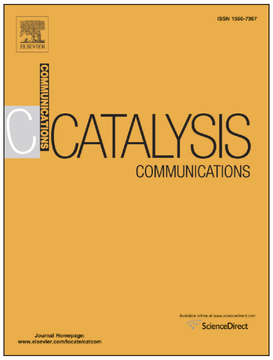

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In situ generated Ni(0)@boehmite from NiAl-LDH: An efficient catalyst for selective hydrogenation of biomass derived levulinic acid to γ-valerolactone

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Abstract

We report *in situ* generation of Ni(0)@boehmite from NiAl-layered double hydroxide (LDH) under reaction conditions which showed superior catalytic activity in the hydrogenation of levulinic acid (LA) to γ-valerolactone (Gvl) with quantitative yield in aqueous medium. Formation of Ni(0)@boehmite in course of the reaction was confirmed by PXRD, TEM, TGA and FT-IR. This catalyst shows superior conversion compared to a series of simple Ni based homogeneous as well as heterogeneous catalysts. The Ni(0)@boehmite catalyst is recyclable, and active even at higher concentrations of LA (25 wt%).

Keywords

Levulinic acid; γ-valerolactone; Hydrogenation; Nickel; Boehmite; Layered double hydroxides

1. Introduction

The consumption of energy is increasing with an increase in world population. Fossil fuels constitute the main source of this energy whose cost is largely governed by the availability as its reserves are diminishing. Another concern is the increase in the emission of greenhouse gases (GHG). A viable and sustainable alternative to the use of these fossil fuels is biomass as its usage would maintain the CO_2 level in the atmosphere [1-4]. Lignocellulosic biomass is one of the major categories of biomass which comprises carbohydrates that are present in the plant cell wall [5]. Several research groups across the globe have been working to obtain chemical building blocks from carbohydrate biomass [6]. Levulinic acid (LA), one of the biomass derived platform chemicals, is easily obtained from C_6/C_5 sugars by acid catalysed transformations. LA is a precursor for the production of biofuels, polymers, and various chemical intermediates [7-12]. The hydrogenation of LA forms three different products namely γ-valerolactone (Gvl), 1-4-pentanediol, and 2-methyltetrahydrofuran. All the three products are industrially relevant, particularly Gvl, a sustainable feedstock for energy and carbon-based chemicals [13,14]. Gvl has diverse applications such as production of biofuels in the form of valeric esters, aromatic hydrocarbons and liquid alkanes [15-17], polymer intermediates such as α-methylene-γ-valerolactone, 1,4-pentanediol and adipic acid [18-21]. Gvl itself acts as a solvent for many organic transformations and as a green reaction medium in biomass conversion [22,23].

Several research groups are working on the effective production of Gvl by selective hydrogenation of LA, and for this transformation various homogeneous and heterogeneous catalysts are reported using diverse hydrogen sources such as H_2, formic acid, and alcohols. The Ru and Ir metal containing phosphine based homogeneous complexes gave good LA conversion with Gvl selectivity but have a serious drawback of separation of catalysts from the reaction mixture, besides being energy intensive and expensive. On the other hand, different heterogeneous catalysts are also explored for this reaction. The precious metal catalysts like Ru, Pt, Pd and Au on different supports like carbon, TiO_2, Al_2O_3, SiO_2, H-ZSM5, H-β, Nb_2O_5, polyethersulfone, DOWEX resin, HMS, MCM-41, polyethersulfone, and hydroxyapatite are used for the reaction. Few reported studies used different co-catalysts, for example Amberlyst-70, Sn, Re etc., for efficient hydrogenation [24,25]. Although, these catalysts gave good conversion and selectivity for this reaction, their high cost and sparse availability preclude their use for bulk scale production of Gvl.

