Sustainable Synthesis and Characterization of Ni–Al-Containing Double-Layered Nanocatalysts and Their Catalytic Activity

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ABSTRACT: Sustainable synthesis of Ni–Al double-layered catalysts by the coprecipitation method is described. Synthesized double-layered catalysts have been characterized by X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared, and thermogravimetric analyses, which confirmed a hydrotalcite-like structure. In addition, the impact of aging time and temperature on the activity of catalyst has been investigated. Furthermore, it has been confirmed by SEM and TEM analyses that the recovered catalyst has retained its structure. It has also been observed that the prepared material has potency to catalyze the reaction without loss in the yield. To explore the reactivity of the material, the catalyst has been examined in the synthesis of N-(2-hydroxyphenyl)benzamide under solvent-free conditions. The overall process afforded the product with high purity and high yields within short time.

1. INTRODUCTION

Double-layered nanocatalysts consist of a cationic brucite layer and anionic compounds in the interlayer with stable active sites. Double-layered nanocatalysts have unique properties such as recyclability, effective dispersion, safe in handling, separability, and friendliness. Hydrotalcite (HT)-like materials have formula $\left[M(II)_{x}M(III)_{y}(OH)_{z}\right]^{n+}\left[(A^{n-})_{m}\cdot yH_{2}O\right]^{n-}$ in which $MII$ and $MIII$ represent a divalent metal cation and a trivalent metal cation, respectively, $A^{n-}$ represents the interlayer anion, $x$ is the molar ratio of $MII/(MII + MIII)$, and $y$ is the molar volume of the intercalated water. Hydrotalcite-derived metal oxides have exhibited high thermal stability, large metal surface areas, and uniformity of the active species. Herein, the reasons for selecting Ni and Al are the lower price and availability of nickel and aluminum compared to those of other noble metals. In hydrotalcite-derived materials, Ni–Al-like material having interaction between NiO and Al$_2$O$_3$ resultant, NiO was reduced at higher temperature. Benzamide derivatives exhibit biological activities such as antihelminthic, antifungal, antibacterial activity. Oxyclozanide (benzamide structure) was discovered in 1969 as an antihelminthic agent for the treatment of liver fluke infection. For the synthesis of benzamide, many catalysts are routinely used. Pasha et al. have reported a trace amount of zinc dust, and Moghadam et al. have reported zirconyl trflate, pyridine, triethyl amine, and sodium hydroxide. However, catalysts that have been used for amide synthesis suffer many drawbacks such as the requirements of harsh conditions, exclusive reagents, long time duration, elevated temperature, and higher loading of catalyst; unwanted impurity generation; and thermal and hygroscopic unsteadiness of reagents. As a result, an efficient methodology is required for the preparation of benzamide. Chemoselective access is an alternative for cost reduction by preventing unwanted impurities, which have an immense importance in organic reactions. However, the reaction of a particular functional group selectively toward synthesizing highly reactive reagents is a challenging endeavor.

In the present work, we describe the synthesis, characterization, and catalytic activity of Ni–Al hydrotalcites as heterogeneous catalysts in chemoselective synthesis of N-(2-hydroxyphenyl)benzamide with high yield under solvent-free conditions. In this study, we have prepared and screened different hydrotalcites for chemoselective synthesis of benzamide. This is the first report on the synthesis of benzamide using Ni–Al hydrotalcite as a heterogeneous catalyst. The coprecipi-
tation method has been employed for the preparation of Ni–Al hydrotalcites having molar ratio of 3.0 and characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), thermogravimetric (TG), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) analyses.23–29

In continuation of these studies, herein, we report a sustainable synthesis and characterization of a Ni–Al hydrotalcite material with good catalytic activity and recyclability (Scheme 1).

Scheme 1. Synthesis of N-(2-Hydroxyphenyl)benzamide

\[
\begin{align*}
\text{OH} + \text{C} &= \text{NH}_2 \rightarrow \text{NH}_2 \text{OH} + \text{C} \\
\text{O} \text{H} \text{N} \text{H} &= \text{OH} \rightarrow \text{OH} \text{N} \text{H}  \\
\text{R} \text{N} \text{H} \text{N} &= \text{NH}_2 \rightarrow \text{NH}_2 \text{OH} + \text{C} \\
\text{Ni} &+ \text{Al} \rightarrow \text{NiAlHT}
\end{align*}
\]

