Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supplementary Information

Reagents and Chemicals

All chemicals for precursor solutions were reagent grade and were used as received. Aluminium nitrate ($Al(NO_3)_3.9H_2O$ ≥99%), was purchased from Acros Organics (Geel, Belgium). Sodium carbonate (Na_2CO_3 ≥99%), sodium hydroxide (NaOH ≥98%) and Zinc nitrate ($Zn(NO_3)_2.6H_2O$ ≥99%) were purchased from Sigma Aldrich (Dorset, United Kingdom). Prior to reactions, fresh precursor solutions were prepared by dissolving metal salts in deionised water.

Bench Scale LDH Synthesis

Bench scale synthesis of Zn_2Al-CO_3 LDHs were produced in a counter-current flow reactor arrangement (*Figure 1*). A mixed metal salt solution containing $Zn(NO_3)_2.6H_2O$ (0.067M) and $Al(NO_3)_3.9H_2O$ (0.033M) was flowed up into the reactor at a rate of 10mL min^{-1} (Solution A), while the base (0.125M NaOH) and Na_2CO_3 (0.0167M) flowed down into the reactor at 20mL min^{-1} (Solution B). Pressure in the system was maintained at 24MPa by a back pressure regulator (Pressure Tech, UK), while temperature adjustment of the reaction system was not used and solutions were used at ambient temperature (approximately 20°C). The volumetric flow rate ratio of 2:1 down-flow to up-flow was maintained for all experiments. Following synthesis, the samples were washed by centrifugation (4000rpm), with deionised water until the counter ions were removed. The samples were freeze dried for 48 hours ready for characterisation.

Pilot Scale Synthesis

Pilot synthesis of LDHs was carried out on a pilot scale system with increased flow rates (total flow rate - 600mL min^{-1}). The precursor reagents in the mixed metal solution (Solution A) were maintained at the same concentration as the bench scale system. The reagents in solution B were also maintained at the same concentration as the bench scale system. The volumetric flow rate ratio of down-flow feed to up-flow feed was maintained in the scaling up process at 2:1 down-flow to up-flow. Temperature was maintained at ambient conditions, while pressure was maintained by a back pressure regulator (Pressure Tech, UK) at 24MPa. Following synthesis, the bulk product was held in drums to allow the LDH to settle into a concentrated suspension before washing. The samples were washed by centrifugation with deionised and freeze dried for 48 hours prior to characterisation.

Industrial Scale Synthesis

Industrial scale synthesis was carried with precursor reagents in the Solution A and B, maintained at the same concentration as the bench scale and pilot scale reactions. Temperature was maintained at 18±2°C. Pressure was maintained at 24MPa. The volumetric flow rate ratio of down-flow feed to up-flow feed was maintained in the scaling up process at 2:1 down flow to up flow, however, the total flowrate in the reaction was 1050L h^{-1}. Following synthesis, a sample of the bulk product suspension was taken from an isolation valve. This sample was centrifuged and washed in the same process as bench and pilot scale synthesis and freeze dried. The rest of the bulk suspension was washed with deionised water via a washing system specifically designed for the industrial scale plant.