Recently few research groups have reported non-precious metal catalysts comprising Ni based catalysts such as Raney Ni, Ni supported on MoO_X/C, SiO_2, H-ZSM-5, mesoporous silica, Al_2O_3, TiO_2, Cu based catalysts supported on ZrO_2, SiO_2, Al_2O_3, ZnO, ZrO_2, Co-containing catalysts namely Co/Al_2O_3, reduced Co_3O_4 and mixed metal derived from hydrotalcites like $Ni_{4.59}Cu_1Mg_{1.58}Al_{1.96}Fe_{0.70}$, Cu–Al, Cu–Cr, and Cu–Fe in catalysing LA to Gvl conversion [12, 26-30]. In most of the cases, high energy was needed for the synthesis of catalysts (reduction of the catalyst, calcination etc.) that are often more intensive than that employed for the catalytic reaction. Another drawback being the use of organic medium that was not suitable for bulk scale manufacture of Gvl. To overcome these problems, we demonstrate here *in situ* generated Ni(0)@boehmite from NiAl-LDH (layered double hydroxide or otherwise referred as hydrotalcite-like compounds) as an efficient and recyclable catalyst for the selective preparation of Gvl from LA in aqueous medium under milder reaction conditions (SI. Table 1 in the ESI).

2. Experimental

2.1 Materials

Levulinic acid (98%), γ-valerolactone (99%), methyl levulinate (≥98%) were purchased from Sigma-Aldrich. Metal salts $NiCl_2$, $Ni(NO_3)_2$, $NiSO_4$, NiO, Ni(0) and Al(0) metal powders were purchased from s. d. fine Chemicals Limited, Mumbai, India.

2.2 Catalyst precursor (NiAl-LDH) preparation

Catalyst precursor NiAl-LDH was prepared by co-precipitation method under low supersaturation. The desired amount of metal nitrate solutions (Ni to Al atomic ratio 3:1) were mixed with solution of precipitating agents (i.e., NaOH and Na_2CO_3) slowly and simultaneously in a Schott auto-titrator assembly (Titroline, Schott, Germany) while maintaining pH at 9.5 ± 0.1 under stirring at room temperature. The precipitated solution was aged at 65 °C for 18 h in an oil bath, filtered, washed with deionized water until neutral pH and dried at 100 °C for 12 h.

2.3 Hydrogenation experiments and product analysis

A detailed description of the hydrogenation procedure and product analysis are described in SI. 1 in the ESI.

3. Results and discussion

3.1. Catalyst screening

Initially various commercial and synthesized Ni containing homogeneous and heterogeneous catalysts were used for the selective hydrogenation of LA to Gvl at 2.5 wt% LA , 10 wt% of Ni catalyst with respect to LA, 200 °C, 40 bar H_2 for 6 h. A blank reaction was carried out without using any catalyst which gave only 4% yield of Gvl with 5% conversion of LA (Table 1, entry 1), The commercial homogeneous catalysts like $NiCl_2$, $Ni(SO_4)_2$, $Ni(NO_3)_2$ gave low to moderate LA conversion and yields of Gvl (Table 1, entry 2-4). Commercially available heterogeneous catalysts like NiO and Ni(0) showed almost similar LA conversion of ~ 35%, and Gvl yields (~ 31%) (Table 1, entry 5-6). In literature, a hydrotalcite catalyst (Cu-Fe) was reported with 90% selectivity of Gvl with >98% of LA conversion at 200 °C and 70 bar H_2 in 10 h [31]. From this observation, here we have explored NiAl-LDH as catalyst for the reaction, and observed 100% conversion of LA with quantitative production of Gvl (Table 1, entry 7). Further the catalytic activity was compared with other Ni based catalysts prepared such as $Ni(OH)_2$ which showed lesser activity compared to NiAl-LDH (Table 1, entry 8). Further, comparison with premixed Ni(70)Al(30) catalyst (as metal powders similar to Ni/Al atomic ratio in NiAl-LDH) which also showed very low activity of this catalyst (Table 1, entry 9). Thus, it can be concluded that NiAl-LDH is a superior catalyst for this conversion compared to other Ni-based reported systems. The optimization of reaction conditions was then carried out using NiAl-LDH catalyst.

