Journal of Molecular Catalysis A: Chemical 355 (2012) 96–101

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

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

Platinum nanoparticles supported on zirconia mediated synthesis of N-acyl and N-(*tert*-butoxycarbonyl)amines from nitroarenes and azides

M. Lakshmi Kantam[a,*], R. Sudarshan Reddy[a], K. Srinivas[a], R. Chakravarti[a], B. Sreedhar[a], F. Figueras[b], Ch. Venkat Reddy[c]

[a] *Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500607, India*
[b] *Institut de recherche sur la catalyse et l'environnement de Lyon, UMR 5256 Université Lyon 1-CNRS, 2, Avenue Albert Einstein, F-69626, Villeurbanne, France*
[c] *1311 Gilman Hall, Department of Chemistry, Iowa State University, Ames, IA 50011, USA*

ARTICLE INFO

Article history:
Received 29 August 2011
Received in revised form
29 November 2011
Accepted 1 December 2011
Available online 11 December 2011

Keywords:
Bi-functional
Heterogeneous
Nanoparticles
Amines
Azides

ABSTRACT

A convenient and useful protocol has been designed for the synthesis of *N*-aryl acetamides from the corresponding nitro compounds via a reductive *N*-acylation process using bi-functional, recyclable heterogeneous platinum nanoparticles supported on zirconia [$Pt(0)/ZrO_2$] catalyst, employing molecular hydrogen as the environmentally benign reductant and the corresponding anhydrides as acylating agents. *N*-Boc protected amines were also synthesized in similar lines, from the corresponding azides. The reaction is successfully performed under mild conditions to afford good to excellent yields of the products. The solid bifunctional-catalyst, $Pt(0)/ZrO_2$ is quantitatively recovered by simple centrifugation and reused for multiple cycles with consistent activity and selectivity.

1. Introduction

Organic amines and their derivatives are industrially important intermediates for several pharmaceuticals, agrochemicals, dyes, herbicides, pigments, surfactants, pesticides, cosmetics and polymers [1–4]. Reduction of nitro compounds and azides to their corresponding amines is an important transformation in synthetic organic chemistry, and protection of primary amines with a suitable group plays a major role in multistep synthesis [5]. The most common technique for the synthesis of anilines involves the selective hydrogenation of aromatic nitro-compounds [6]. The classical route practiced in industry for the production of anilines involves the reduction of nitroarenes employing stoichiometric amounts of iron powder in the presence of hydrogen source such as hydrochloric acid or acetic acid [7]. In general, the preparation of *N*-arylacetamides involves two steps, i.e. reduction of nitroarenes to *N*-arylamines followed by the acylation of *N*-arylamines to the corresponding anilides (*N*-arylacetamides). The conversion of nitroarenes to their corresponding acetanilides in a one-pot reaction is an important transformation in organic chemistry under homogeneous conditions [8]. The acetanilides and other type of *N*-arylamide derivatives [9], such as N-aryl chloroacetamides are useful intermediates for the synthesis of oxyindoles [10].

In general, direct conversion of nitroarenes to acetanilides are carried out by iron powder with acetic acid [11], molybdenum hexacarbonyl/acetic acid [12], Other metal catalysts known to catalyze this transformation are Au/Al_2O_3, $Au–Pd/Al_2O_3$ [13], platinum oxide [14], rhodium–platinum oxide [14], palladium [15] and zinc [16]. In addition, the reduction of nitro groups using samarium [17], are also reported. Recently gold catalyzed hydrogenation of nitro compounds is also reported [18–20]. Some of these processes encounter the problem of disposal of a large amount of metal salts generated during the reaction. Although, homogeneous iron carbonyls are used extensively in the reductive acylation of nitroarenes using variety of reducing agents [21], these processes face the difficulty in product isolation from the iron sludge formed during the reaction.

