano catalyst, recoverable, nitro compounds

Introduction

Catalysts have many advantages in organic synthesis, e.g. they may increase the rate of the reaction through reduction of activation energy [1]. They are divided into two general categories, heterogeneous and homogeneous [2]. Both of them have their own advantages and disadvantages. For example homogeneous catalysts are more selective and because of being in a same phase as reactants, they may result in higher reaction speed and higher yields, but they are hard to separate from the reaction media and there for they may contaminate the final products, which can be sometimes very harmful especially in drug synthesis [3]. Metals supported on magnetic nano particles create a new approach to the world of catalysts [4]. By nascent of such catalysts, it became possible to bring the advantages of both kinds of catalysts (homogeneous and heterogeneous) together in a one magnetic nano catalyst [5]. It means one can profit from sustainability with high yields and easy work up [6]. Because of their tiny and nano size particles they have a large surface area as same as a homogeneous catalyst, so they can increase the speed and the yield of reactions [7]. On the other side, they remain insoluble and due to their magnetic characteristic, they can be easily removed by an external magnetic field [8]. Therefore there is no concern about separation of such catalysts and pollution of the products by toxic metals. These catalysts are of high surface area and have a high ratio of surface area to the volume. This property increases the interaction between the reaction components and so causes dramatic increase in reaction rate and yield. Another important aspect is their reusability for several times that reduces the environmental impact and increases the economical advantages [9]. The strong bond and connection between metal and catalyst surface minimized metal leaching during the reaction [10]. As it is known, palladium is a precious metal and is useful in many organic transformations especially in nitro compound reduction reactions.

Methods

Preparation of Fe_3O_4@SiO_2

was synthesized according to the procedure reported in literature [11]

Preparation of Fe_3O_4@SiO_2@3-glycidoxypropyltrimethoxysilane

was synthesized according to the procedure reported in literature [12]

This catalyst was synthesized according to the procedure reported in literature [13]

General Procedure for nitro compound reduction

A mixture of Nitro compound (1 mmol), $NaBH_4$ (10 mmol), and catalyst (0.01 gr) in H_2O (2 mL) was prepared in a flask. The mixture was stirred at room temperature for minutes. The progress of the reaction was monitored by thin layer chromatography (TLC) and gas chromatography (GC). After completion of the reaction, the catalyst was separated by an external magnetic field from the reaction media and corresponding amine compounds were extracted with ethyl acetate after separation of aqua layer, the organic solvent was evaporated by rotary evaporator under reduced pressure. The product was purified by column chromatography or re crystallization method. The separated catalyst was washed two times with methanol, and dried over night at room temperature and then used directly for subsequent reaction runs.

Result and discussion

Characterization of catalyst

The catalyst structure was characterized by field emission scanning electron microscope (FESEM), thermal gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), CHN analysis, vibrating sample magnetometery (VSM) and inductively coupled plasma optical electron spectrometry (ICP-OES). The catalyst shape and size was confirmed by FESEM. The diameter of nano particles is about 50 nm; they are approximately spherical, and mono-sized. Furthermore, it is clear that the Pd (II) nanoparticles are immobilized on the surface homogeneously.

Catalytic experiments

We examined the catalytic activity of catalyst in reduction of 1 mmol nitro benzene as a model reaction. To optimized experimental conditions, the impact of various reducing agent, temperatures, solvents and different amounts of catalyst were

Entry	Substrate	Product	Time	Yield (%)
1	Nitrobenzene	Aniline	15 min	95
2	4-Nitrophenol	4-Aminophenol	5	90
3	3-Nitrotoulene	3-Toluidine	15 min	78
4	4-Nitrotoulene	4-Toludine	15 min	80
5	3-Iodo nitrobenzene	3-Iodo aniline	3 h	70
6	3-Chloro nitrobenzene	3-Chloro aniline	3 h	88
7	4-Chloro nitrobenzene	4-Chloro aniline	3h	70
8	4-Bromo nitrobenzene	4-Bromo aniline	3 h	80
9[b]	Nitrobenzene	Aniline	24 h	trace

[a] All reactions were carried out with Molar ratio: 1 : 10 : 0.01,Substrate/$NaBH_4$/Igr cat., H_2O (2 mL).[b] Without catalyst ($NaBH_4$).

Conclusions

In conclusion, we have used immobilized palladium on Fe_3O_4 nano magnetic core through triazole ligand in Nitro compound reduction reactions in short times and with high yields and purity. Different derivatives of amine compounds were produced by reduction of nitro compounds derivatives and sodium borohydride. The catalyst also was easily removed from reaction media by external magnetic field each cycle, and washed with methanol and reused for 10 more cycles without considerable reduction in its reactivity. The stability of the catalyst to the air, moisture, and heat makes it suitable for reactions at harder conditions. Easy and completely elimination of the catalyst from reaction media is a good reason for using this catalyst in pharmaceuticals and drug synthesis.

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References

[1] G. Ertl, H. Knozinger, F. Schuth and J. Weitkamp in *Handbook of Heterogeneous Catalysis*, *Vol.* Nature Publishing Group, **2008**.

[2] P. Chutia, S. Kato, T. Kojima and S. Satokawa, *Polyhedron,* 2009, **28**, 370.

[3] H. G. Aurich, K. Hahn, K. Stork , W. Weiss, *Tetrahedron,* 1977, **33**, 969.

[4] G. A. Somorjai, H. Frei, J. Y. Park, *J. Am. Chem. Soc.,* 2009, **131**, 16589.

[5] A. Corma , H. Garcia, *Top. Catal.,* 2008, **48**, 8.

[6] R. Schlogl and S. B. Abd Hamid, *Angew. Chem. Int. Ed.,* 2004, **43**, 1628.

[7] A. T. Bell, *Science,* 2003, **299**, 1688.

[8] a) J. A. Melero, R. van Grieken and G. Morales, *Chem. Rev.,* 2006, **106**, 3790; b) V. Polshettiwar and R. Varma, *Green Chem.,* 2010, **12**, 743.

[9] A. H. Lu, E. L. Salabas and F. Schuth, *Angew. Chem. Int. Ed.,* 2007, **46**, 1222.

[10] L. D. P. a. Rothenberg, Appl. Organomet. Chem., 2008**, 22**, 288.

[11] A. Pourjavadi, S. H. Hosseini, S. T. Hosseini and S. A. Aghayeemeibody, *Catal. Commun.* 2012, **28**, 86.

[12] F. M. Moghaddam and S. E. Ayati, *RSC Adv.,* 2015, **5**, 3894.

[13] A. Dadras, MR. Naimi‐Jamal, F.M. Moghaddam, SE. Ayati, Appl.Organometal. Chem. 2017:e3993. https://doi.org/10.1002/aoc.3993