Catal Lett (2008) 123:264–268
DOI 10.1007/s10562-008-9417-5

Swift and Selective Reduction of Nitroaromatics to Aromatic Amines with Ni–Boride–Silica Catalysts System at Low Temperature

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Received: 29 November 2007 / Accepted: 25 January 2008 / Published online: 13 February 2008

Abstract Various nitroaromatics are successfully reduced to amines with 100% conversion and selectivity in methanol at low temperature ($\approx$5 °C), by using versatile system of 5% Ni–SiO_2 catalyst and $NaBH_4$ and in situ generation of Ni boride. The catalytic efficiency of Ni loading (5%, 10% and 15%) with silica or titania as support materials is investigated for reduction of nitrobenzene. The Ni–titania/$NaBH_4$ system recorded lower conversion and selectivity. The IR studies indicate that silica support does not have free –OH group on its surface. Thus the nickel boride is anchored to the silica to facilitate the catalytic process.

Keywords Impregnation · Ni–SiO_2 catalysts · $NaBH_4$ · Nitrobenzene · Reduction

1 Introduction

Aromatic amines are important class of compounds, which are used industrially as intermediates for the manufacture of dye stuffs, pharma, agricultural chemicals, photographic chemicals, additives, surfactants textile auxillaries, chelating agents, and polymers [1–5]. These are generally prepared by reduction of nitroarenes, mostly aromatic amines with metals such as Pd or Raney Nickel [6–10]. The main limitations of earlier reported work were the necessity of high temperatures, >50 °C and high H_2 pressures, >5 bar for catalytic activity of Pd, Pt and Ni. Further, the selection of metal and its support, the hydrogen source and operational simplicity, which are the important parameters for effective transformations are restricted.

A variety of metal catalysts were also reported as homogeneous catalysts for the reduction, but these procedures generally generate vast waste products [11]. With homogeneous complexes such as iron porphyrin, the selectivity is hindered by the formation of different intermediates. For most of these reactions drastic conditions such as high temperature and pressure are demanded [11–13].

Due to inherent advantages such as easy recovery and reusability, various heterogeneous catalysts were also explored for these reactions. The reduction of nitro compounds to the corresponding amines, using triethyl ammonium formate and palladium on charcoal as catalyst at reflux temperature was reported [14]. High temperatures, pressures and long reaction times preclude the wide use of such catalysts [15]. To mention a few, Kantam et al. [16] reported good conversions at room temperature in reduction of nitro aromatics to their aromatic amines with Pd–MCM(II) catalysts. Han and Jang [17] reported the reduction of nitro aromatics using montmorillonite clay (K-10) with anhydrous hydrazine (1:6 molar ratio) in ethanol under reflux conditions in nitrogen atmosphere for 2 h. Carlini et al. [18] investigated many mono [19–21] and diphosphine [22–26] modified complexes, such as diphsophine polymer-bound palladium complexes, which can be prepared in few steps, as catalysts, but gave low conversions. Sudalai et al [27] reported hydrogen transfer reaction of nitro aromatics on Ni–zirconia catalysts at reflux temperature, which required the use of stoichiometric amounts of base to enhance the reaction. With Raney Nickel [28] which is pyrophoric and can reduce –NO_2, –C=O, –C–X etc., controlling the reduction rates is difficult

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under extreme conditions. Sudalai et al [27] have also reported the use of Zirconia modified with Cr, Mn, Fe, Co and Ni plus additives as catalyst for NO_2 reduction under reflux conditions. Acosta et al. [29] reported nickel supported on different supports like rehydroxylated perlite, zeolite or alumina for reduction of nitrobenzene, which required elaborate procedure to prepare the catalysts.

Since 1980, the amorphous metal–metalloid alloys received special attention for its excellent catalytic selectivity and activity properties. In recent years, nickel based catalysts are attracting much attention for use in various industrially important reactions such as hydrodesulphurization, reduction of nitriles, etc. The Ni and Co containing amorphous alloys have properties that are of interest in catalysis, such as the presence of a large number of surface coordinating unsaturated sites and the lack of crystal defects [30].

The main question this manuscript addresses is avoiding the high temperature and high hydrogen pressure conditions, to minimize thermal risks during production. The second question addressed is the achievement of high conversion and selectivity using mild reducing agent, to produce the desired chemical reliability in the required quality. Additional features looked for are the operational simplicity, safe and energy efficient procedure and scope to recover the investment and developmental costs in a reasonable time. Thus, the objective of this work is to study the capability of Ni loaded support catalysts, silica and titania for the $NaBH_4$ facilitated selective reduction of nitroaromatics to corresponding amines at low temperatures, the effect of the Ni loading on the process and to evaluate catalytic aptitude of the system for a potential use in industrial process.