The reduction of azides to amines is an important and widely practiced reaction in organic synthesis. It is especially useful because of the ease of synthesis and high stereoselectivity associated with the preparation of the precursor azides and the reduction represents a pivotal step in a stereoselective sequence for the preparation of amines. Azides can be introduced by displacement of a suitable nucleofuge or direct conversion of an existing amine by a diazotransfer reaction. Furthermore, azides are resistant to many reaction conditions and can be easily reduced to amines

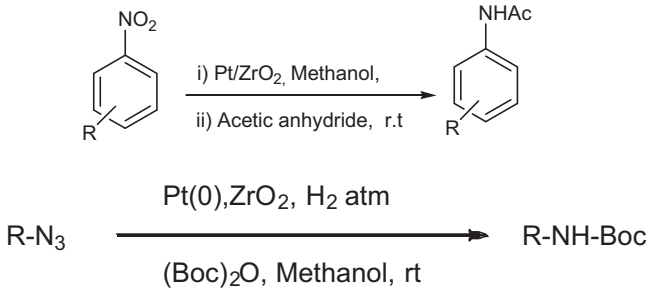
* Corresponding author. Tel.: +91 40 27193510; fax: +91 40 2716 0921.
E-mail address: mlakshmi@iict.res.in (M.L. Kantam).

1381-1169/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2011.12.002

either generally (hydrogenation, metal hydrides, etc.) or orthogonally (Staudinger reaction) [5]. Substitution of a leaving group by the azide anion, reduction of the azide to an amine, and protection of the amine as *tert*-butoxycarbamate (R-NH-Boc) is a standard process in organic synthesis.

Tert-butoxycarbonyl (Boc) is among the most common protecting groups for amines, amino acids, and other nitrogen compounds due to its chemical stability and ease to deprotection [22]. To save time and to avoid secondary or parallel reactions or losses of material during the isolation of certain amines, the reduction and protection steps are frequently performed in one-pot. However, there are only few reports in the literature for the direct conversion of azides to the corresponding *N*-Boc-amines, such as using phosphines [23,24], $Pd(OH)_2/C$ in ethanol [25], Fe/NH_4Cl in methanol under sonication [26], and Pd–C [27]. In recent years a number of heterogeneous catalysts are also reported for the direct conversion of azides to the corresponding *N*-Boc-amines [28,29]. These catalysts offer several advantages over their homogeneous counterparts with respect to recovery, recycling as well as minimization of undesired toxic wastes. Baralt and Holy reported reduction of nitrobenzene to aniline using polymer anchored anthranilic acid palladium complexes under high pressures of 500–800 psi at 70–100 °C [30]. Hydrogenation of mono and poly-nitro aromatics are realized with high yields by Pd/C catalyst via hydrogen transfer using cyclohexene in ethanol under reflux conditions [31]. Recently, Shi et al. have reported the reduction of nitroarenes over nickel–iron mixed oxide catalyst using hydrazine hydrate under reflux conditions while Huang et al. reported the same reaction using a platinum nanocatalyst [32,33]. Thus, high temperatures, pressures and longer reaction times accompany these methods of reduction of nitro compounds. But, there are few reports on the one-pot conversion of nitroarenes to the corresponding *N*-arylacetamides [34,35]. Of late, we have reported reductive acylation of nitroarenes by Fe^{3+} montmorillonite [36], and other reports are available in the literature on the reductive acylation of 3-nitro indoles [37], as well as 2- and 3-nitro pyrroles by Pd/C in methanol [38]. Recyclable heterogeneous catalysis is particularly attractive due to the ready separation of large quantities of products using small amounts of catalysts and less contamination of final products [39].

In an endeavor to design newer industrially feasible protocols for clean, efficient and selective synthesis of various industrially important organic amines utilizing mild and benign reductants, we have earlier reported the reduction of nitrobenzene by molecular hydrogen using heterogeneous nanopalladium and nanoplatinum catalysts [39,40]. Herein, we report a one-pot synthesis of anilides and *N*-Boc protected amines from the reduction of nitro and azido compounds with molecular hydrogen followed by the reaction with an acid anhydride to afford the corresponding products at ambient temperature with good to excellent yields using heterogeneous platinum(0) supported on zirconia [$Pt(0)/ZrO_2$] as a recyclable catalyst (Scheme 1).



Scheme 1. Reductive acylation of aromatic nitro compounds to amides and azides to N-Boc protected amines.

2. Experimental

2.1. General

Nitrobenzene was purchased from S. D. Fine Chemicals Ltd. Mumbai. ACME silica gel (100–200 mesh) was used for column chromatography and thin-layer chromatography was performed on Merck-precoated silica gel 60-F_{254} plates. All other substituted nitrobenzenes were purchased from Aldrich or Fluka and used as received. All the other solvents and chemicals were obtained from commercial sources and purified using standard methods. The particle size and external morphology of the samples were observed on a Philips TECNAI F12 FEI transmission electron microscope (TEM). NMR spectra were recorded on a Varian Gemini (200 MHz), Bruker Avance (300 MHz), Varian Unity (400 MHz) spectrometer using TMS as an internal standard in $CDCl_3$. Mass spectra were obtained at an ionization potential of 70 eV [scanned on VG 70-70H (micro mass)].

