

Simple, Practical and Eco-friendly Reduction of Nitroarenes with Zinc in the Presence of Polyethylene Glycol Immobilized on Silica Gel as a New Solid–liquid Phase Transfer Catalyst in Water

Kiasat, Ali Reza^{*†}; Zayadi, Maryam; Mohammad-Taheri, Fatemeh

Department of Chemistry, Faculty of Science, Shahid Chamran University,

P.O. Box 61357-4-3169 Ahvaz, I.R. IRAN

Fallah-Mehrjardi, Mehdi

Department of Marine Chemistry, Khoramshahr Marine Science & Technology University,

Khoramshahr, I.R. IRAN

ABSTRACT: Polyethylene glycol was easily grafted to silica gel and used as a solid–liquid phase transfer catalyst in the reduction of aromatic nitro compounds. This silica-grafted polyethylene glycol is proved to be an efficient heterogeneous catalyst in the reduction of nitroarenes to the corresponding aromatic amines with zinc powder in water. The reduction reactions proceeded efficiently with excellent chemoselectivity without affecting other sensitive functional groups.

KEY WORDS: Phase transfer catalyst, Reduction, Zinc, Aromatic nitro compounds, Aromatic amines.

INTRODUCTION

Water is a desirable solvent for chemical reactions for reasons of cost, safety, and environmental concerns, and the study of organic reactions in aqueous solvents has an intriguing history. Unfortunately the use of water is limited by low solubility of organic compounds in water. A variety of strategies have been developed in order to expand the scope of water-based organic synthesis, the most important of these being the use of phase transfer catalyst [1].

Phase Transfer Catalysis (PTC) is a very useful approach that typically involves simple experimental operations, mild reaction conditions, inexpensive,

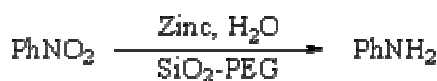
environmentally benign reagents and solvents and large-scale reaction [2]. One practical limitation to the phase transfer method however, is that many of the catalysts used; promote the formation of stable emulsions [3]. Immobilization of the phase-transfer catalyst on an insoluble polymeric matrix can provide a simple solution to this problem. This technique would have considerable advantages. Not only the catalyst recovery and product isolation would be greatly simplified, but also, owing to the three-phase nature of the system, continuous flow methods could be employed making the technique particularly attractive for industrial applications.

^{*} To whom correspondence should be addressed.

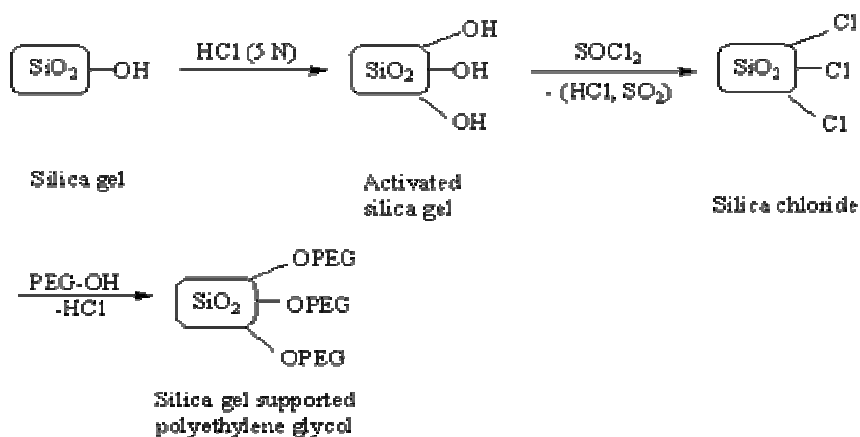
[†] E-mail: akiasat@scu.ac.ir

1021-9986/11/2/37

5/\$/2.50



Scheme 1.



Scheme 2.

Aromatic amines are important starting materials and intermediates for the manufacture of a variety of chemicals such as dyes, photographic materials, surfactants, polymers, pharmaceutical products, agricultural chemicals and as antioxidants. The reduction of aromatic nitro compounds is one of the most common methods for preparing the corresponding aromatic amines. Recently, many novel reducing agents have been reported in the literature. The most commonly used reagents are zinc, iron, or tin, in the presence of an acid [4], catalytic hydrogenation using Ni, Pd/C, and PtO₂ [5]. Other reagents include sodium hydrosulfite [6], Sm [7], In [8], hydriodic acid [9], RhCl₃ [10], Au/SiO₂ [11], N₂H₄/Fe₂O₃/MgO [12], NaBH₄/Pt-Ni [13], NaBH₄/BiCl₃ [14] and Al/NH₄Cl [15]. Each of the above methods has at least one of the following drawbacks: 1) harsh reaction condition 2) significant limitations based on safety and handling considerations, 3) destroy many sensitive functional groups, 4) expensive and/or moisture-sensitive reagents, 5) a high-pressure hydrogen reactor and 6) non-chemoselectivity in reduction reaction. We wish to report a simple, efficient and practical approach for the reduction of nitroarenes in the presence of PTC in water.

