



Rapid and selective reduction of aldehydes, ketones, phenol, and alkenes with Ni–boride–silica catalysts system at low temperature

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ABSTRACT

A superior process for reduction a range of 17 aliphatic and aromatic functional groups with 100% conversion and selectivity is achieved with 5% Ni loaded on SiO₂ support as catalyst and NaBH₄, by *in situ* generation of Ni–boride in methanol, in short reaction duration (5 min) at low temperature ($\approx 0^\circ\text{C}$). Seventeen, substituted aromatics with functional groups C=O, C–X, and C=C were converted to their respective products with 100% conversion and 100% selectivity in 5 min. Phenol is transformed to cyclohexanol with 100% selectivity, but with 20% conversion efficiency.

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1. Introduction

Aromatic compounds, with preferred functional groups are key in chemical industries, as they are intermediates for the manufacture of dye stuffs, pharmaceutical, agricultural and photographic chemicals, additives, surfactants textile auxiliaries, chelating agents, and polymers [1–3]. Aromatic alcohols are generally prepared by reduction of aromatic aldehydes, mostly by reduction with metals such as Raney Nickel [4] and Al₂O₃–NaBH₄ [5,6] or calcined Ni–Al hydrotalcite [7]. A wide variety of homogeneous and heterogeneous catalytic systems such as Pt, NiO, Ru, Rh, Au, Ir, and Co [8–14] in combination with different hydrogen donors have been employed to selectively reduce major functional groups attached to aliphatic and aromatic structures [15]. However, it has been observed that controlling the reduction rates is quite difficult with the homogeneous catalysts [16].

The main limitations of earlier reports were the need for high temperatures (>50 °C) and high H₂ pressures (>5 bar) for catalytic activity of metals such as Pd, Pt and Ni [17]. The selection of metal and its support, hydrogen source and operational simplicity are the important parameters for effective transformations. Kantam et al. reported that reduction of nitro, and alkyl aromatics with Pd(II)–MCM-41 catalysts gave aromatic amines, and aromatics in good conversions, but reactions took longer duration of time [18,19].

Phase transfer catalysts with NaBH₄ reported is take more time for acetophenone, benzophenone, cyclohexanone, and cyclopentanone formations [20]. Sudalai and co-workers [21] reported the use of zirconia modified with Cr, Mn, Fe, Co and Ni with additives under reflux conditions for NO₂ reduction, but it leads to byproducts due to difficulty in controlling the reduction rates [22]. The use of heterogeneous catalysts offers several advantages over the homogeneous systems, such as ease of recovery, recycling and enhanced stability. Over the decades Raney Nickel catalyst has been extensively used in combination with hydrazine hydrate or propan-2-ol as a hydrogen source for reductions. Raney Nickel [22] is pyrophoric and does not show any selectivity towards functional groups such as C–X, C=O, C=C, and NO₂, reducing them all. It has been observed that the use of Raney Ni for the reduction of aromatic ketones leads to reduction of alcohols quite easily at the benzylic positions [21]. For the past two decades, the amorphous metal–metalloid alloys received special attention for their excellent catalytic selectivity and activity properties. Among the materials used are silica and titania as supports because of its chemical inertia and the feasibility for controlling the surface by means of appropriate transformations [23,24]. Use of *in situ* generated Ni–boride as reductant for reduction of nitriles has been reported by Caddick et al. [25]. Earlier, we communicated on the selective and swift reduction of nitro aromatics to aromatic amines with Ni–boride–silica catalysts system at low temperature [26]. The main objective of this work is to study the capability of Ni loaded support catalysts, silica and titania for the NaBH₄ facilitated selective reduction of aldehyde and ketones to aromatic alcohols and other functional moieties

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such as toluene, styrene, and phenol to their respective products which leads to evaluate its catalytic aptitude for a potential use as an 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 non-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 ($20 \pm 1^\circ\text{C}$) 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 vacuum to evaporate the water. The catalyst material is dried in an oven at 100°C for 12 h [26].

2.3. Typical reduction procedure

Anisaldehyde (2.0 mmol) with 10.0 ml methanol solvent and addition of catalyst (200 mg) followed with slow addition of sodium borohydride (200 mg) at (0°C). In case of silica-supported catalysts, sodium borohydride was added in 5 min and for titania, it took 10 min as the formation of nickel boride was slower. The reaction mixture is magnetically stirred continuously. The reaction progress is monitored by TLC, normally till the starting material is consumed. Then the reaction mixture is quenched with diionized 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 *p*-methoxy benzyl alcohol which is then subjected to column chromatography to afford pure *p*-methoxy benzyl alcohol product. The final product is characterized by ^1H and ^{13}C NMR (400 MHz Bruker Instrument). GC-MS was samples were run on Agilent 6890 GC/5973, MS Column: J&W HP5-MS. GC results were characterized on GC System 6820, Agilent Technologies equipped with flame ionization detection (FID) and a carbovax OVI capillary column and compared with standard sample.