2.2. Preparation of the catalyst

The $Pt(0)/ZrO_2$ was prepared by the following procedure. Zirconium hydroxide was precipitated from $ZrOCl_2$ (Loba, L.R. grade) at constant pH 10 with the help of NH_4OH. The precipitate was aged at room temperature for 12 h, filtered and washed several times with deionized water until free from chloride ions, dried at 120 °C for 24 h and calcined at 500 °C in a flow of air. The ZrO_2 thus obtained showed a surface area of 105 $m^2\ g^{-1}$. To prepare Pt^{2+}/ZrO_2, 0.2708 g of H_2PtCl_6 was dissolved in 50 mL of distilled water, 5.0 g of calcined ZrO_2 added, then the beaker was placed on the hot plate stirred with a glass rod for several hours. Water was evaporated while on the hot plate, yielding the Pt^{2+}/ZrO_2 as a light yellow powder (5.2 g). The final catalyst $Pt(0)/ZrO_2$, a grey color solid, was obtained after hydrogenation at 523 K for 3 h under the hydrogen flow (30 mL min^{-1}) and used for the reductive acylation of nitro compounds and for the synthesis of N-Boc protected amines from azides at room temperature. The elemental analysis the Pt content in the catalyst was 0.102 mmol/g (Pt content: 2 wt%). TiO_2 (surface area: 200 $m^2\ g^{-1}$) was purchased from Fluka and similar procedure was followed to prepare $Pt(0)/TiO_2$. 1% Pt/C and 1% Pt/Al_2O_3 were purchased from Sigma–Aldrich and used for the reductive acylation of nitro compounds. The catalyst $Pt(0)/ZrO_2$ is well characterized by XRD, TEM, XPS, TPR, EDX analysis (see Supporting information, SI).

The solid used as support is zirconia, as evidenced from the XRD spectrum Fig. S1a, SI. After loading with Pt, an amorphous phase was observed by XRD (Fig. S1b, SI), after reduction the original pattern of zirconia was restored (Fig. S1c, SI). The XPS analysis of the unreduced Pt/ZrO_2 sample by XPS gave a spectrum containing a doublet at 73.6 (Pt $4f_{7/2}$) and 77 eV (Pt $4f_{5/2}$) (Fig. S2a, SI), characteristic of cationic Pt, while after reduction the presence of the doublet at 71.4 and 74.7 (Fig. S2b, SI) attributed to metallic platinum [41]. The TPR data shows the cationic platinum species converted to metallic platinum at 250 °C (Fig. S3, SI).

2.3. General procedure for the reductive acylation of nitro compounds

The catalyst [$Pt(0)/ZrO_2$] (0.015 g, 0.15 mol%) was suspended in methanol (2.0 mL) and a hydrogen balloon was fitted to the flask through a rubber septa. The suspended catalyst was stirred under hydrogen atmosphere for 10 min at room temperature and then a solution of nitro compound (1.0 mmol) dissolved in methanol

(2.0 mL) was added to the above stirred solution. The resultant solution was stirred under hydrogen atmosphere at room temperature for the specified period. The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of first step, the hydrogen balloon was removed and acetic anhydride was added (0.122 g, 1.2 mmol) using a syringe, to the same flask. The reaction mixture was stirred further at room temperature and the progress of the reaction monitored by TLC. After completion of the reaction, the crude mixture was centrifuged, ethyl acetate (10 mL) was added to the reaction mixture, then filtered the catalyst, and the remaining acetic anhydride and acetic acid produced during the reaction was neutralized with a saturated solution of sodium bicarbonate. The aqueous and organic layers were separated and the excess solvent was removed under reduced pressure. The crude reaction mixture was purified by using short-path column chromatography on silica gel. The resulting products were analyzed by ^{1}H NMR and mass spectrometric methods.