2. RESULTS AND DISCUSSION

2.1. Characterization of Catalyst. Figure 1 shows the powder XRD pattern of Ni–Al hydrotalcite (HT) after being reduced. The characteristic diffraction pattern of the synthesized hydrotalcite (HTlc)-like layered structure has shown hydrotalcite (HTlc) precursors, which were successfully synthesized. Apparent diffraction peaks at 7.83, 3.90, and 2.61 Å are observed, which are corresponding to the diffraction lattice planes (003), (006), and (009), respectively.30 Diffraction patterns have interlayer lattice distance “c” of 23.93 Å, and basal reflections are recorded at 8.11, 3.94, and 2.59 Å (c = 24.33 Å) for the hydrothermally treated sample NiAl-HT. On the other hand, the diffraction is recorded at 1.530 Å (a = 3.06 Å) because of planes (110).

FT-IR spectra are depicted in Figure 2. FT-IR analysis of Ni–Al hydrotalcite was performed to identify the interlayer anions. Ni–Al−NO3− exhibits a broad band around 3480 cm⁻¹, which is attributed to the OH-stretching. The band at around 1380 cm⁻¹ is assigned to the NO3− anion. A small band is observed at 1718 cm⁻¹, which is assigned to the C=O vibration close to the bending vibration of water at 1615 cm⁻¹.30

The TG curve of Ni–Al hydrotalcite shows mass loss in three steps, corresponding to three endothermic peaks (Figure 3). TG analysis of the double-layered Ni–Al nanocatalyst demonstrated 10% weight loss up to 150 °C, corresponding to the broad endothermic effect with the elimination of water, physically absorbed on the external surface of the particles.31 A further decrease in weight of about 7% observed above 200 °C may be attributed to the removal of water from the brucite layer.32 In the third peak, 9% of mass loss was found up to 800 °C.

Figure 4 shows the typical SEM image of Al–Ni–NO3− hydrotalcite. It has been observed that the particles are found with almost spherical aggregates of hexagonal plateletlike sheets.33 When XRD analysis of hexagonal (analyzed by SEM) Ni–Al hydrotalcite was performed, XRD has shown characteristic results, which confirmed the Ni–Al hydrotalcite-like structure. This observation by SEM and XRD is in good agreement and confirmed the hydrotalcite-like structure.34

The morphology of Ni–Al hydrotalcite was examined by TEM analysis, and micrographs are shown in Figure 5. Reduction of Ni–Al hydrotalcite results in round-shaped nanoparticles of Ni, despite a higher loading of NiO. Size distribution of Ni nanoparticles was narrow with a mean size of 4 nm obtained by the Scherrer equation, which confirmed that the Ni–Al HT precursor produced a well-dispersed Ni-HT catalyst.35 The crystallite size obtained by the Scherrer equation is listed in Table 1. In the XRD pattern, the characteristic diffraction peak at 48° (2θ value) can be indexed to the (110) plane of face-centered cubic Ni.36 These observations by TEM and XRD are in good agreement and confirmed the Ni–Al hydrotalcite structure with good dispersion of Ni. The literature has also confirmed the good dispersion of Ni nanoparticles in Ni-containing solid catalysts by TEM and XRD analyses.37

Crystallinity of the catalyst can be affected by hydrothermal aging. Cavani et al. have discussed some aspects of the hydrothermal treatment of hydrotalcite-like compounds.4 The hydrothermal treatment was also applied to improve the crystallinity of some layered double hydroxides (LDHs) containing nickel: Ni–Al and Ni–Cr,52 Ni–Al–Cr and Ni–Al–Fe,53 and Ni–Fe.34 The hydrothermal treatment of Ni–Al LDHs using microwave heating was also reported.35,36 A longer aging time was in favor of an increase in the crystallinity, resulting in good catalytic activity.37 At different aging times, crystallite size has been calculated using XRD. Results of XRD analysis have been given in Table 1. Initially, at 0 h, poor crystallinity was observed, which has improved at 3.0 h and at 110 °C. A marked increase of the LDH crystallite size (calculated using Scherrer’s formula) was observed after 6–9 h. To confirm the crystallinity, scanning electron microscopy has also been carried out, which showed a well-defined platelet and layered structure. As shown in Figure 6, crystallinity was low at 0 h aging time. Increment in crystallinity was found further at 110
°C temperature for 3 h (hydrothermal treatment temperature), which increased sharply at 6–9 h. Results of the hydrothermal treatment have shown increase in the crystallinity of the HTlc Ni–Al sample. From the results, it is clear that the aging time and temperature have an impact on the crystallinity of hydrotalcite because of the increase in the crystallite size on increasing the aging time at 110 °C. The catalyst that was aged at 9.0 h showed good catalytic activity in chemoselective synthesis and was used in the present study. Results showed that crystalline nature improved the catalytic activity of the catalyst and showed excellent yield in chemoselective synthesis of benzamide.