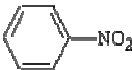
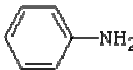
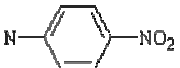

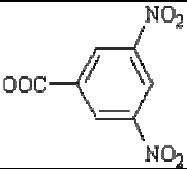
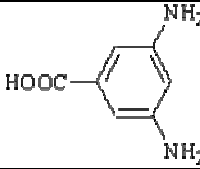
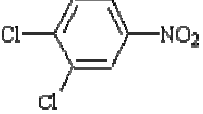
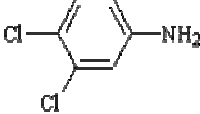


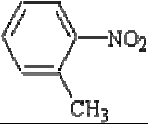
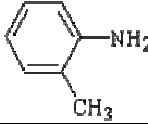
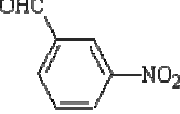
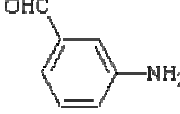

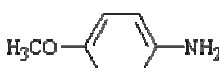


RESULTS AND DISCUSSION

Looking for “cleaner” alternatives to classical syntheses and in developing green chemistry and also

in pursuing our new interest in developing inexpensive and non polluting reagents [16-21], very recently, we described a new efficient covalent immobilization method for preparation of silica-grafted polyethylene glycol and its successful application as a solid-liquid phase-transfer catalyst for regioselective azidolysis of epoxides using NaN₃ in water [22]. Herein, we wish to report application of this solid-liquid phase-transfer catalyst in the facile reduction of aromatic nitro compounds to their corresponding amines with zinc powder as reducing agent (Scheme 1).

The functionalization of layered mineral supports (grafting) is a frequently employed, useful strategy for preparing the inorganic support for the immobilization of catalyst molecules. Grafting reactions can occur by establishing covalent bonds between the reactive groups of the layer and an adequate reactant molecule, which ensures higher chemical, structural and thermal stability for the compound [23]. In 1965, a report by *Baverez* [19] outlined the immobilization of PEG-300 on silica gel surface via covalently bond by heating of silica gel and PEG in toluene. The obtained product indicated that the degree of functionalization was 0.33 mmole of PEG per gram of silica gel [24]. Here we report that PEG can be efficiently immobilized on silica gel by reaction of silica chloride with PEG. The reaction is very clean and not requiring any work-up procedure because the evolved

Table 1: Reduction of nitro compound with zinc in the presence of PEG immobilized on silica gel.

Entry	Substrate	Substrate: reagent (mole)	Condition	Time (h)	Product ^a	Yield (%) ^b
1		1:7	r.t.	1		88
2		1:7	r.t.	0.5		84
3		1:7	r.t.	3		92
4		1:14	r.t.	3		76
5		1:7	r.t.	5		68
6		1:9	reflux	2		86
7		1:7	deflux	0.5		81
8		1:7	reflux	2		72
9		1:9	reflux	1.5		78

a) Products were identified by compared of their physical and spectral data with those of authentic samples, b) Isolated yields, c) 10 drops of ethanol was added to the reaction mixture.

HCl gas can be removed from the reaction vessel immediately. Scheme 2 described the facile immobilization of PEG on silica gel. This supported catalyst, has been found to be stable to acid, base, O₂, high oxidation systems and NaBH₄ reduction systems [23]. The amount of PEG supported on silica gel was determined by gravimetric and was 0.7 mmol/g of silica gel.

To optimization of reaction conditions, the conversion of nitrobenzene to aniline in the presence of supported

catalyst in water was investigated. The optimum molar ratio of the catalyst was found to be 0.1g/1mmol of nitrobenzene. Reduction of different nitroarenes carrying activated and deactivated groups were carried out by using PEG-supported on silica gel and zinc powder in water. The results of reduction of various nitroarenes were shown in Table 1.

The reduction of nitroarenes took place smoothly, cleanly and easily to afford the corresponding amines

as exclusive and virtually pure products according to TLC and ^1H NMR. It is worthy to note that the azoxy, azo and hydrazo compounds as the usual side products of reduction of nitroarenes were not observed in this method. In addition the present method was highly chemoselective and some sensitive functional groups such as aldehyde, acid, and halide groups were unaffected during reduction reaction.

The promoting effect of supported catalyst was definitely confirmed by reaction of nitrobenzene with zinc powder under similar conditions, without adding catalyst. TLC analysis of the reaction mixture did not show completion of the reaction after 10h. It is worthy to note that the polymeric catalyst can be reused several times without loss of activity. The PEG immobilized on silica gel, recovered by filtration and washed with dilute HCl, water and methanol and then it has been reused four times to convert nitrobenzene to the aniline. The catalyst doesn't show any loss in its activity and produced aniline in 88%, 85%, 86% and 83% yield, respectively.