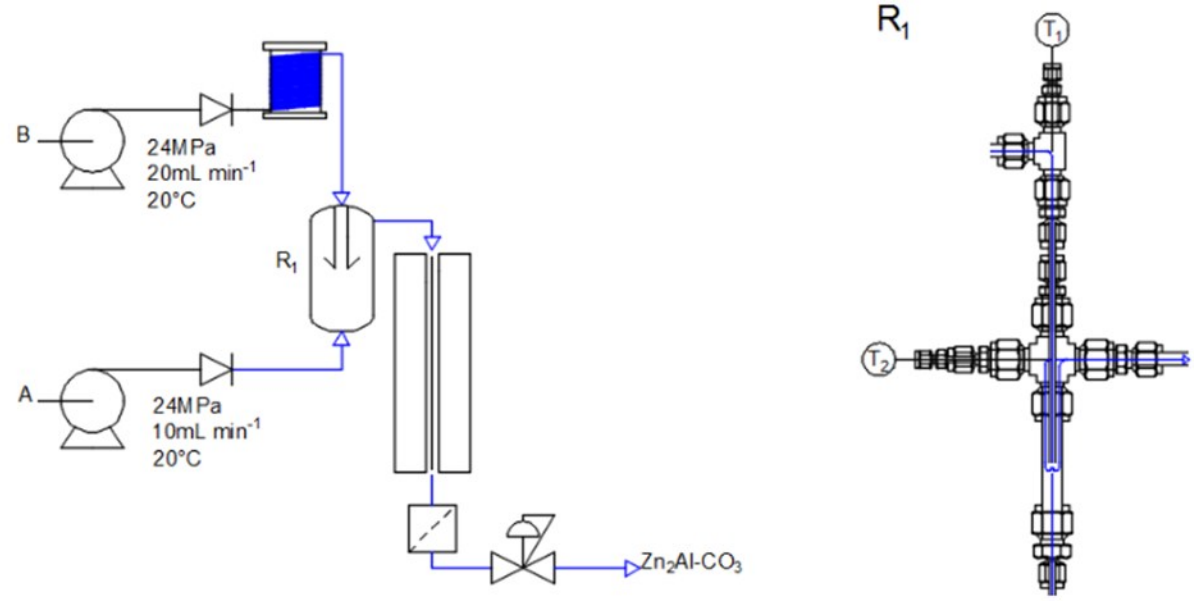

Figure 1 Bench Scale Reaction Schematic and technical drawing of reactor piece

Space-Time Yield Calculation

Space-time yields were calculated based on the approximate amount of dried mass produced per hour (m_P) of synthesis, and the volume of the reactor section covering the length of the inner tube (Figure 2)

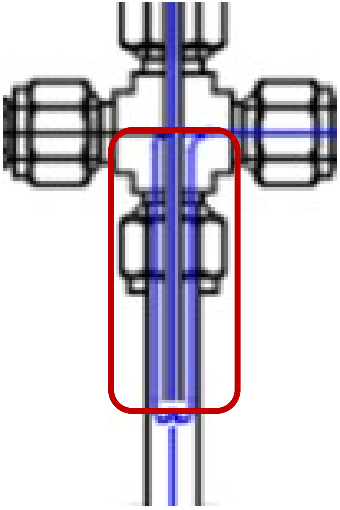

Figure 2 Space-time yield reactor volume (V_R)

$$STY = \frac{m_P}{V_R}$$

Bench scale reactor

		Units
Reactor piece internal volume (V_R)	0.00079	L
Production rate (m_P)	0.005	kg h^{-1}
Precursor flowrate	1.8	L h^{-1}
Space-time yield of bench scale reaction	6.3	kg L^{-1} h^{-1}

Materials Characterisation

X-Ray diffraction on dried samples was carried out on a Bruker D8 Advance Diffractometer. The analysis range was 5-70° 2θ, at a scan rate of 1.5° $\min^{-1}$. For calculation of crystal domain length, scan rate was reduced to 0.075° $\min^{-1}$ in order to reduce background radiation as much as possible to be in-line with a LaB_6 standard sample. Crystal domain length was calculated using the FWHM of the (003) and (110) reflections from the diffractogram and the Scherrer equation. Morphology and surface topography were investigated using a Phillips XL30 SEM with a tungsten filament and acceleration voltage was 20kV. Chemical analysis of the LDHs was completed on the same Phillips XL30 with an Oxford Instruments EDS detector with a spectral range of 0-10eV. Platelet size and further investigation of crystallite size was performed on a JEOL 2100+ TEM where acceleration voltage was set to 200kV. Surface area analysis was carried out on Micromeritics Tristar 3020 instrument. Adsorption isotherms were collected on degassed samples (under vacuum at 100^oC overnight) using nitrogen as the adsorptive gas. Specific surface area was calculated using the BET isotherm at partial pressures between 0.05 and 0.3 P/P_o. Pore diameter and pore volume were calculated from the Barret-Joyner-Halenda (BJH) model using the desorption branch of the adsorption isotherm.