3. Results and discussion

The fast and selective reduction of aldehydes and other substituted moieties is an fascinating area of research, particularly when other potentially reducible moieties are present in the molecule. A representative reaction was examined for *p*-anisaldehyde to *p*-methoxy benzyl alcohol with 5% Ni SiO_2 - NaBH_4 . The reaction was fast and got completed in 3 min at (0°C). It gave 100% conversion with single product. All these catalyst materials used are uncalined. This interesting result lead us to look at the activity of 10 and 15% loaded Ni/ SiO_2 under similar conditions. The results obtained from duplicate experiments are summarized in Table 1. With 10% Ni loading it took 5 min for 100% conversion, while with 15% Ni loaded catalyst, even longer, 8 min. Both had 100% conversion with one product. Thus, the order of reactivity of Ni catalyst is 5% Ni/ SiO_2 > 10% Ni/ SiO_2 > 15% Ni/ SiO_2 . To establish the optimum loading of Ni on SiO_2 , experiments were conducted with 2% Ni loaded silica under identical conditions. While selectivity was 100%, conversion was observed low at 75% after 7 min.

Experiments were repeated with similar loading of Ni on TiO_2 support in place SiO_2 under other wise identical conditions. TiO_2

Table 1

Selective reduction of *p*-anisaldehyde to 4-methoxybenzyl alcohol in methanol.^a *p*-Anisaldehyde = 2.0 mmol, catalyst = 200 mg, sodium borohydride = 200 mg.

Support	Ni loading (%)	Reaction time (min)	Conversion (%)	Selectivity (%)
SiO_2^{b}	2	7	75	100
	5	3	100	100
	10	5	100	100
	15	8	100	100
TiO_2^{c}	5	10	95	100
	10	12	95	100
	15	15	75	100

^a Means duplicate runs.

^b NaBH_4 addition duration 3–5 min.

^c NaBH_4 addition duration 10 min.

supported catalysts too recorded good selectivity, but had poorer conversions and longer duration of reaction times (Table 1). With all the loadings of Ni/Silica catalysts 100% selectivity was intact. During the course of our studies on *in situ* generated nickel boride on silica, it was observed that the aromatic ring of *p*-anisaldehyde is intact under similar conditions; unlike with Raney Ni as catalyst [21]. Further with Raney Ni, reactions take 5 h for complete conversion. These interesting results lead us to investigate the activity of Ni catalyst on titania support for the title reaction. 5% Ni loaded titania gave 95% conversion and 100% selectivity in 10 min, while the 10% Ni/ TiO_2 took 12 min for 95% conversion and 100% selectivity (Table 1). With 15% Ni loaded titania, even after 15 min reaction duration only 75% conversion could be achieved, but selectivity remained 100%.

Identifying that 5% Ni/ SiO_2 as the ideal catalyst and optimum condition, the reduction of 17 different aliphatics and aromatics with different functional groups were investigated and the results obtained were found reproducible (Table 2). The conversion of benzaldehyde to benzyl alcohol was 100%. Similarly the conversion of benzophenone to benzhydrol and acetophenone to 1-phenethanol were 100%. As reported by Sudalai and co-workers, with Ni-Zr catalysts, it took 5 h under reflux conditions, for the conversions of benzophenone to benzhydrol and acetophenone to 1-phenethanol [21]. In the current study, the conversions of 4-hydroxybenzaldehyde to 4-hydroxy benzyl alcohol and 2-hydroxybenzaldehyde to 2-hydroxy benzyl alcohol were 100%. Further, 4-bromobenzaldehyde got converted to 4-bromobenzyl alcohol with bromo group intact with 100% conversion and selectivity in 5 min.

Kantam et al. [19] reported the use of Pd on MCM-41 for reduction of aldehyde and bromo groups and Choudary et al. [7] reported for conversion of 4-bromobenzaldehyde to 4-bromobenzyl alcohol in 22 h employing calcined Ni-Al hydrotalcite. In the current studies, the conversions of 4-hydroxy acetophenone to 4-hydroxyphenethanol and 2-hydroxy acetophenone to 4-hydroxyphenethanol were 100% and in 5 min reaction time. The conversion crotonaldehyde to 1-butanol was also 100% in 5 min duration.

