Layered double hydroxides as iodine sorbents

Frederick L. Theiss, Michael J. Sear-Hall, Sara J. Couperthwaite, Godwin A. Ayoko, and Ray L. Frost

Chemistry Discipline, Faculty of Science and Technology, Queensland University of Technology, Brisbane Queensland 4001, Australia. r.frost@qut.edu.au

Introduction

This study investigates the potential of a Zn/Al layered double hydroxides (LHDs) as an adsorbent for the removal of iodine species from potable water (Theiss et al., 2011b). In this paper the resultant materials were characterised using powder x-ray diffraction (XRD) and thermogravimetry (TG) coupled with evolved gas mass spectrometry (EGMS) (Frost, et al, 2005, Rives, et al, 2001).

Experimental Procedure

Synthesis and Thermal Activation of the Zn/Al LDH

The Zn/Al LDH was prepared using a variation of the co-precipitation method previously described by Theiss et. al. (2011a, b). The LDH was collected and dried before being thermally activated in a furnace. The thermal activation temperature chosen for this experiment was 280°C over a period of one hour (Theiss et al., 2011b). Samples of the LDH were treated with solutions containing potassium iodide and iodine (prepared by reacting potassium iodide and potassium iodate under acidic conditions) as described in (Theiss et al., 2011b).

Powder X-Ray Diffraction

Powder X-ray diffraction (XRD) was carried out on samples of Zn/Al LDH collected before thermal activation, after thermal activation, after the sorption of iodide and iodine. A Philips X'pert wide angle X-ray diffractometer, with Cu Kα radiation (1.54052 Å) was used to collect the XRD patterns.

Thermogravimetry

Thermogravimetric analysis (TG) was performed on samples of Zn/Al LDH treated with iodide and iodine solution. A TA® Instruments incorporated high resolution thermogravimetric analyser (series Q500) was used for thermal analysis experiments with a flowing nitrogen atmosphere ($40cm^3$/min). The samples were placed in an open platinum pan and heated from room temperature at a rate of 2.5°C/min to a maximum temperature of 1000°C. TG and DTG curves where obtained.

Results

Powder X-Ray Diffraction

The powder XRD patterns obtained from samples of the LDH collected before thermal activation and after reformation in the solutions containing the iodine species (Figure 1) show remarkable similarity. The material corresponded to the reference pattern 00-038-0486 for a Zn/Al LDH.

The $d_{(003)}$ spacing was found to increase only slightly after treatment with the iodide and iodine solutions (Table 1). Other phases that may be present in the sample include: zinc and aluminium oxides as well as gahnite ($ZnAl_2O_4$).

