

Oxidation of Benzylic Alcohols and Lignin Model Compounds with Layered Double Hydroxide Catalysts

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Catalyst Preparation

Ni-Cu-Cr-LDH

The metal solution contained $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (30.92 g, 0.128 mol), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (38.71 g, 0.133 mol), and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (53.24 g, 0.133 mol) in 212 mL of deionized water. The base solution contained NaOH (2.73 M) and Na_2CO_3 (0.85 M). The pH was maintained between 7.3 and 7.8 during precipitation of the LDH.

Cu-Cr-LDH

Cu-Cr-LDH was prepared as for Ni-Cu-Cr LDH. The metal solution contained $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (62.12 g, 0.257 mol), and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (53.16 g, 0.133 mol) in 211 mL of deionized water. The base solution contained NaOH (2.82 M) and Na_2CO_3 (0.86 M). The pH was maintained between 7.7 and 8.1 during the precipitation of the LDH.

Ni-Cr-LDH

The metal solution contained $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (38.74 g, 0.133 mol) and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (26.67 g, 0.067 mol) in 210 mL of deionized water. The base solution contained NaOH (1.42 M) and Na_2CO_3 (0.57 M). The pH was maintained between 9 and 10 during precipitation of the LDH.

Mg-Al-LDH-1

Mg-Al-LDH-1 was prepared as for Ni-Cr-LDH. The metal solution contained $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (38.47 g, 0.150 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (18.76 g, 0.05 mol) in 210 mL of deionized water. The base solution contained NaOH (1.45 M) and Na_2CO_3 (0.60 M).

Mg-Al-LDH-2

Mg-Al-LDH-2 was prepared as for Ni-Cr-LDH. The metal solution contained $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (41.02 g, 0.160 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (15.01 g, 0.04 mol) in 210 mL of deionized water. The base solution contained NaOH (1.46 M) and Na_2CO_3 (0.60 M).

Ni-Al-LDH-1

Ni-Al-LDH-1 was prepared as for Ni-Cr-LDH. The metal solution contained NaOH $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (38.98 g, 0.134 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (24.71 g, 0.066 mol) in 210 mL of deionized water. The base solution contained NaOH (1.41 M) and Na_2CO_3 (0.60 M).

Ni-Al-LDH-2

Ni-Al-LDH-2 was prepared as for Ni-Cr-LDH. The metal solution contained $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (43.61 g, 0.150 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (18.72 g, 0.05 mol) in 210 mL of deionized water. The base solution contained NaOH (1.41 M) and Na_2CO_3 (0.60 M).

Catalyst Leaching Study

1-phenyl ethanol (2 mmol), phenyl ether (10 mL), and Ni-Cr (2:1) LDH (0.5 g) were added to a three-necked flask equipped with an oxygen bubbler, a reflux condenser, and a glass stopper. The reaction was stirred at 150 °C for 1 h and then hot filtered to remove the catalyst. A sample of the filtrate was taken for GC-FID analysis and the remainder was added to a fresh three-neck flask equipped with an oxygen bubbler, a reflux condenser, and a glass stopper. The reaction mixture was stirred at 150 °C for an additional 23 h. Conversion, selectivity, and yield were determined *via* the GC-FID method below. The amount of metal leached was determined by ICP-OES.

Catalyst Reusability

The study was carried out using the same proportions of catalyst, solvent, and starting material as in the general procedure. Before each use, the Ni-Al-LDH-1 catalyst was thermally pretreated at 175 °C for 3 h (no thermal pretreatment was performed on the Ni-Cr-LDH). The reaction mixture was stirred at 150 °C, sample aliquots (0.1 mL) being taken at 0.5 h, 1 h, 2 h and added to 0.9 mL of toluene. Each sample was filtered with a PTFE membrane syringe filter (0.2-0.45 µm). After the reaction was finished, the reaction was quenched in an ice bath and THF (10-15 mL) was added to the reaction mixture. The contents were then filtered through a PTFE membrane (0.2-0.45 µm) and the catalyst was washed with THF and hexanes. The catalyst was then placed in a vacuum oven overnight at 50 °C to dry. Conversion, selectivity, and yield were determined using the GC-FID method below. After the third cycle, 0.2 g of the catalyst was washed with 50 g of 10% Na₂CO₃ in deionized water. The mixture was allowed to stir overnight. The mixture was then centrifuged and washed (cyclically) with DI water until the supernatant was of neutral pH. After drying overnight in a vacuum oven, the Ni-Al-LDH-1 catalyst was thermally pretreated at 175 °C for 3 hours (no thermal pretreatment was performed on the Ni-Cr-LDH) and then added to the reaction mixture in the same proportions as noted in the general procedure.