EXPERIMENTAL SECTION

Procedure for the covalent coupling of polyethylene glycol on silica gel

Preparation of silica chloride

To the dried activated silica gel (20 g) was added dropwise SOCl_2 (45 mL) under nitrogen atmosphere and at room temperature. Evolution of copious amounts of HCl and SO_2 occurred instantaneously. After stirring for another 4 h, the excess unreacted thionyl chloride was distilled out and the resulting greyish silica chloride was flame dried, stored in airtight container and used as it is for the reactions [25].

Immobilization of polyethylene glycol on silica gel

To a well-stirred silica chloride (20 g) in dry CH_2Cl_2 (40 mL) was added dropwise PEG-300 (10 g) under nitrogen atmosphere and at room temperature. HCl was instantaneously evaluated. After stirring for another 2 h, the obtained silica gel supported PEG was removed by filtration. For elimination of any additional PEG, the PTC was washed several times by acetone and dried.

General procedures for the reduction of nitro compounds in water

To a mixture of nitro compound (1 mmol) and water (5 mL), silica gel supported PEG (0.1 g) and zinc powder

(7-14 mmol) were added. The reaction mixture was stirred for the time shown in Table 1. The progress of the reaction was monitored by TLC using THF/n-hexane (1/5) as eluent. The insoluble PTC was filtered off and the filtrate was acidified with HCl solution (10%) until the pH of the reaction mixture reached 1. The combined filtrate was extracted with CH_2Cl_2 (2×15 mL). The aqueous layer was separated and the pH of the mixture adjusted to about 9 with a solution of NaOH (10%). The aqueous layer was extracted again with Et_2O (15 mL) and the combined extracts were dried over anhydrous Na_2SO_4 and evaporated to give the product in 72-94% isolated yields.

CONCLUSIONS

In conclusion, we have demonstrated an environmentally friendly route for chemoselective reduction of aromatic nitro compounds to aromatic amines with zinc metal in water that can be used for laboratory synthesis and we feel that it may be a suitable addition to methodologies already present in the literature.

Acknowledgments

Partial support for this work by Shahid Chamran University Research Council is gratefully acknowledged.

Received : Des. 20, 2009 ; Accepted : Sep. 15, 2010

REFERENCES

- [1] Starks C.M., Liotta C.L., Halpern M., "Phase-Transfer Catalysis, Fundamental, Applications, and Industrial Perspectives", Chapman & Hall, New York, (1994).
- [2] Sun H., Li J., Cai X.C., Jiang D., Dai L.Y., Ionic Liquids as Efficient Phase-Transfer Catalysts for the Solid Base-Promoted Monoalkylation of Diethyl Malonate, *Chin. Chem. Lett.*, **18**, p. 279 (2007).
- [3] Keller W.E., "Phase Transfer Reactions", Fluka-Compendium, 3, Georg Thime Verlag, Stuttgart, (1992).
- [4] Mahdavi H., Tamami B., Reduction of Nitro-Aryl Compounds with Zinc in the Presence of Poly[N-(2-Aminoethyl)Acrylamido] Trimethyl Ammonium Chloride as a Phase-Transfer Catalyst, *Synth. Commun.* **35**, p. 1121 (2005).
- [5] Smith G.V., Nothessiz F., "Heterogeneous Catalysis in Organic Chemistry", Academic Press, New York, (1999).
- [6] Scheuerman R.A., Tumelty D., The Reduction of Aromatic Nitro Groups on Solid Supports Using Sodium Hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$), *Tetrahedron Lett.* **41**, p. 6531 (2000).

