



# Journal of Applied Sciences

ISSN 1812-5654

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## Adsorbents Derived from Mg-Al Hydrotalcite-Like Compounds for High-Temperature Hydrogen Storage

R. Ibrahim and Y. Lwin

Department of Chemical Engineering, Universiti Teknologi PETRONAS, 31750, Tronoh, Malaysia

**Abstract:** The coprecipitation method was used to prepare Mg-Al Hydrotalcite-like compounds (HTLcs). The precipitated and calcined Mg-Al HTLcs were characterized using powder X-Ray Diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. The XRD patterns for the materials indicated the presence of the hydrotalcite structure. The IR spectrum for calcined Mg-Al HTLcs with Mg/Al molar ratio of 2 showed reduction in water and CO<sub>2</sub> characteristics due to their removal during calcination. Subsequent to the calcination, the materials were reduced using Temperature Programmed Reduction (TPR) in order to determine the H<sub>2</sub> uptake. The H<sub>2</sub> gas consumption was found to be very small and further modifications of the material synthesis are required to yield better results.

**Key words:** H<sub>2</sub> storage, hydrotalcite, mixed Mg-Al oxide, calcination, temperature programmed reduction

### INTRODUCTION

Hydrogen has gained tremendous attention as a promising fuel which can be used to lower CO<sub>2</sub> emissions and at the same time act as a replacement for the dwindling fossil fuels (Chen and Zhu, 2008). The many advantages of H<sub>2</sub> include its possession of the highest heating value per weight among all chemical fuels apart from being regenerative and also environmentally friendly (Zuttel, 2004). The application of H<sub>2</sub> as a fuel is mainly in H<sub>2</sub> fuel cells with the highest potential market in the fuel cell vehicles (Walker, 2008).

Following its production, H<sub>2</sub> must either be stored, distributed or both (Walker, 2008). The separation and direct storage of H<sub>2</sub> after its production at high temperature may be able to save costs as the reactor system can be operated at lower temperatures (Rawadieh and Gomes, 2009). Compressed gas and liquid storage are the conventional methods of storing H<sub>2</sub>. Alternatively, H<sub>2</sub> may also be stored as physically bound H<sub>2</sub> where H<sub>2</sub> gas is physisorbed to a high surface area adsorbent. A number of potential H<sub>2</sub> adsorbents have been investigated such as metal hydrides (Chio *et al.*, 2008) and also carbon materials (Xu *et al.*, 2007). However, each of these materials comes with its own set of limitations and researches on other materials are necessary.

Another material that is worth investigating for the purpose of H<sub>2</sub> storage is hydrotalcite-like compounds (HTLcs). The HTLcs is also known as Layered Double

Hydroxides (LDHs) and can exist naturally or are synthetically produced (Kustrowski *et al.*, 2005). The HTLcs are ionic and basic clays which are composed of brucite-like (Mg(OH)<sub>2</sub>) structure with trivalent cations substituting for divalent cations resulting in a layer charge. This positive charge is counterbalanced by the anions in the interlayer (Frost *et al.*, 2005). The cations are located at the centers of octahedral sites of the hydroxide sheet. On the other hand, the vertex of the hydroxide sheet contains hydroxide ions where each -OH group is shared by three octahedral cations and points to the interlayer regions (Yong and Rodrigues, 2002). The general formula that can be used to represent HTLcs is  $[(M^{2+}_{1-x}M^{3+}_x(OH)_2)^{x+} (A^{n-})_{x/n}mH_2O]^x$ , where  $M^{2+} = Mg^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Mn^{2+}$  etc.,  $M^{3+} = Al^{3+}, Fe^{3+}, Cr^{3+}$  etc.,  $A^n = CO^{2-}_3, SO^{2-}_4, NO^-_3, Cl^-, OH^-$  etc. (Yong *et al.*, 2001). Meanwhile, x is the molar ratio of  $M^{3+}/(M^{2+}+M^{3+})$  (Lwin *et al.*, 2001) and the value of x is usually between 0.17 and 0.33 (Frost *et al.*, 2005; Yong and Rodrigues, 2002). The stabilization of the structure is achieved by hydrogen bonds among interlayer water molecules, anions and the hydroxyl layers. Besides that, it is also stabilized by the electrostatic interactions between the layers and the anions (Han *et al.*, 1997).

The HTLcs can possess more than two types of metal cations which makes it flexible for improved cation selection for various applications (Yu *et al.*, 2006). This material is commonly applied in catalysis (Nieto *et al.*, 1995), dye removal (Auxilio *et al.*, 2009), adsorption of surfactants from aqueous solutions (Pavan *et al.*, 2000) and also gas adsorption (Hutson and Attwood, 2008).