2 Experimental

2.1 Materials

All chemicals were synthesis grade reagents available from (Merck).

2.2 Preparation of Catalysts

The catalysts were prepared by impregnation method by dissolving nickel nitrate nona-hydrate (2.5 g) in distilled water (20.0 ml) and adding to it silica gel or titania (5.0 g) and stirring for 2 h using a magnetic stirrer at room temperature (20 ± 1°C) and ageing at room temperature for overnight. The excess water is removed by heating the mixture on water bath and using a rota-vapor under mild vaccum to evaporate the water. The catalyst material is dried in an oven at 100 °C for 12 h [29].

2.3 Typical Reduction Procedure

Nitrobenzene (2.0 mmol) with 10.0 ml methanol solvent and addition of catalyst (400 mg) followed with slow addition of sodium borohydride (400 mg) at (0–5 °C). In case of silica supported catalysts, sodium borohydride was added over 5 min period. For titania, as the formation of nickel boride was slower borohydride addition took about 10 min. The reaction mixture is magnetically stirred continuously. The reaction progress is monitored by GC, normally till all the starting material is consumed. Then the reaction mixture is quenched with di-ionized water and extracted with ethyl acetate. The organic layer is dried on sodium sulfate and solvent is evaporated on Rota-vapor to give crude product of aniline, which is then subjected to column chromatography to afford pure aniline product 0.93 g is obtained. The final product is characterized by H^1- and C^{13}-NMR (400 MHz Bruker Instrument). GC MS samples were run on Agilent 6890 GC/5973, MS Column: J&W HP5-MS. The samples were characterized on GC System (Agilent Technologies, GC 6820) equipped with flame ionization detector (FID) and a carbovax OV1-capillary column and compared with standard samples. In the reactions, where the conversion and selectivities are 100%, the carbon balance of the product is estimated and found fully accounted for.

3 Results and Discussion

The reduction of nitrobenzene to aniline with 5% $Ni–SiO_2$ (uncalcined)–$NaBH_4$ at (0–5 °C) was fast and the reaction got completed in 10 min. It gave 100% conversion with a single product. This positive result lead us to look at the activity of 2%, 10% and 15% loaded $NiSiO_2$ under similar conditions. The results obtained are summarized in the Table 1. For the operational convenience, for most of the reactions, it is attempted to monitor the time required for 100% conversion, where the starting material is completely consumed rather than the half-reaction time. With 2% Ni loading the completion of reaction took 15 min and 10% Ni loaded took 20 min for 100% conversion, while with 15% Ni loaded catalyst, even after 25 min duration, conversion was only 90%. All had 100% selectivity resulting in one product. Thus, the order of reactivity of Ni catalyst is 2% $Ni–SiO_2 < 5\%$ $Ni–SiO_2 > 10\%$ $Ni–SiO_2 > 15\%$ $Ni–SiO_2$. Identifying that 5% $Ni–SiO_2$ as the ideal catalyst and optimum condition, all the reactions were studied in duplicate and the results were reproducible.

These interesting studies lead us to investigate the activity of Ni catalyst on titania support for the title reaction under otherwise similar conditions. 5% Ni loaded titania gave 100% conversion and 90% selectivity in

Table 1 Selective reduction of nitrobenzene to aniline in methanol
Nitrobenzene = 2.0 mmol, catalyst = 400 mg, sodium borohydride = 400 mg

Support	Ni loading (%)	Reaction time (min)	Conversion (%)	Selectivity (%)
SiO_2*	2	15	100	100
	5	10	100	100
	10	20	100	100
	15	25	90	100
TiO_2**	5	35	100	90
	10	45	100	90
	15	60	75	100