Synthesis of Lignin Model Compounds

Synthesis of Compounds 4d and 5d

A suspension of guaiacol (16.56 g, 138 mmol), potassium carbonate (21.1 g, 153 mmol), and acetone (140 mL) was cooled to 0 °C and 2-bromo-4'-methoxyacetophenone (24.3 g, 106 mmol) was added slowly. After the addition, the reaction was heated to reflux and held overnight. The mixture was then allowed to cool, filtered through a pad of Celite®, and concentrated *in vacuo*. The resulting solid was dissolved in ethyl acetate (200 mL) and then washed with 1 M sodium hydroxide (75 mL x 3), followed by brine (100 mL x 2), and dried over anhydrous sodium sulfate. After filtration, the product was concentrated *in vacuo*. The resulting red-brown solid was recrystallized using acetone/water resulting in a white solid (20.3 g, 71%).

yield). GCMS: m/z 272.1 (20%), 135.1 (100%), 121.1 (7%) and $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 8.04-7.98 (m, 2H), 6.98-6.94 (m, 2H), 6.92-6.78 (m, 4H), 5.15 (s, 2H), 3.36 (s, 3H), 3.17 (s, 3H). The $^1\text{H-NMR}$ spectrum is consistent with spectra previously reported by Dawange *et al* [45]. Compound **5** was synthesized in an analogous manner to compound **4**. The synthesis of compound **5** resulted in a white powder (29.7 g, 94% yield): GCMS: m/z 272.1 (24%), 135.1 (100%), 77.1 (15%) and $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 8.02-7.96 (m, 2H), 6.98-6.82 (m, 6H), 5.28 (s, 2H), 3.88 (s, 3H), 3.87 (s, 3H). The $^1\text{H-NMR}$ spectrum was consistent with the spectrum previously reported by Lee *et al* [46].

Synthesis of Compounds **4** and **5**

Following the synthesis of **4d**, a solution of tetrahydrofuran (150 mL), methanol (300 mL), and **4d** (8 g, 29 mmol) were cooled to 0 °C. Sodium borohydride (1 g, 26 mmol) was then added and the reaction mixture was allowed to stir at room temperature overnight. The reaction was then concentrated *in vacuo* and extracted with ethyl acetate (100 mL x 2). The resulting organic layer was then extracted with brine (50 mL x 3) and dried over anhydrous magnesium sulfate. The solvent was then removed *in vacuo* to afford a white solid with a low melting point (*ca.* 40 °C) (8.1 g, 99% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 7.37-7.7.35 (d, 2H), 7.01-6.89 (m, 6H), 5.08-5.02 (d, 1H), 4.17-4.12 (d, 1H), 4.0-3.92 (dd, 1H), 3.89 (s, 3H), 3.81 (s, 3H). The $^1\text{H-NMR}$ spectrum was consistent with spectra previously reported by Dawange *et al* [45]. Compound **5**, previously reported by Ren *et al* [47], was synthesized in an analogous manner to compound **4**. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 7.40-7.7.35 (d, 2H), 6.94-6.80 (m, 6H), 5.08-5.02 (dd, 1H), 4.04-3.90 (m, 2H), 3.82 (s, 3H), 3.77 (s, 3H).

Synthesis of Compound **6**

Compound **4d** (3.5 g, 12.8 mmol) was added to a suspension of formaldehyde [37% in water, (1.6 g, 19.2 mmol)], potassium carbonate (2.3 g, 15.4 mmol), and ethanol (205 mL). The suspension was stirred at room temperature for approximately 2 h before the addition of sodium borohydride (1.7 g, 44.8 mmol).

The reaction mixture was then stirred at room temperature for 1 h. After filtration, the reaction mixture was concentrated *in vacuo*, quenched by slowly adding a saturated ammonium chloride solution (20 mL), and filtered. The resulting oil was purified by gradient column chromatography (50% → 100% ethyl acetate in hexanes). After chromatography the product was concentrated *in vacuo*, resulting in a pale yellow oil (1.8 g, 46% yield). ¹H-NMR (400 MHz, CDCl₃) δ: 7.40-7.34 (m, 2H), 7.34-7.29 (m, 2H), 7.15-6.86 (m, 12H), 5.02- 4.98 (m, 2H), 4.18-4.00 (m, 2H), 3.92 (s, 3H), 3.89 (s, 3H), 3.80, (d, 6H), 3.68-3.58 (m, 2H), 3.50-3.40 (m, 2H), 2.74 (br. s., 2 H). The ¹H-NMR spectrum was consistent with spectra previously reported by Dawange *et al* [45].