2.4. General procedure for synthesis of N-(tert-butoxycarbonyl)amines

In a typical experimental procedure, Pt(0)/ZrO_2 (20 mg, 0.2 mol%) was added to a mixture of organic azide (1.0 mmol), di-*tert*-butyl dicarbonate (436 mg, 2.0 mmol) in methanol (5 mL) at room temperature. The resultant solution was stirred under hydrogen atmosphere at room temperature for specified periods. The progress of the reaction was monitored by TLC and upon completion of the reaction, the catalyst was filtered, washed with ethyl acetate (20 mL) and the excess solvent was removed under reduced pressure, the crude material was purified by silica gel chromatography (60–120 mesh) to afford the corresponding *tert*-butoxycarbonyl amine.

3. Results and discussion

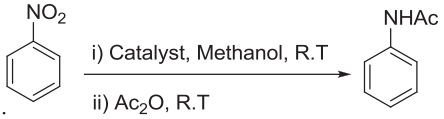
3.1. Screening of catalysts and solvents

In a quest for the best suited catalyst for the one-pot synthesis of organic amines, we have investigated the catalytic activities of a number of solid catalysts. The results are furnished in Table 1.

As can be seen in Table 1, among the different catalysts screened, Pt(0)/ZrO_2 catalyst showed the best result for the reductive acylation reaction using nitrobenzene as the typical substrate (Table 1, entry 5) and methanol as the solvent.

To find out the best catalytic system, along with the chosen catalyst, Pt(0)/ZrO_2, a range of solvents having varied physical and chemical properties and differing immensely in polarities have been investigated for the reaction among which methanol provided the best result (Table 2, entry 5; Table 3, entry 5). Ethanol on the other hand proved to be ineffective in providing the desired solvent effect in promoting the reaction (Table 2, entry 3), in spite of being a widely used proton donor solvent [42,43]. The reason for this cannot be predicted at this point. In THF, the reaction is very sluggish yielding barely 5% of the product (Table 2, entry 1). In toluene, the yield of the product is poor (Table 2, entry 4). Strickingly, DMF, which is widely used in high temperature hydrogenation also resulted in poor yields. The reason cannot be stated very certainly, but it may be due to the conflict between Lewis acidic character of the ZrO_2 and the Lewis basic character of the solvent. Thus it can be stated, in accordance to the observations reported by Li et al., Liu et al. and our group, that the reaction proceeds well without the addition of any base in the reaction mixture and utilizes merely the well dispersed Pt nanoparticles to mediate the reaction [40,42,43]. The reaction was found to proceed at room temperature in methanol in the presence of Pt(0)/ZrO_2 catalyst under hydrogen atmosphere followed by the addition of acetic anhydride in the next step in the same pot for the protection of the formed amine. This step is also well facilitated by the Lewis acidic nature of the catalyst and the proton donating solvent e.g. methanol follows a nucleophilic substitution process in which the electrophilic carbon centre formation for the subsequent attack of the amine is facilitated by the Lewis acidic support [44]. Therefore it can be summarized by stating that the bi-functional catalyst works successfully in the first step through the metal centre by binding the molecular hydrogen in the oxidative insertion step and then finally hydrogenating the nitro compounds and undergoing the subsequent reductive elimination step [45]. In the second step of this sequential reaction, the Lewis acidic support facilitates the reaction majorly by helping in the formation of the carbocation.

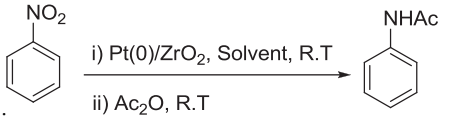
Table 1
Screening of various solid catalysts in the reductive acylation[a]



Entry	Catalyst	Time [h]	Yield [%][b]
1	ZrO_2	3.5	0
2	Pt/Al_2O_3	3.5	15
3	Pt/C	3.5	70
4	Pt(0)/TiO_2	3.5	75
5	Pt(0)/ZrO_2	3.5	93

[a] *Reaction conditions*: nitrobenzene (1 mmol), catalyst (0.15 mol%), methanol (3 mL), H_2 balloon (1 atm), Ac_2O (1.5 mmol), room temperature.
[b] Conversion determined by GC.

Table 2
Screening of various solvents in the reductive acylation[a]



Entry	Solvent	Time [h]	Yield [%][b]
1	THF	3.5	<5
2	DMF	3.5	<5
3	Ethanol	3.5	<5
4	Toluene	3.5	12
5	Methanol	3.5	93

[a] *Reaction conditions*: nitrobenzene (1 mmol), Pt(0)/ZrO_2 (0.15 mol%), solvent (3 mL), H_2 balloon (1 atm), Ac_2O (1.5 mmol), room temperature.
[b] Conversion determined by GC.