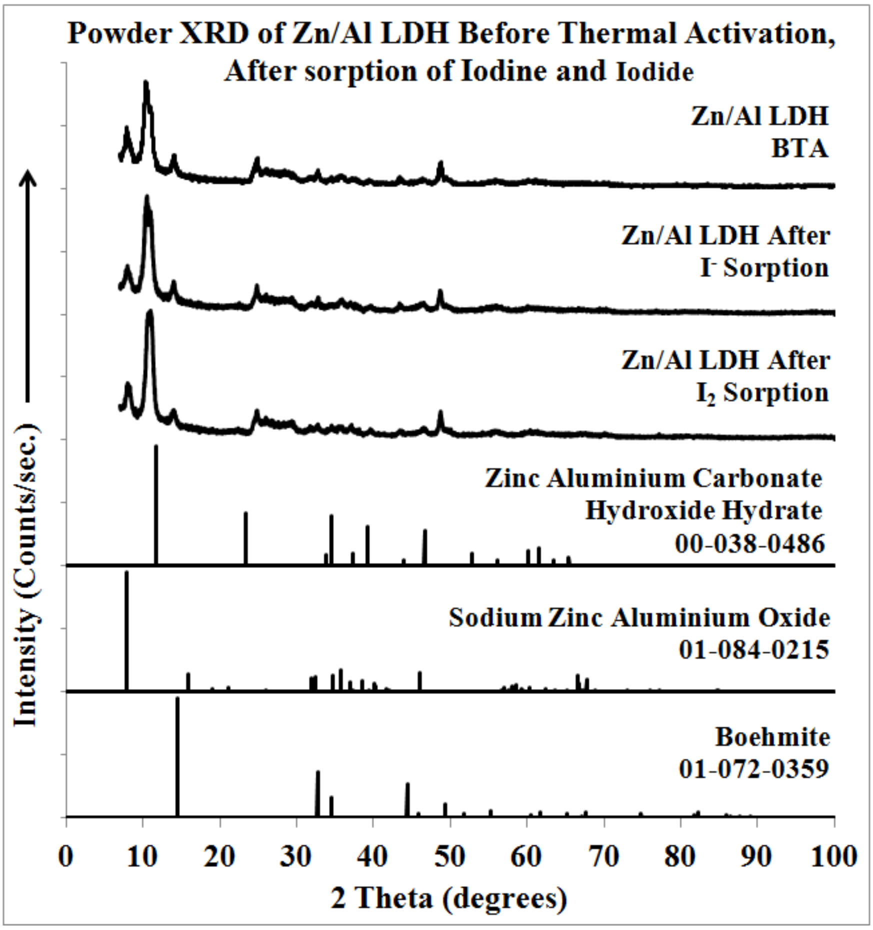

Fig 1. Powder XRD patterns of Zn/Al LDH before thermal activation and after reformation in iodide or iodine solution.

Table 1. Comparison of the $d_{(003)}$ spacing of the LDHs.

Sample	$d_{(003)}$ Spacing (Å)
Before thermal activation	8.07
Treatment with iodide solution	8.59
Treatment with iodine solution	8.41

Thermogravimetry

Both samples appeared to decompose through a similar mechanism that could be divided into three main steps. The first mass loss occurred at approximately 40°C accounted for only 1-2% of the total mass lost. This feature is attributed to the loss of weakly absorbed surface water. The second mass loss occurred at approximately 140°C, accounting for 5-6% of the total mass lost. This feature is assigned to the removal of interlayer water. The third mass loss at approximately 200°C, accounted for 5-8% of the total mass lost. This feature is attributed to dehydroxylation of the brucite like layers.

A mass loss also occurred at approximately 500°C in both samples accounting for 2-4% of the total mass lost. Additional mass losses also occurred at higher temperatures, however, as the temperature at which this mass loss occurred was too high for reformation, they were not investigated further.

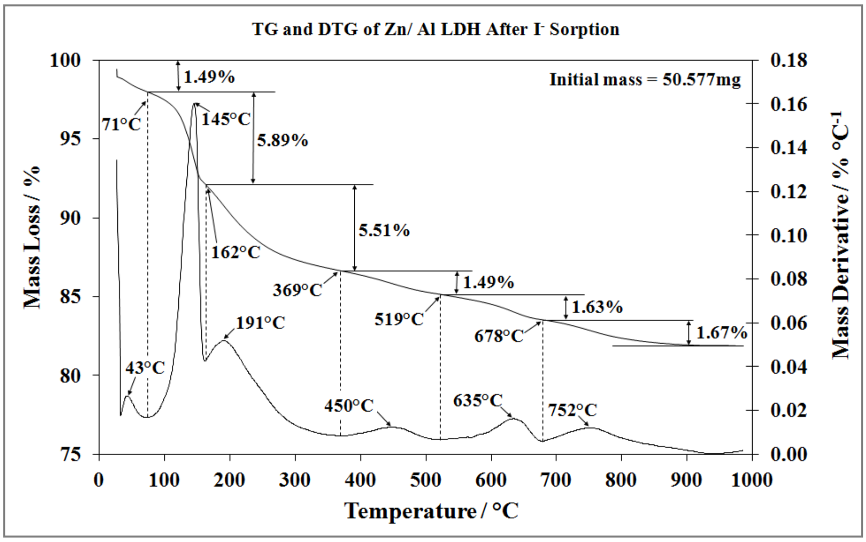

Fig 2. TG and DTG of bulk Zn/Al LDH after reformation in iodide solution.