Gas Chromatography analysis

Gas chromatography (GC) analysis was carried out on an HP 6890A GC equipped with a J&W Scientific DB-Wax Column (30 m x 0.53 mm x 0.50 μm). A 1 μL sample was injected and the inlet was run in split mode (Split Ratio 2.5:1). Helium was used as the carrier gas and the column was held under constant pressure at 20 psi. The flame ionization detector was held at 240 °C. Method A, used for analysis of the oxidation product of **1**, employed an isothermal inlet temperature of 220 °C. The initial oven temperature was 50 °C and was immediately increased to 150 °C at a rate of 5 °C/min and held isothermally for 2 min, resulting in a total run time of 22 min. Method B, used for analysis of the oxidation products of **2**, was similar to Method A with the following changes: The initial oven temperature was 50 °C and was immediately increased to 230 °C at a rate of 10 °C/min and held isothermally for 6 min, resulting in a total run time of 24 min. The inlet temperature was also lowered to 180 °C. Method B was slightly altered by raising the inlet temperature to 220 °C to create Method C, which was used for the analysis of the oxidation products of **3**. All products from the reactions of **1** and **2** were quantified using response factors generated from an external calibration curve created by the use of authentic standards and an internal standard of anisole or guaiacol. When **3** was used as a starting material, 1,4-dimethoxybenzene was used as an internal

standard in the reaction mixture and yields were determined from response factors generated from a calibration curve.

Catalyst Acidity and Basicity Measurements

Pulsed CO₂ chemisorption and NH₃-TPD were performed on a Micromeritics AutoChem II analyzer using 200 mg of sample. In each case, the sample was first outgassed at 120 °C under argon for 1 h. For pulsed CO₂ chemisorption measurements, the sample was then cooled to room temperature and pulsed with CO₂ (100%, 30 sccm) until saturated as indicated by a thermal conductivity detector (TCD). CO₂ was assumed to titrate base sites on a 1:1 molar ratio.

In the case of NH₃-TPD, the pre-treated sample was cooled to room temperature and then saturated with NH₃ (1% in helium, 50 sccm) for 1 h. Next, the sample was purged (helium 100%, 120 sccm) for 1 h. The sample was then heated to 750 °C at 10 °C/min. Effluent gas was analyzed using a mass spectrometer (Pfeiffer ThermoStar GSD301), the signal at $m/e = 15$ being used to monitor NH₃. NH₃ was assumed to titrate acid sites in a 1:1 molar ratio. It should be noted that during TPD, LDH samples decompose to the corresponding mixed oxide, as has been well documented (decomposition is typically complete at ~450 °C). Therefore, the acidity measured by NH₃-TPD must be regarded as highly qualitative.