3.2. Optimization of reaction conditions

Parameter variation studies were carried out for optimizing reaction conditions using NiAl-LDH catalyst. Initially, the temperature was decreased from 200 °C to 150 °C which drastically decreased the conversion of LA from 100% to 20% but almost maintained the selectivity of Gvl (Table 2, entry 1-2). Then the pressure was decreased from 40 to 30 bar H_2 keeping other conditions constant. 100% LA conversion with 100% yield of Gvl was observed while a further decrease in the pressure from 30 to 20 bar H_2 resulted in a decrease in the conversion of LA from 100 to 91% while maintaining selectivity (Table 2, entry 1 and 3-4). Then for further studies, the pressure was fixed at 30 bar H_2 and temperature at 200 °C. Further, wt% of Ni in the catalyst with respect to LA was varied from 10 to 4 at the above optimized conditions which showed that 7 wt% of Ni in NiAl-LDH catalyst is sufficient for the complete conversion of LA to Gvl (Table 2, entry 1 and 5-8). While maintaining 7 wt% of Ni in the catalyst, the reaction time was reduced from 6 to 4 h which decreased LA conversion to 60% (Table 2, entry 8-9). From the above studies, the optimized reaction conditions were: 200 °C, 30 bar H_2 pressure, 7 wt% of Ni and 6 h for complete conversion of LA (1g) to Gvl (0.86) (Table 2, entry 8).

3.3. In situ formation of Ni(0)@boehmite from NiAl-LDH during the reaction

After the reaction under optimized condition, the recovered catalyst was analysed using powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and Fourier-transformed infra-red (FT-IR) spectroscopy. The PXRD of synthesized NiAl-LDH showed 003, 006, 012, 015, 018, 110 and 113 reflections that are characteristic of hydrotalcite shown in Fig.1, which completely converted to 020, 120, 140, and 051 reflections for boehmite, and 111 with 200 for Ni (0) that matched well with the JCPDF file of boehmite (JCPDS PDF Card No. 01-074-290 and literature [32]) and Ni (JCPDS PDF Card No.: 00-004-0850). TEM images of precursor NiAl-LDH showed platelet-like morphology, which changed completely after the reaction due to the formation of boehmite along with Ni(0) particles. The *in situ* formed boehmite during the reaction (Table 2, entry 8) showed well-defined hexagonal long rod-like morphology with nearly spherical embedded Ni (0) particles with the size of less than 20 nm as shown in Fig. 2. The morphology of this boehmite phase matched well with the reported morphology in literature [33]. The *in situ* formation of Ni(0)@boehmite was further confirmed by using FT-IR (Fig. 3); NiAl-LDH showed characteristic bands at 3450 cm^{-1}, 1640 cm^{-1}, and 1380 cm^{-1}, correspondingly attributed to OH stretching of hydroxyl groups from the layers and interlayer water molecules, bending mode of water molecules in the interlayer space and asymmetric stretching vibrations of carbonate that matched well with reported literature [34]. After the reaction, FT-IR of the used catalyst matched well with reported boehmite [35]. Two strong bands observed at 3309 cm^{-1} and 3095 cm^{-1} corresponds to Al-OH, and the band at 1639 cm^{-1} corresponds to adsorbed water in the crystal of boehmite, while the bands at 1158 cm^{-1} and 1070 cm^{-1} are ascribed to the symmetrical bending vibrations of hydrogen bonds of Al-OH….OH-Al and the bands at 750 cm^{-1}, 627 cm^{-1} and 474 cm^{-1} refers to vibration modes of Al-O and Al-O-Al. Furthermore, TGA (Fig.4) also supported the formation of boehmite wherein generally NiAl-LDH exhibits a sharp weight loss between 200-350 °C corresponding to removal interlayer water molecules along with partial dehydroxylation of the material that was not observed for the material after the reaction. Instead, a weight loss was observed (between 370-550 °C), which may be attributed to the removal of strongly held hydroxyl groups of boehmite. To surmise, PXRD, TEM, TGA and FT-IR analysis corroborated the transformation of NiAl-LDH to Ni(0)@boehmite under the reaction conditions. Thus, the high selectivity observed with *in situ* generated Ni(0)@boehmite catalyst is due to uniform dispersion of Ni nanoparticles on boehmite support (as witnessed from TEM) which probably were not observed for the other Ni-based catalysts (Table 1, entry 2-6 and 8-9).

Mechanistically, partial decomposition of the layered lattice of NiAl-LDH under higher reaction temperature and hydrogen environment renders a mixed metal oxide/oxyhydroxide of NiO and AlOOH (boehmite) wherein the former undergo hydrogenation to Ni(0) resulting in Ni(0)@boehmite catalyst [SI.2 in the ESI]. This was also witnessed by the colour change from green of NiAl-LDH to grey due to the formation of Ni(0) (black), and boehmite (white). In addition, the absence of peaks at positions at $2\theta=37.1$, 43.3, and 62.8^{o} in PXRD of the used catalyst suggests the absence of NiO.