2.2. Chemistry. We report a study on the reaction between benzyol chloride and 2-aminophenol to obtain N-(2-hydroxyphenyl)benzamide in the presence of a double-layered catalyst (Scheme 1). Initially, to optimize the reaction conditions, the reaction of benzyol chloride and 2-aminophenol was carried out with different catalysts (Table 2). The influence of bases such as Al(OH)₃, Ca(OH)₂, Al(NO₃)₃·H₂O, and Ni(NO₃)₂·6H₂O was examined. It is clear that excellent yield was obtained with double nanocatalyst (Ni–Al–NO₃⁻) (Table 2, entry 4). The catalyst Al–Co–Cl⁻ showed moderate yield as compared to that with remaining base catalysts.
Next, to optimize the amount of catalyst, the reaction of benzoyl chloride and 2-aminophenol was studied under solvent-free conditions in the presence of the double-layered catalyst (Ni−Al−NO3−). Table 3 showed that when the concentration of catalyst was increased from 0.02 to 0.1 g, the yield also increased (99%). However, there was no significant impact of a higher concentration of catalyst (0.15 g) on the yield and reaction time. Hence, it could be concluded that 0.1 g of catalytic amount was optimal.

We also examined the effect of temperature and time. As shown in Table 4, excellent yield was obtained at 60 °C, which decreased at lower temperature. It has been shown that a temperature of 60 °C is suitable to perform the reaction. From Table 4, the best yield was observed at 30 min, which decreased with reaction time. Therefore, it can be concluded that the optimum time for completion of the reaction is 30 min.

Substituted benzamides have been synthesized under optimized reaction conditions with excellent yield. The yield of target products (range 89−99%) has been mentioned in Table 5, which shows no impact of electron-donating and electron-withdrawing groups.

Substituted N-(2-hydroxyphenyl)benzamides (3a−h) have been synthesized successfully. Compounds 3a−d were characterized by reported melting points and spectral data (mass, IR, 1H, and 13C NMR). The compound 3a is known in the literature, and the identity of this compound was confirmed by the comparison of melting point. The IR spectra showed a strong absorption at 1710 cm−1, which can be ascribed to the C=O group. The IR band at ≈3300 cm−1 confirmed the O−H stretch, and a stretch band has been found at 1516 cm−1 because of the N−H stretch of the amino group. The 1H NMR spectra showed a characteristic singlet of methoxy proton (−OCH3) at δ 3.81, and other protons of phenyl moieties appeared in the aromatic region δ 8.11−6.96. The characteristic peaks appeared at 10.65 and 9.52 ppm for O−H and N−H, respectively. The wagging band at 1300 cm−1 has confirmed a chlorine group in 3c, and the stretching bands at 1517, 1347, and 852 cm−1 have been assigned to the NO2 group in product 3b. The bands at 2950, 2835, 1247, and 2000−1650 cm−1 (overtone combination region) confirmed the methoxy group in compound 3d.

The reusability and effectiveness are the key features of the catalytic activity for industrial and commercial applicability. The catalyst has been reused successfully without loss of significant yield of the target product. The recovered catalyst has been characterized by SEM (Figure 5C) and TEM images (Figure 6C), which confirmed that the catalyst has retained its structure after recyclability. XRD data of recovered hydrotalcite also showed a profile similar to the one of the fresh catalyst, which confirmed that the layered structure of hydrotalcite was maintained after the reaction (Figure 7).

3. CONCLUSIONS

We have developed a Ni−Al double-layered catalyst for the chemoselective synthesis of N-(2-hydroxyphenyl)benzamide derivatives using 2-aminophenol and benzoyl chloride with excellent yield in short reaction time under solvent-free conditions. The morphology and characterization of the catalyst were confirmed by XRD, IR, TG, SEM, and TEM analyses. XRD

![Figure 5. TEM image of the Ni−Al hydrotalcite fresh catalyst at (A) 100 nm and (B) 50 nm and of (C) recovered catalyst at 100 nm.](image-url)
analysis demonstrated diffraction patterns that confirmed the hydrotalcite structure. TG analysis (TGA) and IR analysis have been performed to identify the interlayer anions and confirmed the structure. The effect of aging time at 110 °C has been investigated, and it was found that aging time has affected the particle size of the nanomaterial and high crystallinity was achieved. It was observed that crystallinity was increased after