Catalyst Characterization

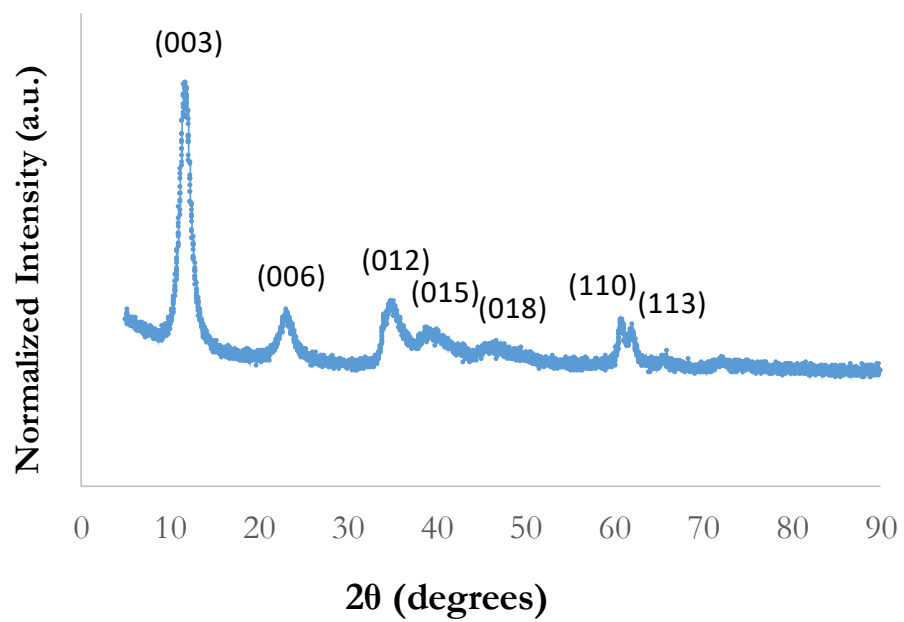


Fig. S1. X-ray diffractogram of Ni-Al-LDH-1 pre-treated at 160 °C

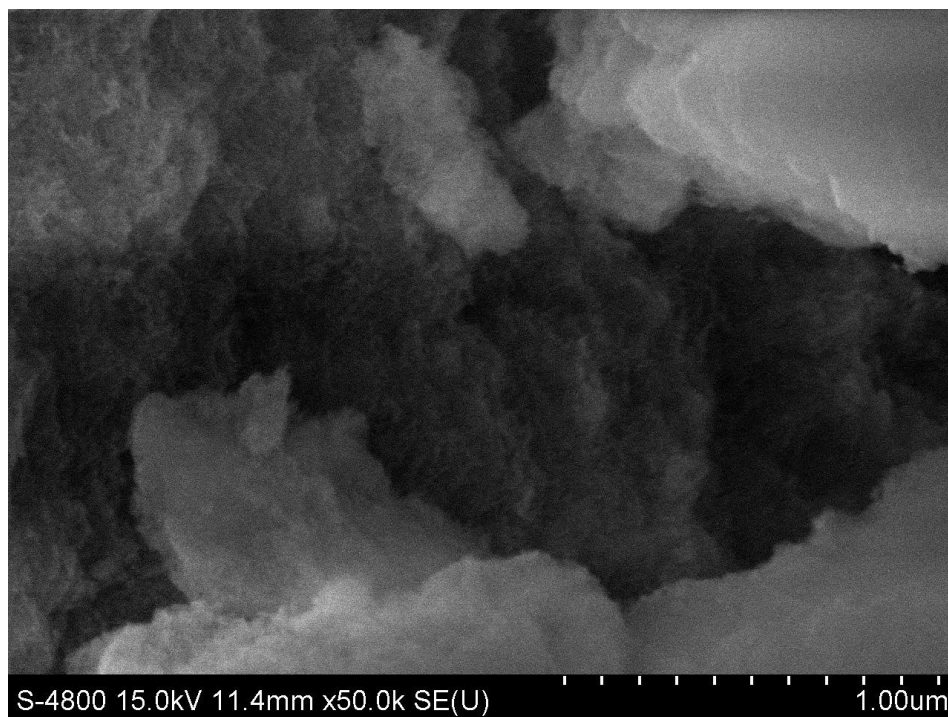


Figure S2. Scanning electron micrograph of Ni-Al-LDH-1

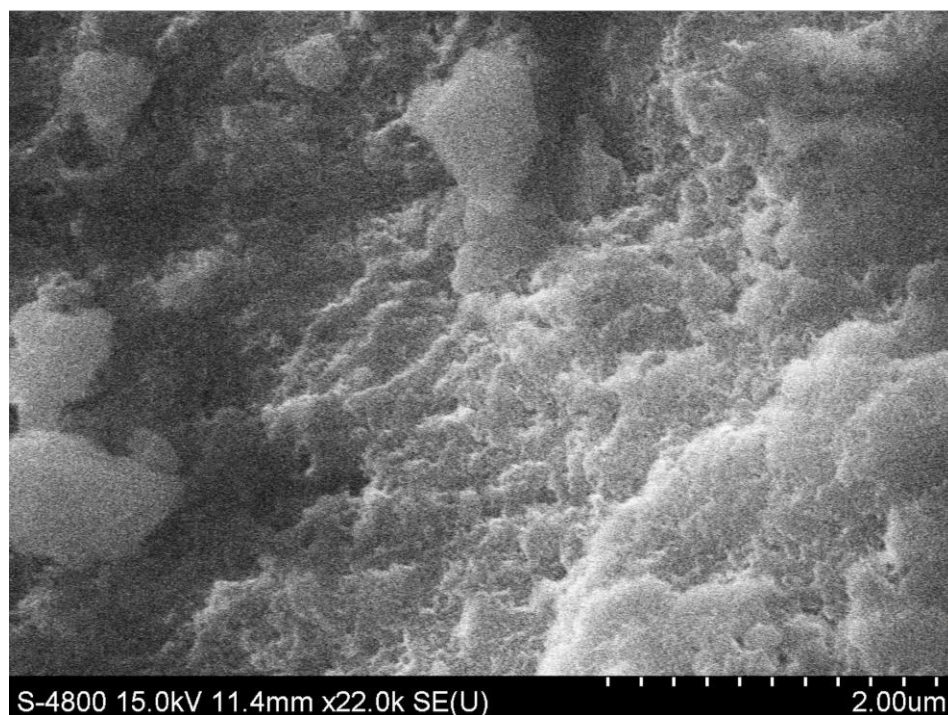


Figure S3. Scanning electron micrograph of Ni-Cr-LDH

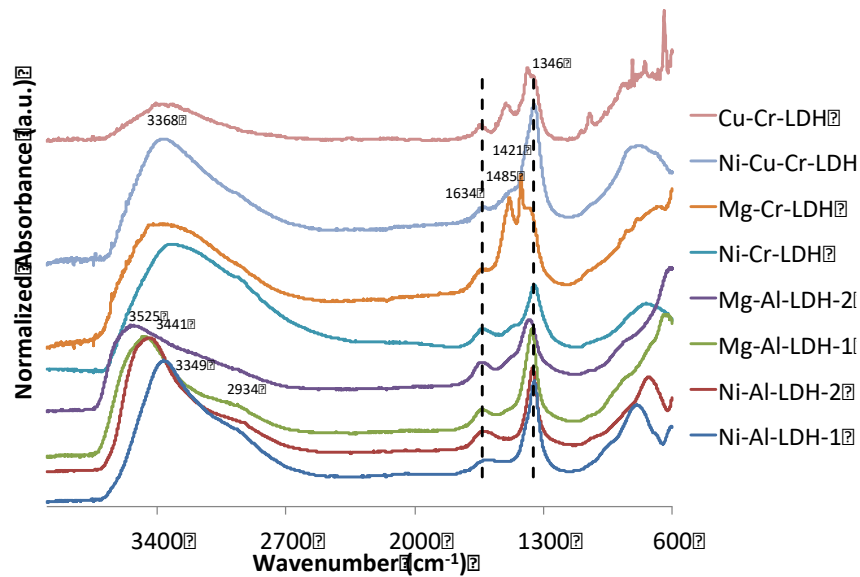


Figure S4. FT-IR analysis of LDH catalysts

Bands at *ca.* 1634 cm^{-1} and *ca.* 1346 cm^{-1} correspond to the bending mode of interlayer water and asymmetric carbonate stretching, respectively (Figure S4) [48]. A similar band at *ca.* 1635 cm^{-1} has been reported for Ni-Al-LDHs [49–51] and Ni-Cr-LDH [52].