3.4. Recyclability of catalyst

Assessment of recyclability of the catalyst is beneficial for industrial applications. After the reaction, the catalyst was removed from the product mixture by simple centrifugation, washed with deionised water and further used for 2^{nd} cycle. Interestingly, it showed good activity similar to first cycle indicating that the *in situ* generated Ni(0)@boehmite is the active species for the reaction. The recyclability studies were conducted for up to four cycles and observed some decrease in the conversion of LA in each cycle while the selectivity of Gvl was maintained as illustrated in Table 3. The decrease in the conversion of LA is due to the decrease in the amount of Ni with respect to LA as it leached into solution in each cycle as elucidated from ICP. The ICP of the product mixture showed Ni leaching in the range of 0.1 to 0.4 wt% of Ni (with respect to LA) in every cycle.

3.5. Scale-up study

The catalytic activity was successfully demonstrated at 10 g scale of LA and achieved 100% of Gvl yield under similar reaction conditions which was used for 1g (Table 2, entry 10). After the reaction, Gvl was extracted from aqueous product mixture using ethyl acetate which was later evaporated resulting in a maximum isolated yield of 99% for Gvl (8.5 g). The evaporated solvent was further used for next cycles and it has good recyclability. The structural integrity of the recovered Gvl was confirmed by using ^{1}H-NMR (SI.Fig.1 in the ESI), ^{13}C-NMR (SI.Fig.2 in the ESI), FT-IR (SI.Fig.3 in the ESI), and whose purity was ~100% as elucidated from UHPLC (SI.Fig.4 in the ESI) and HR-MS (SI.Fig.5 in the ESI) studies.

4. Conclusion

We report *in situ* generated Ni(0)@boehmite from NiAl-LDH as an active catalyst for the selective hydrogenation of LA to Gvl. Nearly stoichiometric conversion of LA with 100% selectivity of Gvl was observed at 200 °C, 30 bar H_2 pressure in aqueous medium in 6 h. The formation of Ni(0)@boehmite was ascertained by various physicochemical techniques namely PXRD, FT-IR, TEM and TGA. The active catalyst (Ni(0)@boehmite) was recyclable up to four cycles with slight decrease in the conversion of LA in each cycle, however, maintained the Gvl selectivity. Further, the catalyst was successfully demonstrated at 10 g scale of LA and achieved nearly 100% Gvl yield under similar reaction condition as that of small scale (1g). The structural and functional characteristics of the isolated Gvl was ascertained by both spectroscopic and chromatographic techniques whose purity was 100%.

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Table 1 Screening of nickel catalysts for LA hydrogenation to Gvl

S.No	**Catalyst**	**LA conv. (%)**	**Gvl yield (%)**
1	Blank	5	4
2	$NiCl_2$	23	16
3	$Ni(SO_4)_2$	22	17
4	$Ni(NO_3)_2$	44	37
5	NiO	35	31
6	Ni(0) metal	34	32
7	NiAl-LDH	100	100
8	$Ni(OH)_2$	75	75
9	Ni(70)Al(30)	44	38

Reaction conditions: LA 2.5 wt% (0.0086 moles (1g)) in aqueous medium (40 ml), 10 wt% of Ni with respect to LA, 200 °C, 40 bar H_2, 6 h.

Table 2 Reaction conditions optimization studies using NiAl-LDH catalyst precursor

S.No	**Temp. (°C)**	**Pressure (H_2) in bar**	**Catalyst wt(%)**	**Time (h)**	**LA conv. (%)**	**Gvl yield (%)**
1	200	40	10	6	100	100
2	150	40	10	6	20	20
3	200	30	10	6	100	100
4	200	20	10	6	91	90
5	200	30	8	6	100	99
6	200	30	6	6	90	89
7	200	30	4	6	44	43
8	200	30	7	6	100	100
9	200	30	7	4	60	60
10[b]	200	50	7	6	100	99

Reaction condition: LA 2.5 wt% (0.0086 moles (1g)) in aqueous medium (40 ml), 4-10 wt% of Ni with respect to LA, 150-200 °C, 20-40 bar H_2. [b]LA 25 wt% (0.086 moles (10 g)) in aqueous medium (40 ml).

