



Selective reduction of aldehydes to alcohols by calcined Ni-Al hydrotalcite

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Received 29 January 2003; accepted 9 May 2003

Abstract

Several aromatic and heterocyclic aldehydes are reduced at atmospheric pressure by calcined Ni-Al hydrotalcite and the catalyst is reused for several cycles with consistent activity and selectivity.

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Keywords: Reductions; Calcined Ni-Al hydrotalcite; Aldehydes; Hydrogen; Alcohols; Heterogeneous catalysis

1. Introduction

The reduction of carbonyl functionality is a fundamental reaction in organic chemistry and found numerous applications in fine chemical industry and laboratory. Basically varieties of reducing systems are available to effect reductions, for instance, nickel–aluminium (Ni–Al) alloy [1], $\text{Al}_2\text{O}_3\text{--NaBH}_4$ [2,3], Cu/Ru complexes [4–6], PHMS [7], $\text{HCO}_2\text{Na}/\Delta/\text{pressure}$ [8,9] and MPV reductions [10,11]. The selective reduction of aldehydes in the presence of other functional group vulnerable for reduction constitutes a more difficult task in organic synthesis and in such cases, most of the times it is necessary to use the expensive reagents and/or work at low temperatures. This can be accomplished by using aminoborane [12,13], tributylstannane [14], especially in the presence of

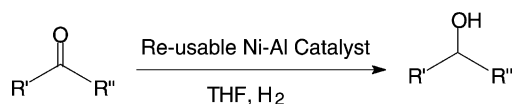
low-valency titanium [15], tetrabutylammonium triacetoxymethylborohydride [16], potassium triphenylborohydride [17] and lithium trialkoxyaluminium hydrides [18]. Raney nickel [19,20] is an effective catalyst to achieve the chemoselective reduction of aldehydes in the presence of ketones. All these methods have their own drawbacks that include the use of high pressure and temperature or both, non-reusable/regenerable and non-selective stoichiometric amounts of reagent which leads to the formation of quantitative amounts of undesirable salts, or the use of pyrophoric catalyst. With this background, there is strong need to develop a new heterogeneous catalyst that can be reusable and efficient under mild conditions.

Layered double hydroxides (LDHs) or hydrotalcite like compounds (HTLCs) have recently received much attention in view of their potential usefulness as adsorbents, anion exchangers [21] and most importantly as basic catalysts [22–29] for a variety of organic transformations. We report in this communication the selective reduction of various aromatic and α,β -unsaturated aldehydes to their corresponding

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Scheme 1. The reduction of aldehydes to alcohols by calcined Ni-Al hydrotalcite catalyst.

alcohols in good yields (Scheme 1) at atmospheric pressure by calcined Ni-Al hydrotalcite.

We have developed a series of heterogeneous Ni-Al hydrotalcites of various Ni/Al compositions for reduction of aldehydes to alcohols. Aromatic and conjugated aldehydes, heterocyclic aldehydes such as 2-pyridinecarboxaldehyde, 3-pyridinecarboxaldehyde, 2-thiophenecarboxaldehyde, and 3-thiophenecarboxaldehyde have been effectively and selectively reduced to the corresponding alcohols in presence of other vulnerable function groups.

2. Experimental

2.1. General

^1H NMR spectra were recorded on a Gemini Varian (220 MHz) spectrometer, using TMS as an internal standard and CDCl_3 as solvent. Mass spectra were obtained at an ionisation potential of 70 eV (scanned on VG 70-70H (micro mass)). Thin layer chromatography was performed on silica gel 60F254 plates procured from E-Merck. Starting materials purchased from Aldrich and Fluka were used as it is without any further purification. X-ray powder diffraction (XRD) data were collected on a Siemens/D-5000 diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$).