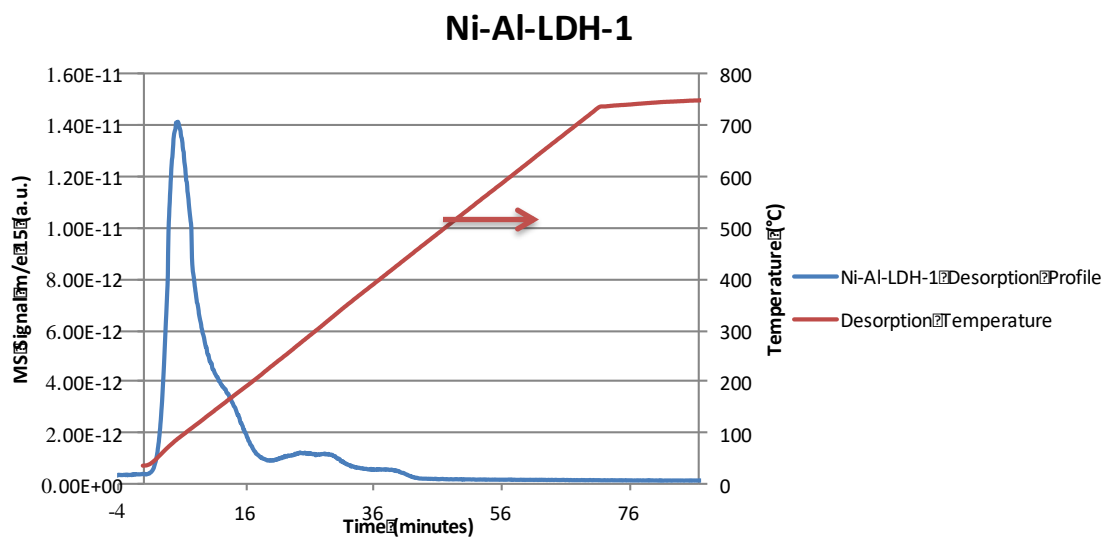


Figure S5. NH_3 -TPD of Ni-Al-LDH-1

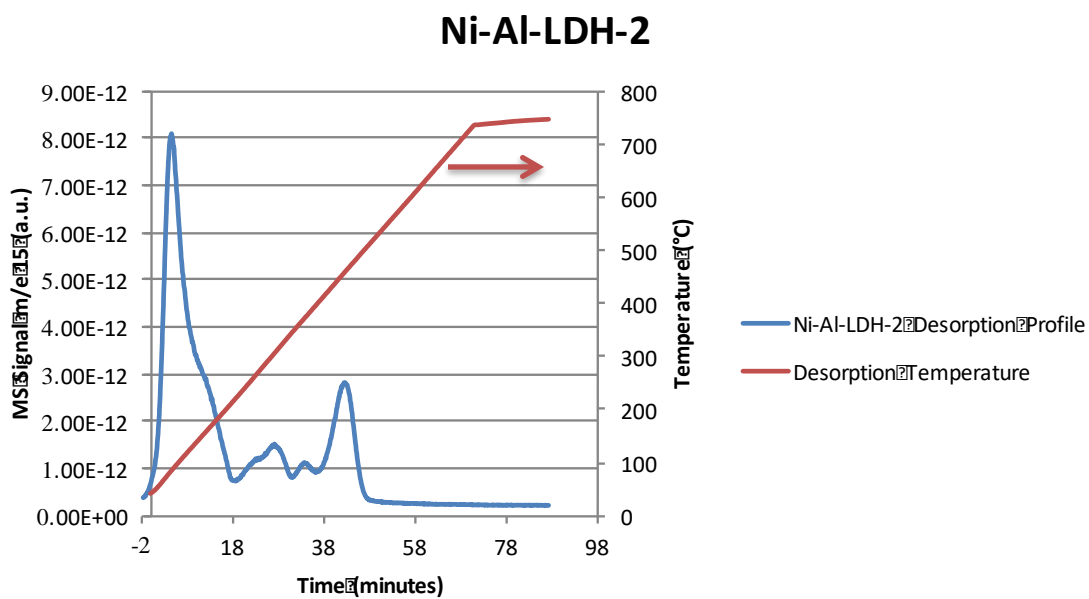


Figure S6. NH_3 -TPD of Ni-Al-LDH-2