SEM-EDS and Molar Ratio

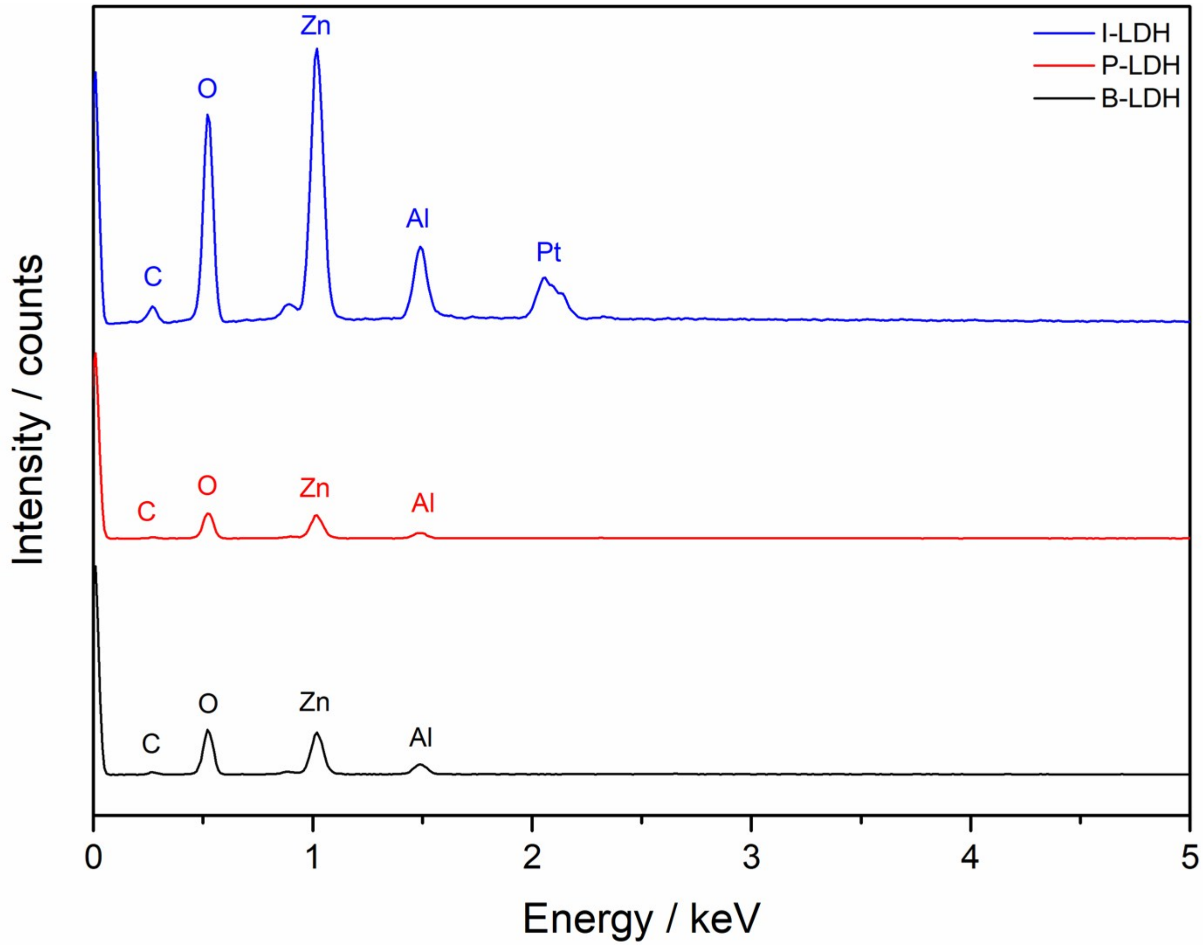

Figure 3 SEM-EDS spectra for bench (B-LDH), pilot (P-LDH) and industrial (I-LDH) scale materials

The SEM-EDS spectra for the I-LDH sample contains platinum from the thin film deposited by vacuum sputter coating (Agar Scientific), for the bench and pilot scale samples carbon was used to generate the conductive surface. The Zn/Al ratio was determined form the molar concentrations of the identified elements in their oxide forms (Table 1)

Table 1 SEM-EDS molecular content of bench (B-LDH), pilot (P-LDH) and industrial (I-LDH) scale samples

Sample	Molecular % Zn	Molecular % Al	Molecular % C	Molecular % O	Zn/Al
B-LDH	29.6	16.3		54.1	1.8
P-LDH	17.6	8.1		74.3	2.2

I-LDH	9.1	3.3	24.5	63.1	2.8

The EDS data in Table 1 illustrates the effect of a Pt coat rather than a carbon coater, as the Oxford EDS analysis accounts for the carbon in the film, but also the carbon intercalated in the interlayer region. This results in a reduction of the total metal content as determined by the EDS spectrum, however the of the platinum would not affect the counts of Zn in the sample. Therefore, the increased scale is the most probable cause of the greater Zn/Al ratio. It is unclear why this is the case however, the overall impact of the increased Zn/Al ratio, did not have any significant impacts on other crystal or structural characteristics. Increased M^{II}/M^{III} ratios have been found to be a cause of reduced adsorption efficiency for anionic compounds [1]. This is due to a reduction in the positivity of the brucite-like layers of the LDH which are caused by electrostatic attractions between the metal hydroxide layers and the interlayer anion [1].

ESI References

1. P. S. Ghosal, A. K. Gupta and S. Ayoob, *Applied Clay Science*, 2015, **116**, 120-128.