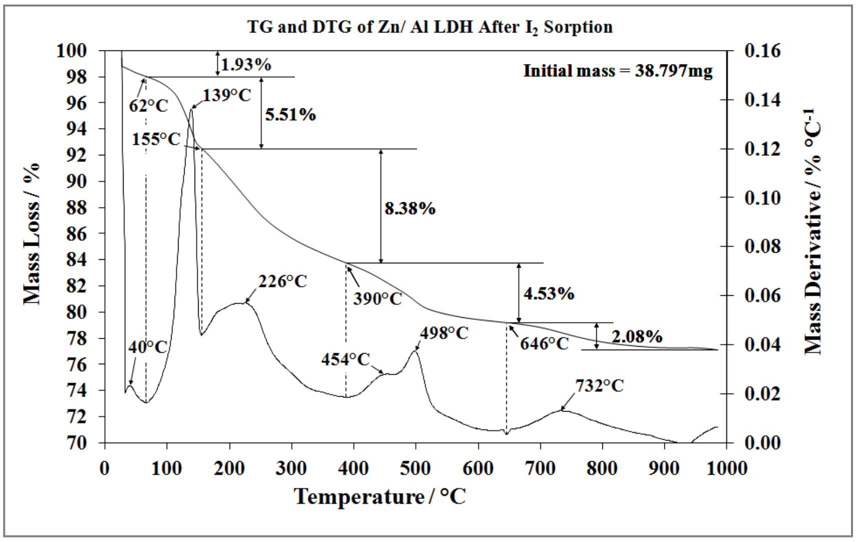

Fig 3. TG and DTG of bulk Zn/Al LDH after reformation in iodine solution.

Conclusions

The XRD patterns obtained for all samples collected corresponded well to the reference pattern 00-038-0486 for a Zn/Al LDH. Additional phases that were identified in the samples included aluminium oxide iodate, zinc iodate and aluminium iodate and gahnite ($ZnAl_2O_4$). The presence of the various oxides indicate that impurities are present in the Zn/Al LDH samples. The presence of metal oxides may also indicate that the LDH may have partially decomposed to a mixed metal oxide. If this is the case using a lower thermal activation temperature may produce better results. The increase in the d_{003} spacing observed for both the iodine and iodide adsorbed samples suggests that intercalation of some anionic species did indeed occur. The overall similarity of the XRD patterns may indicate a similar composition of anions in the interlayer and therefore a similar mechanism of sorption.

Successful anion sorption is achieved using batch processes with relatively short mixing times and without any attempt to reduce sorption of carbonate. The thermal decomposition of all samples investigated appears to occur through a similar mechanism. The total percentage mass loss observed for samples of LDH treated with iodine (22.43%) and iodide (17.68%) is significantly lower than that of the original LDH (42.79%) (Theiss et al, 2011b). Zinc aluminium layered double hydroxides show promise as potential sorbents for the removal of harmful iodine species from water, however, more research is required before the sorption of iodine species by Zn/Al LH materials is completely understood.

Acknowledgments

The financial and infra-structure support of the Chemistry Discipline of the Faculty of Science and Technology, Queensland University of Technology is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the instrumentation.

References

Frost RL, Martens WN, Erickson KL (2005) Thermal decomposition of the hydrotalcite. *Journal of Thermal Analysis and Calorimetry*, **82**, 603-608.

Rives V and Editor (2001) *Layered Double Hydroxides: Present and Future*, New York, Nova Science Pub Inc 439 pp.

Theiss F, Palmer S, Ayoko G., Frost R (2011a) Sulfate intercalated layered double hydroxides prepared by the reformation effect. *Journal of Thermal Analysis and Calorimetry* p. 1-6, doi 10.1007/s10973-011-1369-0.

Theiss FL, Sear-Hall MJ, Palmer SJ, FrostRL (2011b) Zinc Aluminium Layered Double Hydroxides for the Removal of Iodine and Iodide from Aqueous Solutions. *Desalination and Water Treatment*, 2011. Accepted for Publication 14 September 2011.