* $NaBH_4$ addition duration 5 min.; ** $NaBH_4$ addition duration 10 min

Mean of duplicate runs

35 min, while the 10% Ni–TiO_2 took 45 min for 90% conversion and 90% selectivity (Table). With 15% Ni loaded titania, even after 60 min duration only 75% conversion could be achieved. Interestingly, the selectivity for the titania supported system too was 100%. In order to check the activity of the catalysts, blank reactions without $NaBH_4$ were conducted under otherwise similar conditions either with 5% Ni–SiO_2 or bulk NiO and in both cases no reaction occurred. When $SiO_2/NaBH_4$ reactions were conducted under the similar conditions a 60% conversion of nitrocyclohexane was observed, while with $NaBH_4$ alone, only 50% nitrocyclohexane was formed. This confirms that nickel boride on silica is effective system for selective reduction of nitroaromatics to aromatic amines at low temperature. During the course of our studies on in situ generated nickel boride on silica, it was observed that the aromatic ring of nitrobenzene was intact under reaction conditions; unlike with Raney Ni as catalyst, the reaction could proceed to aromatic ring hydrogenation [28]. With all Ni silica catalysts, when sodium borohydride was added over 5 min duration, the reaction turned instantly black, indicating the generation of Ni boride accompanied by hydrogen evolution. This is possibly due to nickel particles adsorbed on the surface of silica support that facilitate the formation of Ni boride. When the reaction mixture is filtered there was no leaching of the metal in the filtrate, which indicates that the nickel boride is well bound to the silica surface. Ni–boride–silica is non-pyrophoric in nature relative to Raney Nickel [28]. The scope of hydrazine hydrate in place of $NaBH_4$, as hydrogen donor for reduction of nitrobenzene was investigated with 5% $NiSiO_2$ catalyst in methanol. After refluxing the reaction mixture for 17 h, it gave only 50% conversion, but with 100% selectivity. Other hydrogen transfer agents, 2-propanol or ethanol even under reflux condition for 17 h with 5% Ni–silica, gave no reduction of nitrobenzene. It appears that the rate of hydrogenation depends upon the rate of $NaBH_4$ decomposition to form Ni boride and H_2.

The use of nickel-based catalysts, the impregnation with nickel nitrate solutions, is the most extensively used method to prepare them. In order to obtain the same active species, the influence of the operation parameters are important during the impregnation process such as order of reactants, speed of agitation, time of aging [31]. The presence of weak interaction between metal and support is due to the little impregnation. Part of electrons can be transferred from boron to nickel and the metallic nickel becomes electron-rich and the boron electron-deficient [32]. Thus, this greatly enhances the catalyst activity, and selectivity for the product. The nitrogen atom of nitro aromatics can also transfer electrons to the oxygen atom. The plausible adsorption mechanisms could be the electronic interaction between the N=O groups in nitro aromatics and the metallic active sites. The forward donation of the electrons from the highest occupied molecular orbital (HOMO) of the N=O bonding, i.e., from the $\pi_{N=O}$ to the dz^2 and s orbits of the metallic Ni atom, and a back donation from the $dx^2 - y^2$ orbit of the metallic Ni atom to the lowest unoccupied molecular orbital (LUMO), i.e., $\pi^*_{N=O}$. As $\pi^*_{N=O}$ is an anti-bonding orbit, the increased back electrons donation to the $\pi^*_{N=O,}$ which resulted from the high electron density on the Ni active sites, can also activate the N=O bond and promote the hydrogenation [32].

In the reduction reactions the activity of the catalysts is attributed to the presence of Ni uniformly distributed on the surface of the silica. All the results and analytical data identify that the Ni in association with silica is the active species and major contributor to maximize the activation of sodium borohydride to form nickel boride on silica support to transfer hydrogen. The observed fast generation of nickel boride on silica compared to titania support, and noticeable lower activity Ni–titania reinforces the above inference. The low metallic surface of nickel on the silica support encourages the nickel oxide crystallized formation. Practically no reactivity with 15% Ni loaded material is possibly due to the formation of nickel basic sites. The presence of weak interaction between metal–support due to multi-layer nickel on the support or the formation of the thick Ni particles. Thus, it contributed to the decrease of the catalytic activity. A similar observation was reported in literature, while studying the oxidation of alcohols using Ni loaded hydrotalcites as catalysts in presence of oxygen [30].

The selective reduction of nitro compounds is an interesting area of research, particularly when other potentially reducible moieties are present in the molecule. Nitro group

Table 2 Selective reduction of nitro aromatics to aromatic amines in methanol with 5% Ni–Silica catalysts #. Substrate = 2.0 mmol, catalyst = 400 mg, sodium borohydride = 400 mg