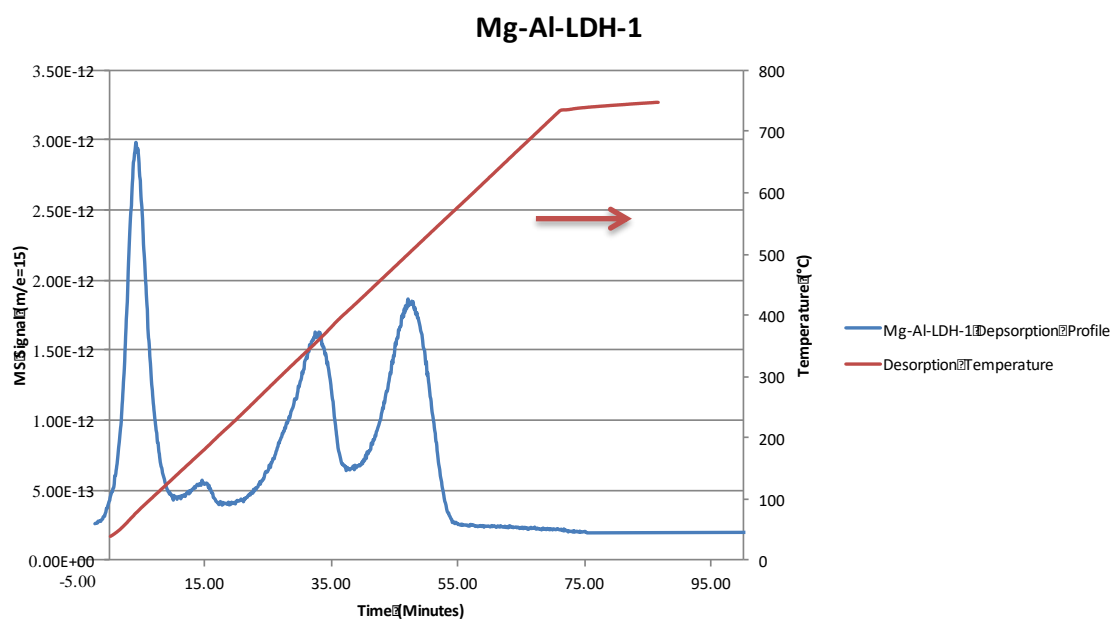


Figure S7. NH_3 -TPD of Mg-Al-LDH-1

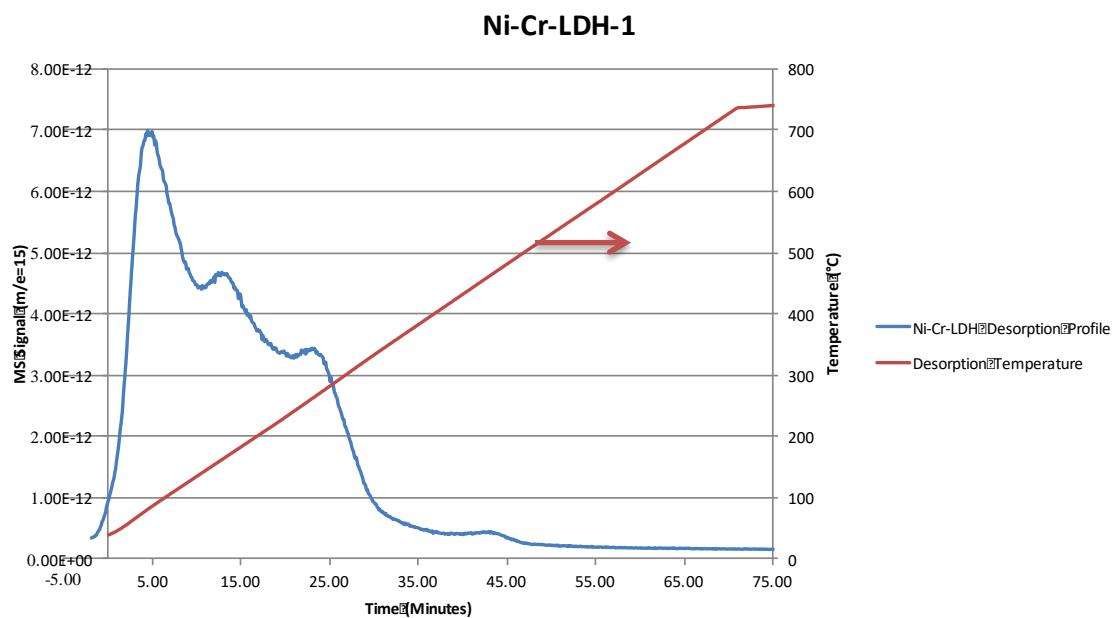


Figure S8. NH_3 -TPD of Ni-Cr-LDH

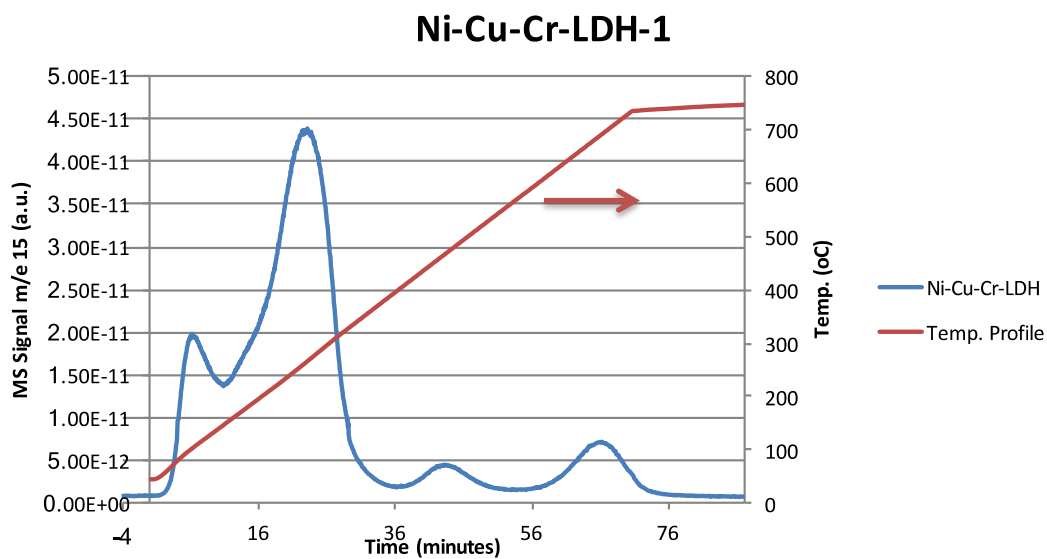