Literature reports that under hydrogen transfer conditions, it needs 12 h under reflux conditions for cyclohexanone to cyclohexanol to achieve 100% conversion [27], while in current studies the transformation of cyclohexanone to cyclohexanol was 70% in 5 min. The cyclopentanone to cyclopentanol and phenol to cyclohexanol reactions recorded poor conversion efficiency (20%).

While for the 100% conversion of styrene to ethyl benzene, the nickel clay catalysts reportedly take 8 h under reflux conditions [28,29], it was achieved in 5 min using the proposed Ni on silica and boride catalyst system. Similarly, while with Ni catalysts it is reported to take 25 min for the hydrogenation of chalcone with

Table 2
 Selective reduction of various substituted aromatics in methanol with 5% Ni-silica catalysts at 0 °C.^a Substrate = 2.0 mmol, catalyst = 200 mg, sodium borohydride = 200 mg. Reaction duration: 5 min.

S. no	Substrate	Product	Conversion (%)	Selectivity (%)
1	C ₆ H ₅ -CHO	C ₆ H ₅ -CH ₂ -OH	100	100
2	4-OCH ₃ -C ₆ H ₄ -CHO	4-OCH ₃ -C ₆ H ₄ -CH ₂ OH	100	100
3	4-Br-C ₆ H ₄ -CHO	4-Br-C ₆ H ₄ -CH ₂ -OH	100	100
4	4-OH-C ₆ H ₄ -CHO	4-OH-C ₆ H ₄ -CH ₂ OH	45	100
5	2-OH-C ₆ H ₄ -CHO	2-OH-C ₆ H ₄ -CH ₂ OH	20	100
6	C ₆ H ₅ -CO-CH ₃	C ₆ H ₅ -CHOH-CH ₃	100	100
7	4-OH-C ₆ H ₄ -CO-CH ₃	4-OH-C ₆ H ₄ -CHOH-CH ₃	100	100
8	2-OH-C ₆ H ₄ -CO-CH ₃	2-OH-C ₆ H ₄ -CHOH-CH ₃	100	100
9	C ₆ H ₅ -CO-C ₆ H ₅	C ₆ H ₅ -CHOH-C ₆ H ₅	100	100
10	C ₅ H ₁₀ CO	C ₅ H ₁₁ C-OH	70	100
11	C ₄ H ₈ CO	C ₄ H ₈ C-OH	65	100
12	C ₆ H ₅ -CO-CH=CHCOC ₆ H ₅	C ₆ H ₅ -CO-CH ₂ CH ₂ COC ₆ H ₅	100	100
13	C ₆ H ₅ -CH=CH ₂	C ₆ H ₅ -CH ₂ CH ₃	100	100
14	C ₆ H ₅ -Br	C ₆ H ₆	75	100
15	CH ₃ CH ₂ CH ₂ CHO	CH ₃ CH ₂ CH ₂ CH ₂ -OH	100	100
16	C ₆ H ₅ -OH	C ₆ H ₁₁ -OH	20	100
17	C ₆ H ₅ -CH ₃	C ₆ H ₁₁ -CH ₃	100	100

^a Means duplicate runs.

conversion 100% [30], the same reaction was achieved in 5 min in the present studies.

Using the title system, in 5 min, bromobenzene was converted to benzene achieving 75% conversion and 100% selectivity, and the same reaction with Pd anchored silica reportedly took 15 h [7]. In the current investigations, the toluene to 4-methyl cyclohexane conversion was 100% in 5 min, while with supported nickel catalysts it took 16 h under vapor phase conditions [3].

For all the substrates investigated in this study, it took much longer times with other reported catalysts in literature, but our catalyst system in most cases achieved 100% conversion with single product in 5 min duration. With all Ni silica catalysts, when sodium borohydride was added slowly for 3–5 min, the reaction mixture turned instantly black confirming the generation of Ni boride accompanied by a sufficient amount of hydrogen evolution. This possibly is facilitated by the nickel particles adsorbed on the surface of silica support. When the reaction mixture is filtered, there was no leaching of the metal in the filtrate, which indicates that the nickel boride is well formed on the silica surface. Unlike the Raney Nickel, Ni-boride silica is non-pyrophoric in nature [22].

The scope of hydrazine hydrate as hydrogen donor was also explored with 5% Ni/SiO₂ catalyst in methanol. It gave 75% conversion only, even after 17 h refluxing, but selectivity remained 100%. Further, to investigate the scope of other hydrogen transfer agents, the activity of 5% Ni-silica in 2-propanol or ethanol under reflux condition was studied and no reactions were observed even after for 17 h reaction. Pure nickel oxide is observed to have no catalytic activity.