S. No	Substrate	Product	Time (min)	Conv (%)	Sel (%)
1.	Nitrobenzene	Aniline	10	100	100
2.	*p*-Nitrophenol	*p*-Aminophenol	15	100	100
3.	3-Nitrophenol	3-Aminophenol	15	100	100
4.	*p*-Nitroaniline	*p*-Phenylenediamine	10	95	100
5.	*p*-Nitroacetanilide	*p*-Aminoacetanilide	10	100	100
6.	*p*-Nitrotoluene	*p*-Toulidine	10	100	100
7.	*o*-Nitrotoluene	*o*-Toulidine	15	75	100
8.	p-Nitrobenzyl alcohol	*p*-Aminobenzyl alcohol	15	100	100
9.	*o*-Nitrophenol	*o*-Aminophenol	20	75	100
10.	*p*-Nitro-4-phenyl-benzyl pyridine	*p*-Amin-4-phenyl-benzyl pyridine	20	100	100

attached to the aromatic ring can withdraw electrons inductively compared to other reducible groups. The presence of an electron-releasing group such as hydroxyl group will retard the reduction of nitro compound. Hence, *p*-nitrophenol and 3-nitrophenol selective reduction to corresponding amines is more challenging. *p*-Aminophenol is the intermediate for the paracetamol synthesis [4]. Using an appropriate catalyst that facilitates the adsorption of nitrobenzene will enhance the efficiency of conversion and selectivity of the reduction reaction. The rate of reduction is decided by the rate of initial adsorption of the substrate on the catalyst surface. The efficiency of the proposed catalyst system for reduction of various substrates was also investigated. Table 2 summarizes the results obtained using 5% Ni–Silica/$NaBH_4$ system and methanol as solvent. A examination of the data indicates that *p*-nitoraniline to phenylenediamine in 95% conv, *p*-nitroacetamide to *p*-nitro acetanilide, *p*-nitro toluene, to *p*-amino toluene, *o*-nitro toluene to *o*-amino toluene in 75% conv, *p*-nitro benzyl alcohol to *p*-amino benzyl alcohol, 4-nitro 4-phenyl benzyl pyridine to 4-amino 4-phenyl benzyl pyridine which are reduced to the corresponding aromatic amines in 100% conv and selectivity is obtained.

3.1 Catalysts Characterization

5% Ni–silica catalysts were characterized by BET surface area, XRD and IR techniques.

3.2 XRD Characterization of 5% Ni–Silica

The XRD spectra (Phillip-PW 1830XRD diffraction spectrometer) showed characteristic diffraction lines of the nickel phase and support, and no mixed nickel oxide support phases were identified. The pattern for the supports was that of crystallized materials with the well-defined broad diffraction lines bands of amorphous SiO_2 support around $2\theta = 45$.

3.3 BET Data for 5% Ni Silica

The specific area i.e. the BET surface area of the catalysts is 180 mg^{-1}. During the impregnation stage of the preparation, surface hydroxyl groups of the support where consumed by reaction with the active phase precursor.

3.4 The FT-IR Spectra of 5% Ni Silica

The examination of IR spectra (Perkin Elmer FT-IR Spectrometer) of 5% and 10 % $NiSiO_2$ fresh catalysts shows that the band at 1,100 cm^{-1} (asymmetrical Si–O–Si) is very perceptive to formation of silicates [22]. SiO_2 does not have free hydroxyl group on the surface, this confirms that nickel boride is formed in situ during the reaction. In the IR results of 5% Ni–SiO_2, the strong and intense absorption band between 1,078 and 1,050 cm^{-1}, shows the presence of Si–O–Ni bonds [22]. Silica do not have free OH group on the surface these results confirms that the nickel boride obtained probably anchored to the support. This attributes to the Ni active species in association with silica for the activation of sodium borohydride with the evolution of hydrogen with immediate formation nickel boride species. These results conclusively demonstrate that 5% Ni–silica catalyst is ideally suited for selective nickel boride silica initiated reduction of nitro aromatic's to aromatic amine's with good conversion and high selectivity.

4 Conclusions

This study confirms that nickel borohydride silica system is superior to the other hydrogen transfer systems for selective reduction of nitro aromatics. Nickel boride generated in situ by the decomposition sodium borohydride on nickel silica reduced various nitro aromatics to aromatic amines with good conversitons and selectivity under mild reaction conditions in short duration of 10–15 min (Table 2). In most cases 100% conversions were achieved. This system applies even to hydroxyl substituted nitro compounds. It is a robust system with no need for any specialized facilities. The catalyst can be loaded with out pre-reduction. Further, this process is economically viable and can be upgraded to large-scale reactions. This forms a new alternative route at low temperature, which excludes harsh reaction conditions and use of additives.

Acknowledgments Authors thank the National Research Foundation, Pretoria and the University of KwaZulu-Natal for financial support of this research.

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