- [7] Banik B.K., Mukhopadhyay C., Venkattman M.S., Becker F.F., A Facile Reduction of Aromatic Nitro Compounds to Aromatic Amines by Samarium and Iodine, *Tetrahedron Lett.* **39**, p. 7243 (1998).
- [8] Cho Y.S., Jun B.K., Kim S., Cha J.H., Pae A.N., Koh H.Y., Chang M.H., Han S.Y., Reduction of Nitro Group Using Indium-wire in Water, *Bull. Korean Chem. Soc.* **24**, p. 653 (2003).
- [9] Kumar J.S.D., Ho M.M., Toyokuni T., Simple and Chemoselective Reduction of Aromatic Nitro Compounds to Aromatic Amines: Reduction with Hydriodic Acid Revisited, *Tetrahedron Lett.*, **42**, p. 5601 (2001).
- [10] Mdleleni M.M., Rinker R.G., Ford P.C., Reduction of Aromatic Nitro Compounds as Catalyzed by Rhodium Trichloride under Water-Gas Shift Reaction Conditions, *J. Mol. Catal. A: Chem.*, **204-205**, p. 125 (2003).
- [11] Chen Y., Qiu J., Wang X., Xiu J., Preparation and Application of Highly Dispersed Gold Nanoparticles Supported on Silica for Catalytic Hydrogenation of Aromatic Nitro Compounds, *J. Catal.*, **242**, p. 227 (2006).
- [12] Kumbhar P.S., Valnte J.S., Figueras F., Reduction of Aromatic Nitro Compounds with Hydrazine Hydrate in the Presence of the Iron(III) Oxide-MgO Catalyst Prepared from a Mg-Fe Hydrotalcite Precu, *Tetrahedron Lett.*, **39**, p. 2573 (1998).
- [13] Ghosh S.K., Mandal M., Kundu S., Nath S., Pal T., Bimetallic Pt-Ni Nanoparticles Can Catalyze Reduction of Aromatic Nitro Compounds by Sodium Borohydride in Aqueous Solution, *Appl. Catal. A: Gen.*, **268**, p. 61 (2004).
- [14] Ren P.D., Pan S.F., Dang T.W., Wu H.S., The Novel Reduction Systems: $\text{NaBH}_4\text{-SbCl}_3$ OR $\text{NaBH}_4\text{-BiCl}_3$ for Conversion of Nitroarenes to Primary Amines, *Synth. Commun.* **25**, p. 3799 (1995).
- [15] Nagaraja D., Pasha M.A., Reduction of Aryl Nitro Compounds with Aluminium/ NH_4Cl : Effect of Ultrasound on the Rate of the Reaction, *Tetrahedron Lett.*, **40**, p. 7855 (1999).
- [16] Kiasat A.R., Fallah-Mehrjardi M., Polyethylene Glycol: A Cheap and Efficient Medium for the Thiocyanation of Alkyl Halides, *Bull. Korean Chem. Soc.* **29**, p. 2346 (2008).
- [17] Kiasat A.R., Badri R., Zargar B., Sayyahi S., Poly(ethylene glycol) Grafted onto Dowex Resin: An Efficient, Recyclable, and Mild Polymer-Supported Phase Transfer Catalyst for the Regioselective Azidolysis of Epoxides in Water, *J. Org. Chem.* **73**, p. 8382 (2008).
- [18] Kiasat A.R., Fallah-Mehrjardi M., PEG- SO_3H as Eco-Friendly Polymeric Catalyst for Regioselective Ring Opening of Epoxides Using Thiocyanate Anion in Water: An Efficient Route to Synthesis of β -Hydroxy Thiocyanates, *Catal. Commun.*, **9**, p. 1497 (2008).
- [19] Kiasat A.R., Fallah-Mehrjardi M., $\text{B}(\text{HSO}_4)_3$: A Novel and Efficient Solid Acid Catalyst for the Regioselective Conversion of Epoxides to Thiocyanohydrins Under Solvent-Free Conditions, *J. Braz. Chem. Soc.*, **19**, p. 1595 (2008).
- [20] Kiasat A.R., Zayadi M., Fallah-Mehrjardi M., Regioselective Ring Opening of Epoxides Using NH_4SCN /Silica Sulfuric Acid: An Efficient Approach for the Synthesis of β -Hydroxy Thiocyanate Under Solvent-Free Conditions, *Chin. Chem. Lett.*, **19**, p. 665 (2008).
- [21] Kiasat A.R., Fallah-Mehrjardi M., Dowex as Reusable Acidic Polymeric Catalyst in the Efficient and Regioselective Conversion of Epoxides into β -Hydroxy Thiocyanates under Solvent Free Conditions, *J. Chin. Chem. Soc.* **55**, p. 1119 (2008).
- [22] Kiasat A.R., Zayadi M., Polyethylene Glycol Immobilized on Silica Gel as a New Solid-Liquid Phase-Transfer Catalyst for Regioselective Azidolysis of Epoxides in Water: An Efficient Route to 1,2-Azido Alcohols, *Catal. Commun.*, **9**, p. 2063 (2008).
- [23] Nakagaki S., Castro K.A.D.F., Guilherme S.M., Matilte H., Sueli M.D., Fernando W., Catalytic Activity in Oxidation Reactions of Anionic Iron(III) Porphyrins Immobilized on Raw and Grafted Chrysotile, *J. Braz. Chem. Soc.*, **17**, p. 1672 (2006).
- [24] Baverez, M., Bastick, J., Action Du Methanol Sur Les Gels De Silice, *J. Bull. Soc. Chim. Fr.*, **12**, p. 3662 (1965).
- [25] Firouzabadi H., Iranpoor N., Karimi B., Hazarkhami H., Highly Efficient Transdithioacetalization of Acetals Catalyzed by Silica Chloride, *Synlett*, p. 263 (2000).