2.2. Preparation of the catalysts

2.2.1. Preparation of calcined Ni-Al hydrotalcite (Ni/Al, 2:1) Cat A [27]

An aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (29.1 g, 0.10 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (18.75 g, 0.05 mol) in 70 ml distilled water was slowly added to an aqueous solution of NaOH (24.0 g, 0.3 mol) and Na_2CO_3 (10.0 g, 0.094 mol) in 100 ml distilled water under vigorous stirring at room temperature. At the end of the addition (30 min) when a milky suspension remained intact, the material was allowed to age at 65°C for

18 h. After cooling to room temperature, the solid was filtered, washed with warm distilled water and dried at 125°C under vacuum over P_2O_5 . The obtained solid (Ni-Al- CO_3 hydrotalcite) was calcined at 450°C in a flow of air for 6 h, then cooled to room temperature and used for the reactions. Ni-Al- CO_3 hydrotalcites, Ni/Al ratios (2.5 and 3) were prepared similarly by taking appropriate ratios of Ni and Al nitrates.

2.2.2. Preparation of Ni-Al rehydrated hydrotalcite (2:1)

Ni-Al- CO_3 hydrotalcite synthesized with Ni/Al in a ratio of 2.0 was first calcined at 450°C in a flow of air at the rate of $10^\circ\text{C min}^{-1}$ to reach 450°C and maintained for 6 h. The solid was then rehydrated at room temperature under flow of nitrogen gas (61 h^{-1}), saturated with water vapour for about 6 h and used for the reaction.

Ni-Al hydrotalcite (cat B) was prepared by coprecipitation using ammonia solution as detailed in the literature [28], then the solid was calcined at 450°C in a flow of air for 6 h, then cooled to room temperature and used for the reaction, Ni/ γ - Al_2O_3 (2, 5, and 10%) catalysts were prepared as described earlier [26].

2.2.3. A typical experimental procedure for reductions

In typical run, the catalyst (0.5 g) and KOH (0.1 g) was suspended in dry THF (10 ml) and treated with molecular hydrogen for 20 min and then 2-pyridinecarboxaldehyde (2 mmol) was added drop-wise. A hydrogen balloon was fitted to the flask and the resultant solution was stirred under reflux for a specified period. The progress of the reaction was monitored by TLC and on completion of the reaction, the reaction mixture was subjected by column chromatography (hexane/ethyl acetate, 9:1 (v/v)) to afford the 2-pyridylcarbinol. ^1H NMR (200 MHz, CDCl_3 , 25°C , TMS): $\delta = 8.5$ (d, 1H, $J = 5.2$ Hz), 7.6–7.7 (t, 1H, $J = 7.3$ Hz), 7.3 (d, 1H, $J = 7.8$ Hz), 7.1 (t, 1H, $J = 6.8$ Hz), 4.7 (s, H), 4.4 (s, broad, 1H), m/z (EI), 109 (M^+ , 62%), 108 (100), 80 (52), 52 (27).

3. Results and discussion

In order to identify and evolve the best catalytic system composed of Ni catalyst and suitable base in

Table 1

Reduction of 2-pyridinecarboxaldehyde to 2-pyridylcarbinol by different nickel catalysts in hydrogen atmosphere

Entries	Catalyst	Time (h)	Yield (%) ^a	Specific activity (mmol g ⁻¹ h ⁻¹) ^b
1	Ni-Al HTLC (2:1, cat A) (calcined)	14	98	0.280
2	Ni-Al HTLC (2:1) (rehydrated)	16	80	0.200
3	Ni-Al HTLC (2.5:1) (calcined)	30	80	0.106
4	Ni-Al HTLC (3:1) (calcined)	30	29	0.038
5	Ni-Al HTLC (2:1) (uncalcined)	30	No reaction	–
6	Ni-Al (cat B) (calcined)	20	47	0.094
7	Ni/ γ -Al ₂ O ₃ (2%) (calcined)	30	79 ^c	0.105
8	Ni/ γ -Al ₂ O ₃ (5%) (calcined)	30	45 ^c	0.060
9	Ni/ γ -Al ₂ O ₃ (10%) (calcined)	30	52 ^c	0.069
10	None	30	No reaction	–

All reactions were performed with 2 mmol of substrate in 10 ml of dry THF using 0.5 g of catalyst and 0.1 g of KOH under 1 atm of hydrogen at refluxing in a specified time.