Table 3 Recycle studies with Ni(0)@boehmite catalyst

S.No	Catalyst	LA conv. (%)	Gvl yield (%)
1	Cycle-1	100	100
2	Cycle-2	96	95
3	Cycle-3	87	84
4	Cycle-4	71	70

Reaction conditions: LA 2.5 wt% (0.0086 moles (1g)) in aqueous medium (40 ml), 7 wt% of Ni (161 mg of NiAl-LDH) with respect to LA, 200 °C, 30 bar H_{2}, 6 h.

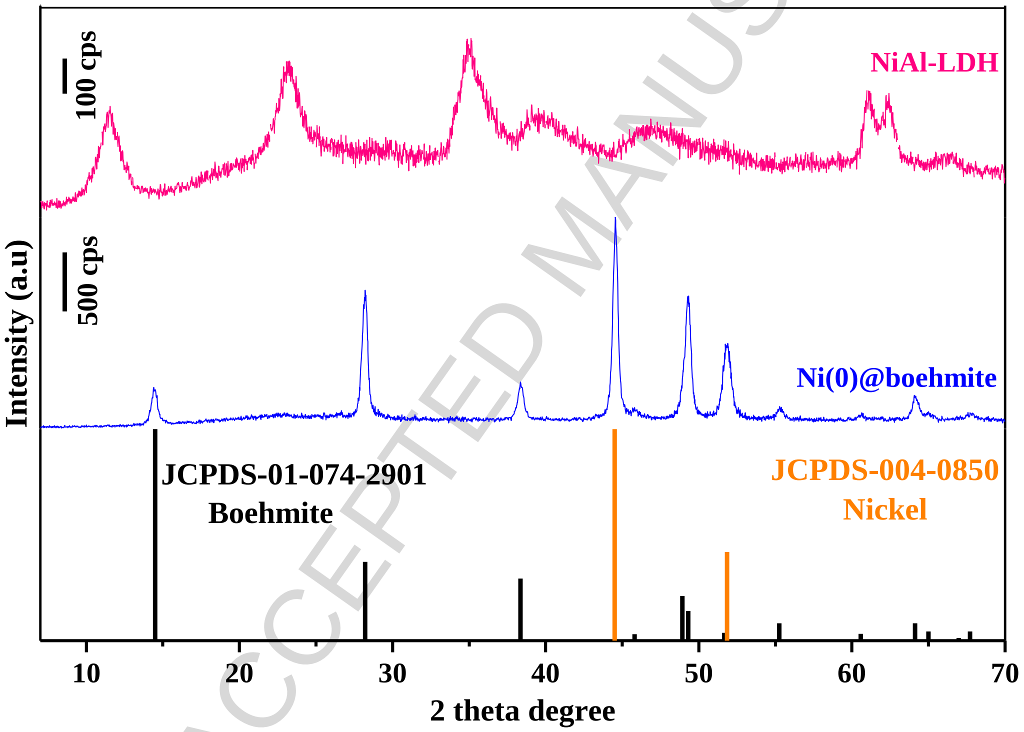
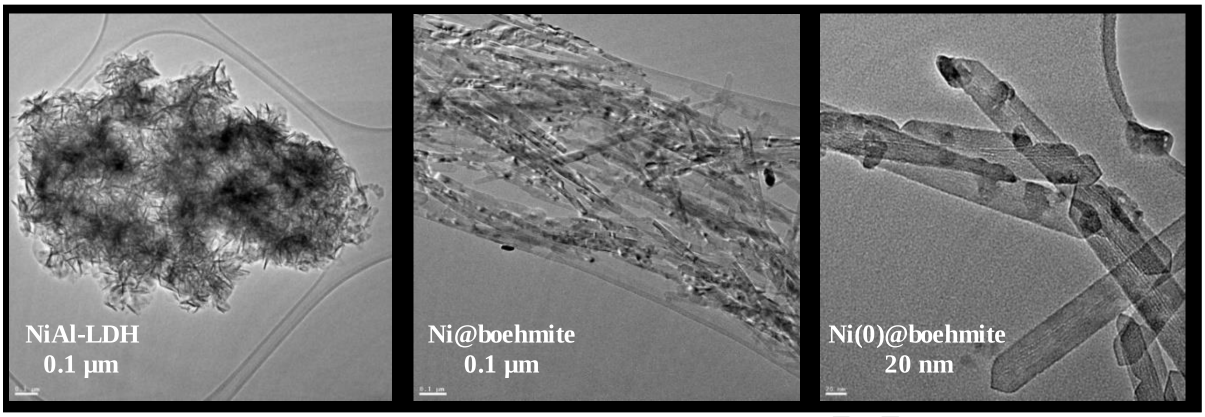