3.2. Scope of the reaction

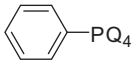
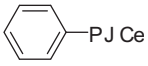
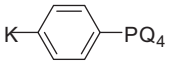
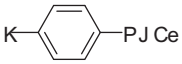
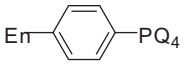
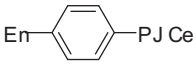
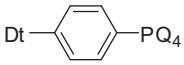
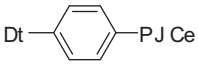
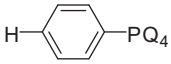
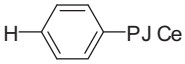
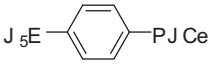
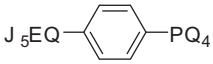
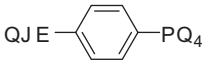
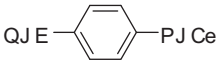
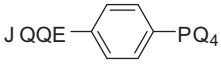
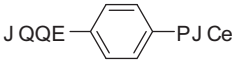
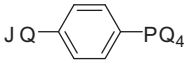
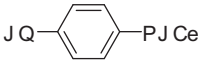
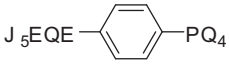
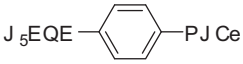
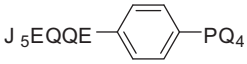
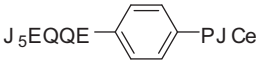
After optimizing the reaction conditions, the scope of the reaction was extended to different aromatic nitro compounds as summarized in Table 4. The halo substituted nitrobenzenes were converted into the corresponding halo-anilines with high yields without any concomitant side reaction forming the

Table 3
Solvent screening for the synthesis of N-Boc amines from organic azides.[a]

Entry	Solvent	Time [h]	Yield [%][b]
1	DMF	8	Traces
2	Ethanol	8	Traces
3	THF	8	<5
4	Toluene	8	18
5	Methanol	8	82

[a] *Reaction conditions*: benzyl azide (1 mmol), $(Boc)_2O$ (1.0 mmol), Pt(0)/ZrO_2 catalyst (0.2 mol%), solvent (4.0 mL), H_2 balloon (1 atm.), room temperature.
[b] Isolated yields after column chromatography.

Table 4
Reductive acylation of various nitroarenes catalyzed by $Pt(0)/ZrO_2$.[a]

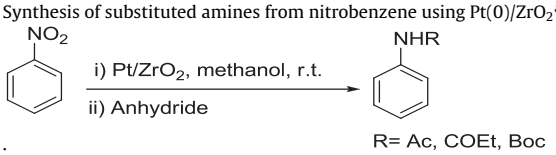
Entry	$ArNO_2$	Amide	Time[b]	Time[c]	Yield (%)[d]
1			3	3.5	93,92,91,91[e]
2			3.5	4	87
3			3.5	4	92
4			3.5	5	91
5			3	3.5	92
6			4	4.5	92
7			4	4.5	88
8			4	4.5	87
9			4	4.5	89
10			3.5	4	93
11			4	5	75
12			4	5	68

[a] *Reaction conditions*: nitroarene (1.0 mmol), $Pt(0)/ZrO_2$ catalyst (0.15 mol%), methanol (4.0 mL), H_2 balloon (1 atm), Ac_2O (1.5 mmol), room temperature.
[b] Time taken for first step (reduction of nitroarene to aminoarene).
[c] Total reaction time.
[d] Isolated yields after column chromatography.
[e] Isolated yield in fourth cycle.

dehalogenated product. Even iodo-aniline was obtained with 87% yield. The catalyst $Pt(0)/ZrO_2$ is highly chemoselective for this purpose. Nitroarenes without substituent groups produced higher yield in shorter reaction time (93%, 3.5 h, Table 4, entry 1). Nitroarenes containing halo substitution at *para* position such as iodo, chloro, bromo and fluoro also smoothly resulted high yields of the corresponding products (89%, 92%, 91%, 92%, respectively, Table 4, entries 2–5) in 3–3.5 h. Nitroarenes containing 4-methyl and 4-methoxy groups afforded corresponding anilides with high yields (entries 6–7). It is worth mentioning here that the critical and useful functionalities in organic synthesis such as aldehyde (entry 8), acid (entry 9), phenolic (entry 10), keto (entry 11), and ester (entry 12) were well tolerated without any side reactions under the present reaction conditions.