^a Isolated yields.

^b Specific activity: mmol of product obtained per gram of catalyst per hour.

^c Reaction was conducted in *n*-hexane.

the activation of molecular hydrogen and aldehyde, a study on various hydrotalcite catalysts of different compositions of Ni/Al prepared by different coprecipitation agents [26] and Ni/ γ -Al₂O₃ of varied Ni content in the reduction of 2-pyridinecarboxaldehyde to 2-pyridylcarbinol with molecular hydrogen was undertaken and the results are presented in the Table 1. A series of hydrotalcite containing different compositions of Ni/Al such as 2:1, 2.5:1 and 3:1 and Ni/ γ -Al₂O₃ of varied nickel content 2, 5, and 10% were screened, and the calcined Ni-Al HTLC (2:1, cat **A**) was found to be the most active. The calcined and rehydrated form of the Ni-Al HTLC (2:1), is found to be the next best catalyst in the reduction of 2-pyridinecarboxaldehyde. The Ni-Al HTLC catalysts with the Ni/Al 2, 2.5, 3:1 as-synthesised composed of anion carbonate are essentially inactive. Ni-Al hydrotalcite cat **B** (Ni:Al, 2:1) prepared by an ammonia coprecipitation method and on subsequent calcination showed moderate activity. The Ni: γ -Al₂O₃ catalysts with different compositions and on subsequent calcination also exhibit moderate activity. Therefore, it is concluded that calcined Ni-Al hydrotalcite cat **A** was the best catalyst for an effective reduction of 2-pyridinecarboxaldehyde to 2-pyridylcarbinol. The observed order of the specific activity in the reduction of 2-pyridinecarboxaldehydes: Ni-Al hydrotalcite (cat **A** calcined, 2:1) > rehydrated Ni-Al hydrotalcite (2:1) > Ni-Al hydrotalcite (2.5:1) > Ni/ γ -Al₂O₃ (2%)

> Ni-Al (cat **B**) > Ni/ γ -Al₂O₃ (10%) > Ni/ γ -Al₂O₃ (5%) > Ni-Al hydrotalcite (3:1); the results are summarised in Table 1.

A TPR profile of all the catalysts [26] indicates that the free NiO is reduced at low temperature 400 °C (T_{\max}) and NiO in association with oxide of aluminium is reduced at higher temperature 500 °C (T_{\max}). The TPR of the samples of Ni/ γ -Al₂O₃ indicates the presence of free NiO only, while the samples of Ni-Al hydrotalcite prepared by coprecipitation agents, NaOH/Na₂CO₃ and ammonia display both free NiO and NiO in association with aluminium oxide. The moderate activity of Ni/ γ -Al₂O₃ in the reduction of aldehydes indicates that the free Ni which is present in these impregnated samples also contributes to the activity in reduction reactions. The activation of molecular hydrogen by all the samples of Ni-Al hydrotalcites, as evident by the reduction of aldehydes is attributed to the presence of Ni in association with aluminium oxide. The TPR profile of Ni-Al hydrotalcites prepared by NaOH/Na₂CO₃ displayed a shoulder at lower temperature which grows on increased free NiO content, namely from Ni:Al ratio 2:1 to 3:1, although XRD analysis showed a crystalline hydrotalcite pattern (Fig. 1a). The rate of reduction of aldehyde which is in the increasing order: 3:1 < 2.5:1 < 2:1 (Ni-Al), is in good agreement with the TPR data of hydrotalcites. The IR spectra of various compositions of Ni-Al hydrotalcite samples