Fig. 1 Powder XRD pattern for NiAl-LDH (catalyst precursor) and Ni(0)@boehmite (catalyst obtained after the reaction - Table 2 Entry 8). The XRD pattern for Ni(0)@boehmite matched well with nickel (JCPDS card no: 004-0850; stick pattern included) and boehmite (JCPDS card no: 01-074-290).



NiAl-LDH before reaction

Insitu generated

Fig. 2 TEM images showing the morphology and crystallinity of NiAl-LDH catalyst precursor and Ni(0)@boehmite catalyst at different magnification (catalyst obtained after the reaction - Table 2 Entry 8).

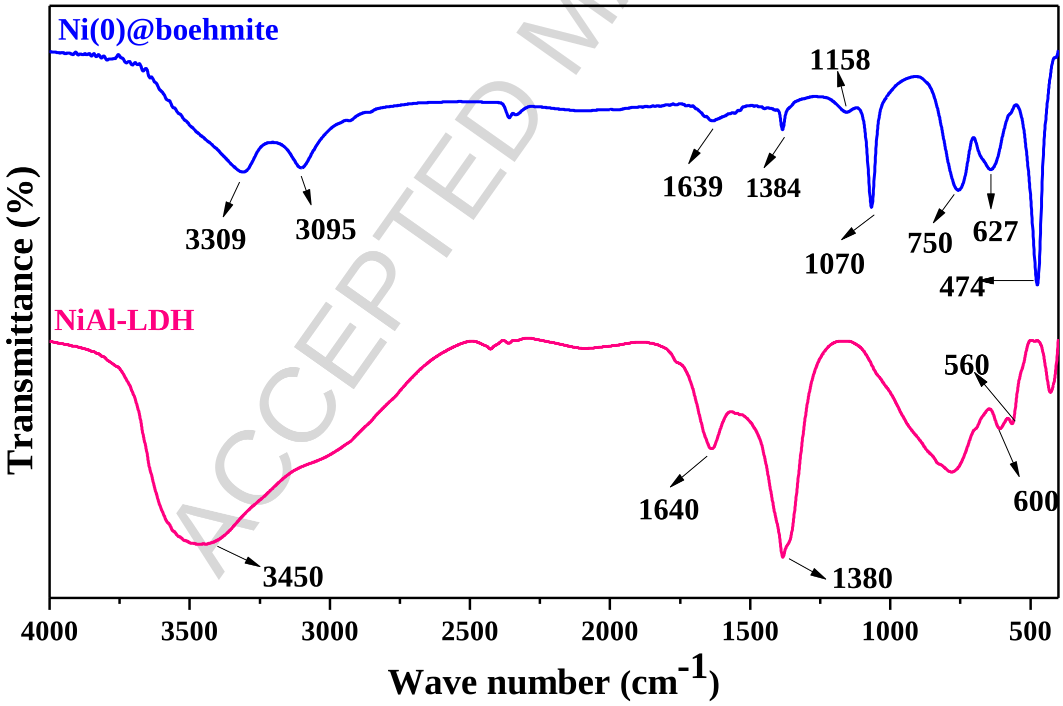


Fig. 3 The FT-IR spectra of NiAl-LDH catalyst precursor and Ni(0)@boehmite catalyst (catalyst obtained after the reaction - Table 2 Entry 8)