We have studied the applicability of various anhydrides as protecting agents by *in situ* generated amine group using nitrobenzene as the model substrate and the results are presented in Table 5. As can be seen from this table, all the anhydrides reacted cleanly and gave amides in good to excellent yields. However, acetic acid showed poor activity under these reaction conditions (Table 5, entry 1). The reason for this may be attributed to the formation of a poor leaving group, OH^- during the course of substitution reaction. The strong leaving groups on the other hand formed in case of Boc, etc. renders the reaction more facile and therefore facilitates the formation of the product in greater yields. In case of *p*-nitrophenol, *p*-aminophenol formed in the first step is cleanly converted in the second step to the corresponding N protected amine (Table 4, entry 10) without any competitive side reaction to form the O protected product. Thus the catalyst is highly selective in facilitating N-protection where reactive substituents are present in the initial nitroarene.We have studied the scope of this reaction with various aliphatic and aromatic azides using our optimized reaction condi-

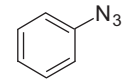
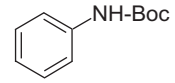
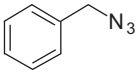
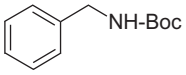
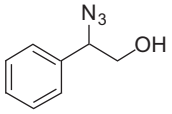
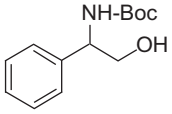
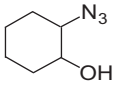
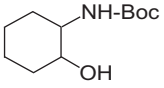
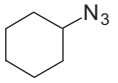
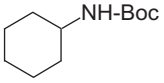
Table 5
Synthesis of substituted amines from nitrobenzene using $Pt(0)/ZrO_2$[a]



Entry	Acylating agent	Time [h]	Yield [%][b]
1	Acetic acid	3.5	40
2	Acetic anhydride	3.5	93
3	$(Boc)_2O$	3.5	79
4	Propionic anhydride	3.5	82

[a] *Reaction conditions*: nitroarene (1.0 mmol), $Pt(0)/ZrO_2$ catalyst (0.15 mol%), methanol (4.0 mL), H_2 balloon (1 atm), Anhydride (1.5 mmol), room temperature.
[b] Isolated yields after column chromatography.

Table 6
Synthesis of various N-Boc amines from azides using $Pt(0)/ZrO_2$.[a]

Entry	Substrate	Prduct	Time [h]	Yield [%][b]
1			7	86
2			8	82
3			8	81
4			10	79
5			10	82

[a] *Reaction conditions*: organic azide (1 mmol), Boc_2O (2 mmol), $Pt(0)/ZrO_2$ (0.2 mol%), methanol (5 mL), H_2 atmosphere, room temperature.
[b] Isolated yields.

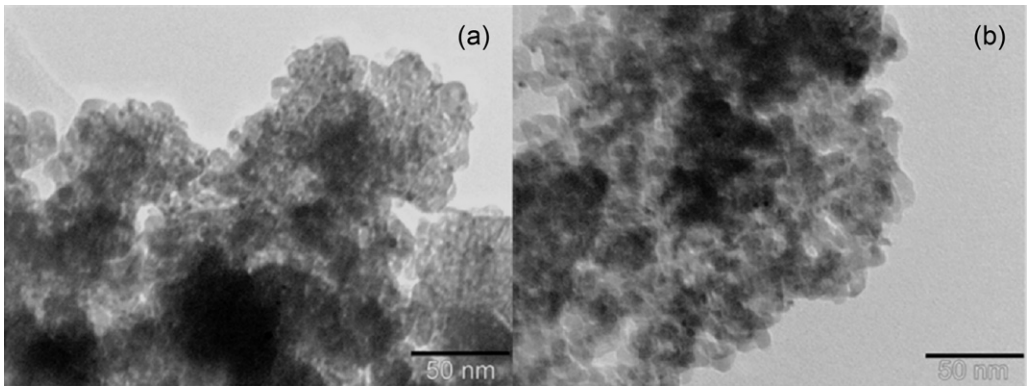


Fig. 1. TEM images of fresh catalyst (a) and used catalyst (b).

tions. As shown in Table 6, all the substrates produced good yields of the product. Aromatic, benzylic azides, and aliphatic azido alcohols underwent clean reductions and sequential protection resulting in good yields of the products under the reaction conditions followed.