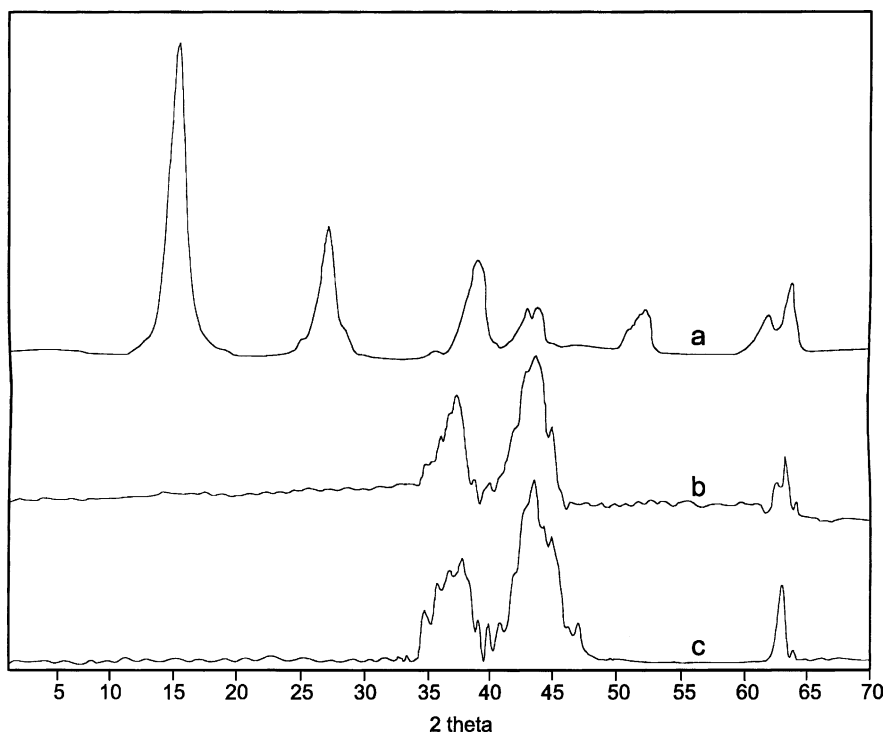


Fig. 1. XRD powder patterns of samples. (a) Ni-Al-CO₃ as-synthesised, (b) calcined Ni-Al hydrotalcite catalyst (cat A) and (c) used cat A.

as-synthesised show that the vibrational stretching frequency of the hydrogen atom in a hydroxide group of the cat A with Ni:Al (2:1) appears at lower wave number (3420 cm^{-1}) and has a smaller half-width than the other composition, which indicates there is a more-ordered cation distribution in the former [26]. The XRD of the Ni-Al hydrotalcite calcined (cat A) shows formation of NiO phase only with Al(III) inside the NiO particles [30] with the disappearance of hydrotalcite pattern concomitantly (Fig. 1b). Despite the rehydration with water for 2 days at room temperature, the calcined sample could not be restructured into hydrotalcite. This is in agreement with the reported results suggesting that the restructure of the calcined Ni-Al hydrotalcite requires stringent conditions [30,31]. The protocol of the calcination does not effect homogeneity (cationic distribution) of the Ni-Al hydrotalcite (cat A) since the restructuring of calcined hydrotalcite into layered one is possible albeit using stringent conditions [30–32]. The used cat A shows a XRD pattern (Fig. 1c) identical to the calcined catalyst indicating that the homogeneous NiO

particles composed of Al(III) ions (ordered cationic distribution) are the active sites that reduce aldehydes to alcohols effectively. The higher specific activity ($0.280\text{ mmol g}^{-1}\text{ h}^{-1}$) by Ni-Al hydrotalcite (cat A) calcined (Table 1, entry 1) in the reduction reactions is thus attributed to the presence of high Ni dispersion in the mixed oxide. All these results identify that the Ni in association with aluminium oxide as the active species and major contributor to maximise the activation of molecular hydrogen. The inactivity of the Ni-Al hydrotalcite as-synthesised reinforces the above inference.

The rehydrated version of hydrotalcite cat A, in which inclusion of hydroxyl ion is incorporated to enhance the basic character shows in fact a slightly lowered specific activity, $0.200\text{ mmol g}^{-1}\text{ h}^{-1}$ (Table 1, entry 2). The presence of moisture in the rehydrated version of hydrotalcite cat A lowers the activity of the catalyst.