**Figure 6.** Relation between SEM and aging study.

**Table 2. Synthesis of N-(2-Hydroxyphenyl)benzamide Using Various Catalysts**

| entry | catalysts         | yield (%) |
|-------|------------------|-----------|
| 1.    | catalyst free    | 35        |
| 2.    | Al−Mn−Cl−        | 56        |
| 3.    | Al−Co−Cl−        | 74        |
| 4.    | Al−Ni−NO−        | 99        |
| 5.    | Al−Cu−Cl−        | 40        |
| 6.    | Al−Mg−NO−        | 52        |
| 7.    | Al(OH)₃          | 35        |
| 8.    | Ca(OH)₂          | 52        |
| 9.    | Al(NO₃)₂·H₂O     | no reaction |
| 10.   | Ni(NO₃)₂·6H₂O    | no reaction |

**Table 3. Effect of Catalyst Concentration**

| entry | Al−Ni−NO₃ (HT in g) | time (min) | yield (%) |
|-------|---------------------|------------|-----------|
| 1     | 0.02                | 30         | 50        |
| 2     | 0.05                | 30         | 75        |
| 3     | 0.07                | 30         | 80        |
| 4     | 0.10                | 30         | 99        |
| 5     | 0.15                | 30         | 99        |

**Table 4. Effect of Temperature and Time**

| entry | time (min) | temperature (°C) | yield (%) |
|-------|------------|------------------|-----------|
| 1     | 60         | 25               | 71        |
| 2     | 60         | 40               | 90        |
| 3     | 60         | 60               | 99        |
| 4     | 60         | 80               | 82        |
| 5     | 30         | 60               | 99        |
| 6     | 90         | 60               | 82        |
| 7     | 180        | 60               | 75        |

**Table 5. Synthesis of Benzamide Derivative Using the Ni−Al Double-Layered Nanocatalyst**

| entry | R | R′ | product | yield (%) |
|-------|---|----|---------|-----------|
| 1     | 3a|    | 99      |
| 2     | 3b|    | 99      |
| 3     | 3c|    | 99      |
| 4     | 3d|    | 91      |
| 5     | 3e|    | 89      |
| 6     | 3f| 2,4-OCH₃ | 90      |
| 7     | 3g| 4-Cl | 91      |
| 8     | 3h| 5-Cl | 94      |

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| entry | catalysts         | yield (%) |
|-------|------------------|-----------|
| 1.    | catalyst free    | 35        |
| 2.    | Al−Mn−Cl−        | 56        |
| 3.    | Al−Co−Cl−        | 74        |
| 4.    | Al−Ni−NO−        | 99        |
| 5.    | Al−Cu−Cl−        | 40        |
| 6.    | Al−Mg−NO−        | 52        |
| 7.    | Al(OH)₃          | 35        |
| 8.    | Ca(OH)₂          | 52        |
| 9.    | Al(NO₃)₂·H₂O     | no reaction |
| 10.   | Ni(NO₃)₂·6H₂O    | no reaction |

**Table 3. Effect of Catalyst Concentration**

| entry | Al−Ni−NO₃ (HT in g) | time (min) | yield (%) |
|-------|---------------------|------------|-----------|
| 1     | 0.02                | 30         | 50        |
| 2     | 0.05                | 30         | 75        |
| 3     | 0.07                | 30         | 80        |
| 4     | 0.10                | 30         | 99        |
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| 7     | 180        | 60               | 75        |

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| 1     | 3a|    | 99      |
| 2     | 3b|    | 99      |
| 3     | 3c|    | 99      |
| 4     | 3d|    | 91      |
| 5     | 3e|    | 89      |
| 6     | 3f| 2,4-OCH₃ | 90      |
| 7     | 3g| 4-Cl | 91      |
| 8     | 3h| 5-Cl | 94      |

**Isolated yield.**
5. EXPERIMENTAL SECTION

5.1. Preparation of Hydrotalicates. Aluminum- and nickel-containing double-layered nanomaterials (ratio 1:3) were synthesized by charging 1 M solution of NaOH (1 mL/min charging rate) in a mixture of 0.1 M Al(NO$_3$)$_3$·9H$_2$O (2.31 g) and 0.3 M Ni(NO$_3$)$_2$·6H$_2$O (8.72 g) until the pH was adjusted to a range of 10–11. Afterward, a slurry was observed with crystallized particles at this pH, which was further stirred for 2 h under heating. Then, the slurry was cooled and the precipitate was filtered followed by washing with 500 mL of deionized water. The wet solid was dried at 100 °C in air oven for 24 h.