3.3. Recycling of the catalyst

After completion of the reaction, the catalyst was separated by centrifugation and washed with methanol followed by acetone and then dried in an oven at 120 °C. The catalyst was then kept stored in a vacuum desiccator until the next run. The catalyst was used for four cycles successively in the reaction of nitrobenzene and acetic anhydride (model substrate) to yield the product with minimum loss of activity (Table 4, entry 1). This proves that the catalyst is efficient and stable for this reaction.

The TEM image of the used catalyst Fig. 1b is similar to the fresh catalyst Fig. 1a and therefore it could be concluded that the morphology of the catalyst is well maintained after several recycles. A few agglomerated spots can be noticed in some places which are responsible for the slight deactivation of the catalyst by the formation of copious amounts of acids as a byproduct from the protection of the amines.

Therefore, a minor reduction in the yield of the product is seen (91% in fourth cycle vs 93% in the first cycle, see Table 4, entry 1) in the subsequent cycles. The presence of acid on the catalyst surface may be responsible for hindering the active catalytic sites from coming into contact with the substrate. No quantifiable amount of leached Pt was detected in the filtrate by AAS analysis.

The effect of the strongly Lewis acidic zirconia as demonstrated in the formation of the *N*-acyl and *N*-Boc-protected amine derivatives, coupled with the absence of any leached metal in the filtrate suggests that the catalytic process is truly heterogeneous and occurs on the solid surface [46,47].

4. Conclusion

In summary, we report a convenient, simple, clean and efficient protocol for the reduction of aromatic nitro compounds, organic azides to amines followed by protection of amines with acetic anhydride or di-*tert*-butyl dicarbonate [$(Boc)_2O$] to give the corresponding *N*-acyl or *N*-(*tert*-butoxycarbonyl)amines using $Pt(0)/ZrO_2$ catalyst. The catalyst can be conveniently recovered and reused several times without any practical loss of activity. This methodology is environment friendly, utilizing only molecular hydrogen as the reductant. The reaction is smoothly conducted under mild conditions affording good yields of the products. These above mentioned advantages make this protocol a cost effective and therefore, industrially attractive one in the age of stringent environmental legislations.

Acknowledgement

R. Sudarshan Reddy, K. Srinivas and R. Chakravarti thank the Council of Scientific and Industrial Research, India for the award of a research fellowship.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.12.002.