The effect of various organic solvents on the reduction of 2-pyridinecarboxaldehyde as the model substrate using cat A was examined and the results

Table 2
Reduction of 2-pyridinecarboxaldehyde to 2-pyridylcarbinol in various organic solvents using cat **A** in hydrogen atmosphere

Entries	Solvent	Time (h)	Yield (%) ^a
1	THF	14	98
2	<i>n</i> -Hexane	14	95
3	Benzene	14	54
4	Toluene	14	88
5	Cyclohexane	14	83

All reactions were performed with 2 mmol of substrate in 10 ml of dry solvent using 0.5 g of cat **A** and 0.1 g of KOH under an hydrogen atmosphere at refluxing in a specified time.

^a Isolated yields.

Table 3
Effect of base for reduction of 2-pyridinecarboxaldehyde to 2-pyridylcarbinol using cat **A** in hydrogen atmosphere

Entries	Base (g)	Time (h)	Yield (%) ^a
1	NaOH (0.1)	14	98
2	KOH (0.1)	14	98
3	KOH (0.05)	14	52
3	KO ^{<i>t</i>} Bu (0.05)	6	45
4	KO ^{<i>t</i>} Bu (0.1)	5	59
6	K ₂ CO ₃ (0.1)	18	50
9	None	36	11

All reactions were performed with 2 mmol of substrate in 10 ml of dry THF using 0.5 g of cat **A** under an hydrogen atmosphere at refluxing temperature of solvent in a specified time.

^a Isolated yields.

are summarised in the Table 2. The polar solvent, THF is found superior over hydrocarbon solvents. The order of activity is: tetrahydrofuran > *n*-hexane > toluene > cyclohexane > benzene.

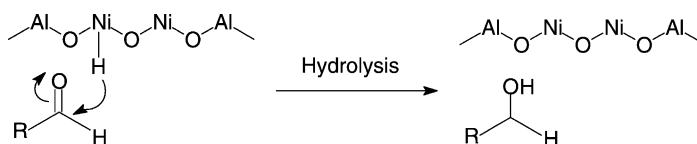
The effect of the bases on the reduction of 2-pyridinecarboxaldehyde to 2-pyridylcarbinol using cat **A** and molecular hydrogen was studied and found that both NaOH and KOH are effective bases and the use of molar equivalents of the base to substrate is required for higher yields (Table 3).

The cat **A**, proved to be the best catalyst in our studies was further evaluated for the reduction of var-

ious kinds of aldehydes such as aromatic, conjugated, heterocyclic ones (Table 4) to their corresponding alcohols using molecular hydrogen as a sole reductant. Although the reduction of benzaldehyde (Table 4, entry 5) with cat **A** is low yielding, the reduction of halobenzaldehydes proceeds in quantitative yields to the corresponding alcohols (Table 4, entries 4, and 13). However, moderate yields are obtained in the reduction of *p*-nitro and -cyano benzaldehydes (Table 4, entries 3, and 6). It is notable that the substituted benzaldehydes are selectively reduced, while the functional groups such as nitro and halo are intact. The naphthyl aldehyde is also reduced with moderate yields. The selective reduction of cinnamaldehyde (Table 4, entry 9) provides excellent yields of corresponding unsaturated alcohol. The heterocyclic aldehydes composed of pyridine (Table 4, entries 1, and 2), thiophene (Table 4, entry 7), furan (Table 4, entry 12), indole (Table 4, entry 8), benzthiophene (Table 4, entry 11) are subjected for reduction using cat **A** under similar conditions. It is significant that the 2-pyridine and 3-carboxaldehydes are reduced effectively and quantitatively. 2-Thiophenecarboxaldehyde is reduced in good yields (Table 4, entry 7). While benzthiophene, furfural and indole aldehydes on reduction under similar conditions offer only moderate yields. The cat **A** is reused for six cycles, which shows almost consistent activity and selectivity in the reduction of 2-pyridinecarboxaldehyde (Table 4, entry 2).