Figure S9. NH_3 -TPD of Ni-Cu-Cr-LDH

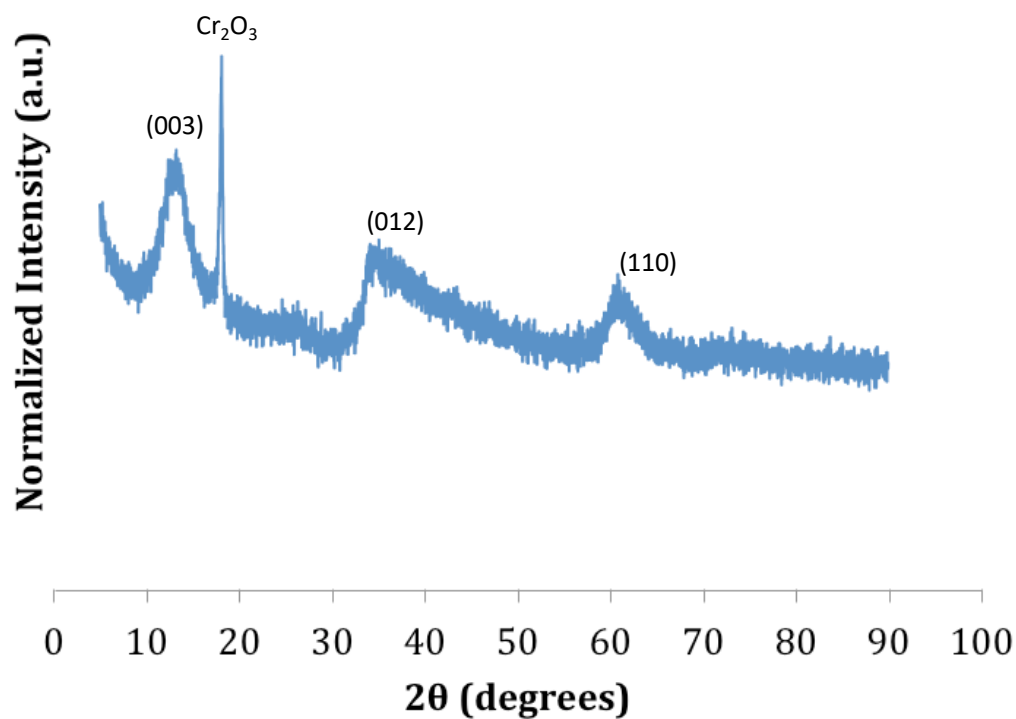


Figure S10. X-ray diffractogram of Ni-Cr-LDH after three cycles of use in the oxidation of 1.