5.2. Synthesis of N-(2-Hydroxyphenyl)benzamide. To a round-bottomed flask equipped with a magnetic stirrer were added benzylo chloride (0.108 g, 1 mmol), 2-aminophenol (0.15 mL, 1.3 mmol), and the prepared catalyst (0.10 g). The resulting mixture was heated at 60 °C. Reaction completion has been monitored by TLC analysis (ethyl acetate/hexane as a solvent; 1:4 ratio, respectively). After completion of reaction that was monitored by TLC, the reaction mixture was cooled to room temperature. Then, acetone was added followed by filtration to obtain N-(2-hydroxyphenyl)benzamide as the target product.

5.3. Characterization Data. 5.3.1. N-(2-Hydroxyphenyl)-4-nitrobenzamide. Mp 165–167 °C; IR (KBr): $\nu$ (cm$^{-1}$) 3410 (O–H stretch), 2950 (C–H stretch aromatic), 1710 (C=O stretch), 1573 (C–C stretch aromatic), 1465 (C=C stretch aromatic), 748 (C–H bending); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 6.81–7.40 (m, SH, Ar–H), 7.73–8.10 (m, 4H, Ar–H), 9.65 (s, 1H, OH), 10.52 (s, 1H, NH); $^{13}$C NMR (75 MHz, DMSO-$d_6$): 166, 139, 133, 130, 128, 128, 127, 124, 120; electrospray ionization mass spectrometry (ESI-MS): m/z Calcd for C$_{13}$H$_{11}$NO$_3$: 213.08. Found [M$^+$] 213.

5.3.2. N-(2-Hydroxyphenyl)-4-nitrobenzamide. Mp 180–182 °C; IR (KBr): $\nu$ (cm$^{-1}$) 3410 (O–H stretch), 2990 (C–H stretch aromatic), 1720 (C=O stretch), 1568 (C–C stretch aromatic), 1516 (N–H stretch), 1465 (C=C stretch aromatic), 1347 (N=O stretch), 852 (C=N stretch Ar–NO$_2$), 748 (C–H bending); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 10.52 (s, 1H, NH), 6.81–7.40 (m, 4H, Ar), 7.73–8.10 (m, 4H, Ar–H), 9.65 (s, 1H, OH); $^{13}$C NMR (75 MHz, DMSO-$d_6$): 166, 157, 131, 130, 129, 128, 124, 123, 120; ESI-MS: m/z Calcd for C$_{13}$H$_{11}$NO$_3$: 258.06. Found [M – H]$^-$ 257.

5.3.3. N-(2-Hydroxyphenyl)-2-chlorobenzamide. Mp 246–248 °C; IR (KBr): $\nu$ (cm$^{-1}$) 3320 (O–H stretch), 1630 (C–O stretch), 1530 (C–C stretch aromatic), 1460 (N–H stretch), 1465 (C=C stretch aromatic). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 10.52 (s, 1H, NH), 7.26–7.99 (m, 4H, Ar–H), 9.36 (s, 1H, OH), 9.65 (s, 1H, NH); $^{13}$C NMR (75 MHz, DMSO-$d_6$): 163, 136, 130, 128, 127, 126, 126, 120, 119; ESI-MS: m/z Calcd for C$_{12}$H$_{10}$ClNO$_2$: 247.04. Found [M$^+$] 246.6.

5.3.4. N-(2-Hydroxyphenyl)-4-methoxybenzamide. Mp 167–169 °C; IR (KBr): $\nu$ (cm$^{-1}$) 3410 (O–H stretch), 2950 (C–H stretch aromatic), 2839 (stretching in OCH$_3$), 1645 (C–O stretch), 1573 (C–C stretch aromatic). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 3.84 (s, 1H, OCH$_3$), 6.81–7.40 (m, 4H, Ar–H), 7.73–8.10 (m, 4H, Ar–H), 9.65 (s, 1H, NH), 9.65 (s, 1H, OH); $^{13}$C NMR (75 MHz, DMSO-$d_6$): 166, 157, 131, 130, 129, 128, 124, 123, 120; ESI-MS: m/z Calcd for C$_{13}$H$_{12}$O$_3$ClNO$_2$: 247.04. Found [M$^+$] 246.6.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01994.

General experimental procedure and details of characterization data of the products (PDF)

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The authors declare no competing financial interest.

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