The functional group on the aromatic ring that inductively withdraw electrons compared to other reducible groups, get reduced easily. Based on the TEM characterization studies of Ni/SiO₂ prepared from nickel nitrate, Hou et al. [31] have reported that the activity of Ni on silica surface depended on the particle size of the metal and lower catalytic activity is observed with increased Ni particle size. With 15% Ni loaded silica they observed that support surface is almost completely covered by nickel particles, suggesting that the Ni could be unevenly distributed which has contributed to the low activity of 15% Ni/SiO₂.

3.1. Catalysts characterization

5% Ni silica catalysts were characterized by BET surface area, XRD and IR techniques reported earlier report [26].

3.2. Nitrogen desorption measurements of 5% Ni silica

As reported earlier, the specific area, i.e., the BET surface area of the catalysts is 180 mg⁻¹. The surface reaction may have caused the decrease of available surface area of the support, probably by closure of the pores [26]. The hydrothermal treatment results in a surface modification, which affects the support surface area. It could be inferred from the increasing specific surface area with time and by the OH stretching band in IR however after 90 h of treatment the BET area decays. When time is increased for hydrothermal treatment, the OH bands show a maximum at 46 h. After that a degradation process can be assumed due to a decreasing in the BET area and a starting crystallization process as can be seen by XRD.

3.3. The FT-IR spectra of 5% Ni silica

As documented in earlier report [26] the IR spectra of 5% and 10% NiSiO₂ showed a band at 1100 cm⁻¹ (asymmetrical Si-O-Si) very perceptible to formation of silicates and strong and intense absorption band between 1078 and 1050 cm⁻¹, showing the presence of Si-O-Ni bonds.

Further, upon hydrothermal treatment of catalysts for 46 h, the observed degradation process can be assumed due to decrease in BET area. Apart from these hydrothermal treatment at 96 h shows OH stretching vibrations by FT-IR [26]. From these results it is assumed that hydrothermal treatment modifies the surface for superficial corrosion creating free places of SiOH during the time of treatment. Haukka reported the broad band at 3500–3680 cm⁻¹ is due to hydrogen bridge bonds [32]. Silica does not have free OH groups. These results confirm that nickel boride is anchored to the surface of silica through the free OH groups over the surface.

The use of nickel-based catalysts, impregnation with nickel nitrate solutions, is the most extensively used method in preparations. In order to obtain the same active species, the operation parameters such as order of reactants, speed of agitation, time of aging are important during the impregnation process [26]. With partial electron transfer from boron to nickel, the metallic nickel becomes electron-rich and boron electron-deficient. It greatly enhances the catalyst activity and selectivity for the product. The nitrogen atom of nitro aromatics could 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 is a forward donation of the

electrons from the highest occupied molecular orbital (HOMO) of the N=O bonding, i.e., from the $\pi_{\text{N=O}}$ to the dz^2 and s orbitals 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., $\pi_{\text{N=O}}^*$. As $\pi_{\text{N=O}}^*$ is an antibonding orbit, the increased back electrons donation to the $\pi_{\text{N=O}}^*$, which resulted from the high electron density on the Ni active sites, can also activate the N=O bond and promote the hydrogenation [26].

Generally, Ni–B alloy involves two major processes which contribute to the alloy's properties, (i) reduction of nickel cation and (ii) decomposition of sodium borohydride. Process (ii) is initiated by nickel atoms formed in process (i) [33]. In the confined environment of silica support, it is possible that process (i) and (ii) are quite fast due to higher activity of nickel on support. Further, the formation of a segregated boron phase is inevitable even with amorphous support. In the aqueous synthesis reactions, for example, the formation of boric acid (HBO₂) on the support via a hydrolysis process is inevitable. In present case of non-aqueous synthesis method, we have found that a large fraction of the boron species formed. The higher stability of Ni–B/SiO₂ suggests that its alloy particles are smaller, and oxygen adsorption on the surface affects a larger proportion of Ni–B interactions.

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 these results 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. Similar observation was reported in literature, while studying the oxidation of alcohols using Ni loaded hydrotalcites as catalysts in presence of oxygen [25].

4. Conclusions

In conclusion nickel boride generated *in situ* from nickel silica and sodium borohydride reduces wide range of aromatic substrates, substituted aldehyde, ketones, alkenes, alkyl aromatics, phenol, aromatic amines in short duration of 5 min (Table 2) under mild reaction conditions with 100% selectivity and conversion efficiency. This proves that nickel borohydride silica system works as superior system to the hydrogen transfer. It is a robust catalyst and easy work up. This system even applies to groups such as OH, which is acidic and also for nitro groups. Further, this process is economically viable and applicable to large-scale reactions. The Ni silica catalysts can be charged into the reactor with out pre-reduction

of the catalyst. This forms a new alternative route for selective reductions with good conversions.

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