References

[1] E. Plattner, G. Seifert, T. Somlo, Eur. Patent 0269563 (1998).
[2] M. Pesson, Ger Offen. 2 (1979) 840910–840920.
[3] K. Sugimoto, K. Yamaguchi, Y. Tanabe, M. Yamazaki, M. T. Yamaguchi, Jpn. Patent 61,189,250 (1986).
[4] C.R. Worthing, The Pesticide Manual (A World Compendium), 8th ed., 1987, p. 599.
[5] E.F.V. Scriven, K. Turnbull, Chem. Rev. 88 (1988) 297–368.
[6] R.S. Downing, P.J. Kunkeler, H.V. Bekkum, Catal. Today 37 (1997) 121–136.
[7] A.W. Dawes, J. Werner, Kirk Othemer, Encyclopedia of Chemical Technology, vol. II, 4th ed., Wiley, New York, 1992, p. 355.
[8] Y. Watanabe, K. Tsuji, Y.T. Kondo, R. Takeuchi, J. Org. Chem. 49 (1984) 4451–4456.
[9] S.Y. Lee, C.W. Lee, D.Y. Oh, J. Org. Chem. 64 (1999) 7017–7022.
[10] A.H. Beckett, R.W. Daisley, J. Walker, Tetrahedron 24 (1968) 6093–6109.
[11] D.C. Owsley, J.J. Bloomfield, Synthesis (1977) 118–120.
[12] T.L. Ho, J. Org. Chem. 42 (1977) 3755.
[13] F.C. Lizana, S.G. Quero, M.A. Keane, Catal. Commun. 9 (2008) 475–481.
[14] R. Adams, F.L. Cohen, Org. Synth. Coll. 1 (1932) 240–241.
[15] G.D. Mendenhall, P.A.S. Smith, Org. Syn. Coll. 5 (1973) 829–833.
[16] T. Tsukinoki, H. Tsuzuki, Green Chem. 3 (2001) 37–38.
[17] L. Wang, L. Zhou, Y. Zhang, Synlett (1999) 1065–1066.
[18] M. Boronat, P. Concepcion, A. Corma, S. Gonzalez, F. Illas, R. Serna, J. Am. Chem. Soc. 129 (2007) 16230–16237.
[19] A. Grirane, A. Corma, H. Garcia, Science 322 (2008) 1661–1664.
[20] A. Corma, P. Serna, Science 313 (2006) 332–334.
[21] J.M. Landesberg, L. Katz, C. Olsen, J. Org. Chem. 37 (1972) 930–936.
[22] T.W. Greene, P.G.M. Wuts, Protective Groups in Organic Synthesis, Wiley, New York, 1991.
[23] X. Ariza, F. Urpi, J. Vilarrasa, Tetrahedron Lett. 40 (1999) 7515–7517.
[24] C.A.M. Afonso, Tetrahedron Lett. 36 (1995) 8857–8858.
[25] H. Kotsuki, T. Ohishi, T. Araki, Tetrahedron Lett. 38 (1997) 2129–2132.
[26] S. Chandrasekhar, C. Narsihmulu, Tetrahedron Lett. 41 (2000) 7969–7972.
[27] S. Saito, H. Nakajima, M. Inaba, T. Moriwake, Tetrahedron Lett. 30 (1989) 837–838.
[28] R.M. Magadalene, E.G. Leelamani, N.M.N. Gowda, J. Mol. Catal. A: Chem. 223 (2004) 17–20.
[29] H.U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner, M. Studer, Adv. Synth. Catal. 345 (2003) 103–151.
[30] E. Baralt, N. Holy, J. Org. Chem. 49 (1984) 2626–2627.
[31] I.D. Entwistle, R.A.W. Johnsone, T.J. Povali, J. Chem. Soc., Perkin Trans. 1 (1975) 1300–1301.
[32] Q. Shi, R. Lu, X. Fu, D. Zhao, Adv. Synth. Catal. 349 (2007) 1877–1881.
[33] K. Xu, Y. Zhang, X. Chen, L. Huang, R. Zhang, Adv. Synth. Catal. 353 (2011) 1260–1264.
[34] R.N. Baruah, Indian J. Chem. Sec. B: Org. Med. Chem. 39 (2000) 300–303.
[35] B.H. Kim, Y.M. Jun, S.W. Suh, W. Baik, B.M. Lee, J. Chem. Res. (S) (1998) 46–47.
[36] M.L. Kantam, K.V.S. Ranganath, M. Sateesh, B. Sreedhar, B.M. Choudary, J. Mol. Catal. A: Chem. 244 (2006) 213–216.
[37] S. Roy, G.W. Gribble, Tetrahedron Lett. 49 (2008) 1531–1533.
[38] G.L. Fu, G.W. Gribble, Tetrahedron Lett. 48 (2007) 9155–9158.
[39] M.L. Kantam, R. Chakravarti, V.R. Chintareddy, B. Sreedhar, S. Bhargava, Adv Synth. Catal. 350 (2008) 2544–2550.
[40] A. Deshpande, F. Figueras, M.L. Kantam, K.J. Ratnam, R. Sudarshan Reddy, N.S. Sekhar, J. Catal. 275 (2010) 250–256.
[41] F.A. de Bruijn, G.B. Marin, J.W. Niemantsverdriet, W.H.M. Visscher, J.A.R. Van Veen, Surf. Interface Anal. 19 (1992) 537–542.
[42] H. Liu, G. Lu, Y. Guo, Y. Wang, Y. Guo, J. Colloid Interface Sci. 346 (2010) 486–493.
[43] C.-H. Li, Z.-X. Yu, K.-F. Yao, S.-F. Ji, J. Liang, J. Mol. Catal. A: Chem. 226 (2005) 101–105.
[44] G.V.M. Sharma, J.J. Reddy, P.S. Lakshmi, P.R. Krishna, Tetrahedron Lett. 45 (2004) 6963–6965.
[45] P. Serna, M. Lopez-Haro, J.J. Calvino, A. Corma, J. Catal. 263 (2009) 328–334.
[46] B.M. Choudary, S. Madhi, S. Chowdari, M.L. Kantam, B. Sreedhar, J. Am. Chem. Soc. 124 (2002) 14127–14136.
[47] K. Mori, T. Hara, M. Oshiba, T. Mizugaki, K. Ebitani, K. Kaneda, New J. Chem. 29 (2005) 1174–1181.