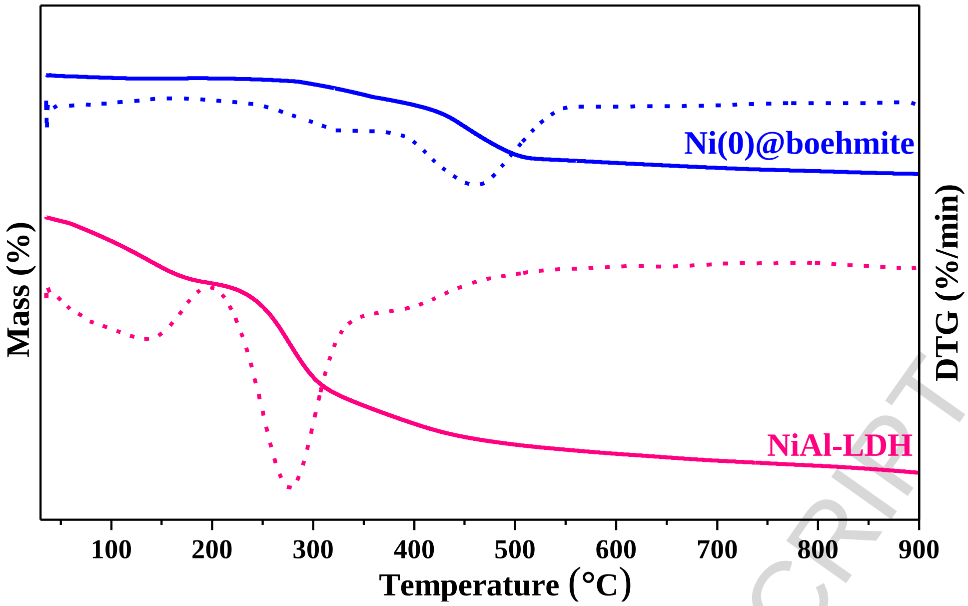
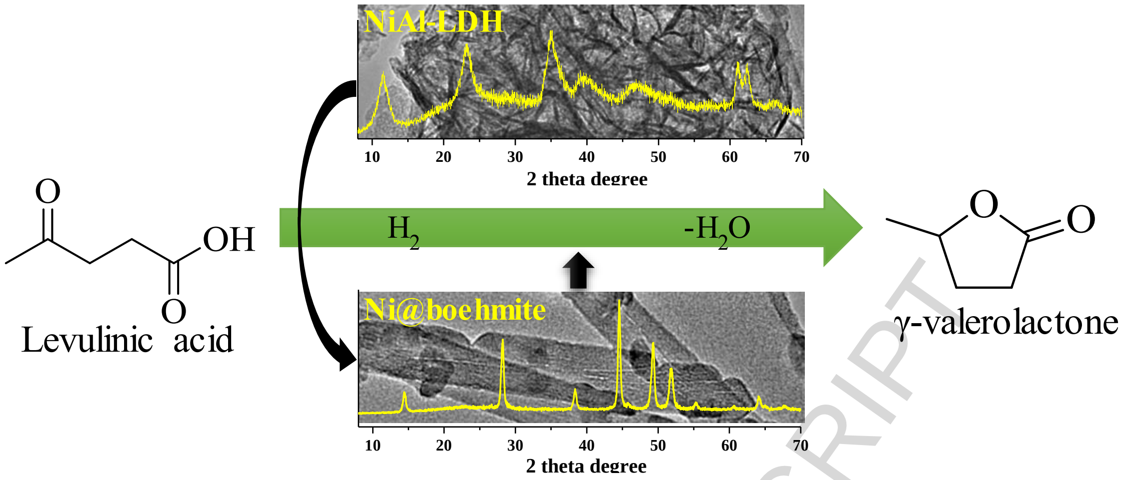


Fig. 4 TGA of NiAl-LDH catalyst precursor and *in situ* derived Ni(0)@boehmite catalyst (catalyst obtained after the reaction - Table 2 Entry 8)

Graphical abstract



Highlights

- NiAl-LDH is reported for the first time for the hydrogenation of levulinic acid to γ-valerolactone
- Stoichiometric conversion with 100% selectivity is obtained under optimized conditions
- During hydrogenation NiAl-LDH converts *in situ* into active catalyst Ni(0)@boehmite
- Formation of Ni(0)@boehmite is confirmed by PXRD, TEM, FT-IR and TGA
- The catalyst is recyclable, active at high LA concentration (25 wt%) and at larger scale