3.1. Plausible reaction mechanism

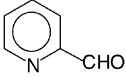
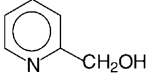
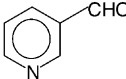
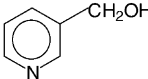

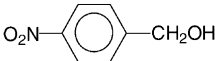
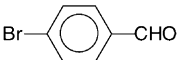
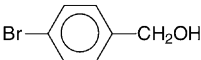
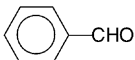
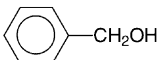
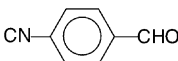
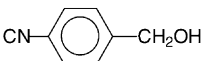
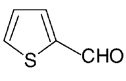
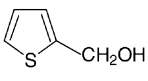
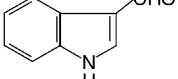
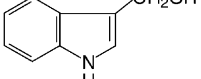
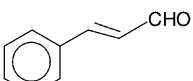
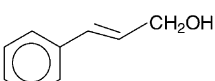
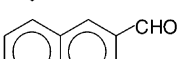
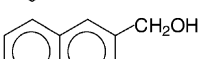

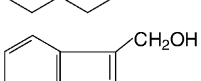
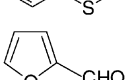
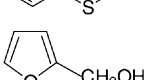
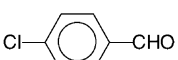
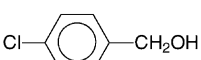
The plausible reaction mechanism (Scheme 2) therefore, involves the formation of nickel hydride on interaction of molecular hydrogen with Ni-Al hydrotalcite. The nickel hydride of the hydrotalcite on reaction with aldehyde forms alkoxide via hydride transfer and eventually generates the alcohol on subsequent hydrolysis with the base used as an additive. Aluminium is well documented both in Oppenauer oxidation and Meerwein-Ponndorf-Verley (MPV)



Scheme 2. Plausible mechanism for the reduction of aldehydes using cat **A**.

Table 4

Reduction of various aromatic aldehydes to alcohols using cat A in hydrogen atmosphere

S. no.	Substrate	Time (h)	Product	Yield (%) ^a
1		14		98
2		15		91 (89) ^b
3		20		37
4		22		90
5		12		51
6		15		60
7		18		83
8		30		48
9		16		85
10		18		40
11		15		35
12		12		35
13		24		92

^a Isolated yields.^b Yield after sixth cycle.

reduction, as well as in the recently reported MPV reduction [25] of ketones by Mg–Al hydrotalcite, to favor the formation of alkoxide, while the neighboring Ni atom facilitates the formation of a hydride species with molecular hydrogen. The hydride transfer from the nickel hydride of hydrotalcite is effected

to the physisorbed carbonyl compound to generate Al alkoxide. Hydrotalcites are homogeneous mixtures of heterobimetallic composition having a periodic composition of M^{II} and M^{III} ions. The cationic order of cat A calcined as revealed by IR on as-synthesised sample suggests that the presence of one aluminium

atom for every two nickel atoms substituted alternately in the hydrotalcite provides optimum use of nickel in cat A better than is possible with the other compositions, and is thus responsible for the display of higher activity [26]. The synergistic activity of nickel and aluminum is conspicuously demonstrated as reflected in the superior activity over Ni/ γ -alumina.

4. Conclusions

In conclusion, calcined Ni-Al hydrotalcite, composed of NiO–Al₂O₃, efficiently reduces a wide range of aldehydes, such as aromatic aldehydes, heterocyclic aldehydes to alcohols by employing molecular hydrogen. This process is not only economically viable but also applicable to large-scale reactions. Moreover, the high yields of reduced products can be obtained in heterogeneous catalysis using hydrotalcites as catalysts. The calcined Ni-Al hydrotalcite can be charged into reactor without pre-reduction of the catalyst. With special reference to the Raney nickel catalyst, the handling of present catalyst does not require any special precautions and it can be used directly by charging into reactor.

Acknowledgements

One of us (Ch. VR) thank the Council of Scientific and Industrial Research (CSIR), India, for providing research grants.

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