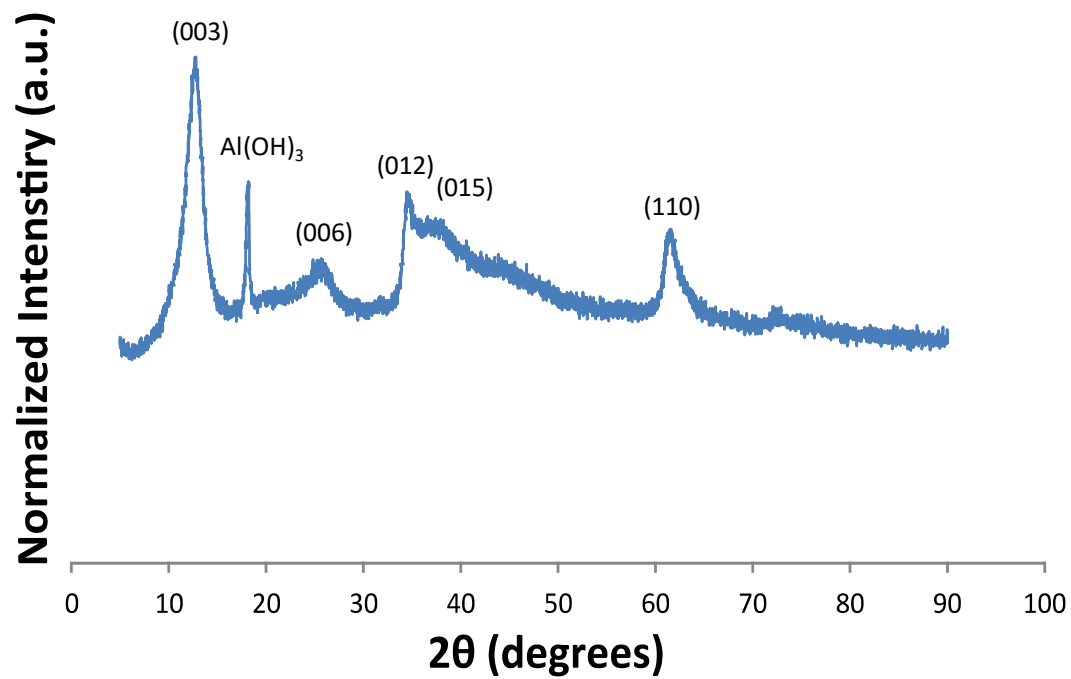


Figure S11. X-ray diffractogram of Ni-Al-LDH-1 after two cycles of use in the oxidation of 1.

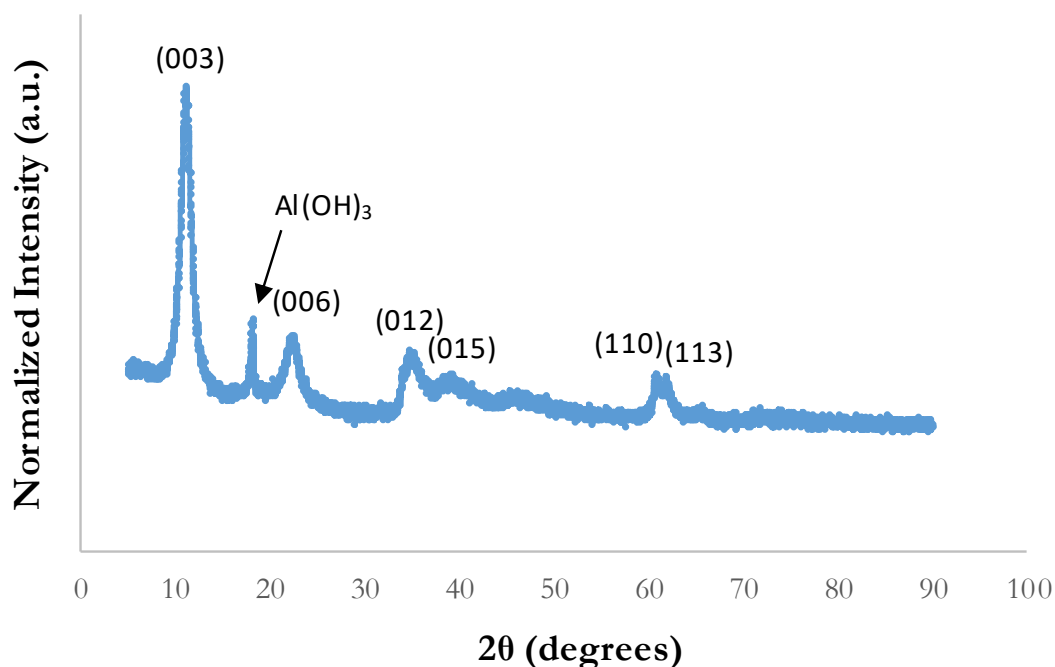


Figure S12. X-ray diffractogram of Ni-Al-LDH-2 after one cycle of use in the oxidation of 2.

References

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