Once calcined at temperatures exceeding 350°C, the HTlcs will produce mixed oxides which can be used for adsorption (Olsbye *et al.*, 2002). Calcined HTlcs have been utilized in many applications including NO<sub>x</sub> reduction catalyst (Yu *et al.*, 2006), transesterification catalyst (Zeng *et al.*, 2008) and also high-temperature CO<sub>2</sub> adsorption (Wang *et al.*, 2008).

However, the use of HTlcs for high-temperature H<sub>2</sub> storage has not been recorded in previous literature. Therefore, this study aims to develop an adsorbent derived from hydrotalcite-like compounds that can be used to store H<sub>2</sub> at high-temperature. In this study, the coprecipitation method was used to synthesize the adsorbents. Additionally, the Mg/Al molar ratios used were 2 to 4 in order to see the effects of composition on the H<sub>2</sub> adsorption. Powder XRD and FTIR were used to characterize the adsorbents. Meanwhile, the H<sub>2</sub> adsorption was carried out using Temperature Programmed Reduction (TPR) and thermogravimetric analysis (TGA).

## MATERIALS AND METHODS

**Synthesis of Mg-Al hydrotalcite-like compounds:** In this study, the Mg-Al HTlcs were synthesized by coprecipitation method with sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) as the precipitating agent. The experimental procedure for the HTlcs synthesis used is similar as the one in previous literature (Lwin *et al.*, 2001). In the coprecipitation, three solutions with Mg/Al molar ratios of 2.0, 3.0 and 4.0 were prepared. Each solution contains 50±1g mixture of magnesium nitrate hexahydrate and aluminum nitrate nonahydrate. Next, each solution was added drop by drop into 250 mL sodium carbonate (0.5 M) solution. During the mixing, the solution was maintained at 313 K and subjected to vigorous stirring. The solution was continuously stirred for 15 min after precipitation. The precipitate was filtered and washed several times using distilled water to remove excess Na<sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions and then dried overnight in an oven at 383 K.

**Material characterization:** Powder X-Ray Diffraction (XRD) was used to characterize the dried precipitate in order to determine the species present and their crystallinity. The crystallite sizes were calculated using the Debye-Scherrer equation as by Kannan (2004). Additionally, the synthesized materials were also characterized by Fourier transform infrared (FTIR) spectroscopy in KBr phase.

**Hydrogen adsorption using TGA and TPR:** In TGA experiments, the H<sub>2</sub> adsorption by the materials was carried out according to a temperature profile which is

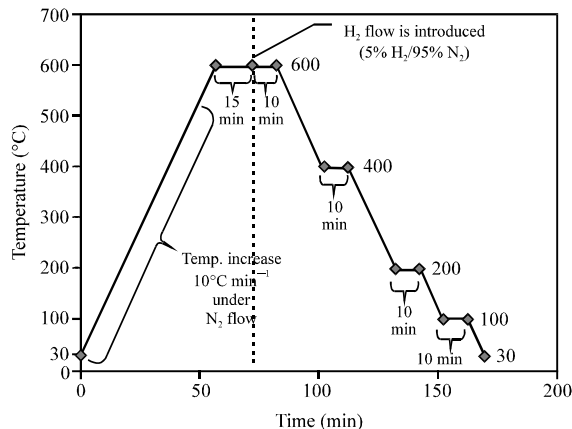


Fig. 1: The programmed temperature profile for hydrogen adsorption

similar to the one used in previous research (Lwin and Abdullah, 2009). As shown in Fig. 1, the system is initially at room temperature (of about 30°C). Then the temperature is raised to 600°C under N<sub>2</sub> flow, with a temperature increase of 10°C min<sup>-1</sup>. After 15 min at 600°C, the H<sub>2</sub> flow will be introduced along with N<sub>2</sub> into the system and the system is maintained at 600°C for another 10 min. Then, the temperature will be lowered to 400°C and the temperature is kept constant at this value for 10 min. Afterwards, the temperature will be lowered and kept constant for 10 min at other holding temperatures as shown in Fig. 1. Meanwhile, the materials will be calcined in air at 450°C for 3 h prior to the TPR experiment to provide mixed oxides for the following reduction process (Lwin and Abdullah, 2009). The TPR of the materials were conducted at 600°C.

## RESULTS AND DISCUSSION

The materials were synthesized with Mg/Al molar ratio of 2 to 4 because the minimum M<sup>2+</sup>/M<sup>3+</sup> molar ratio has to be 2:1 to avoid M<sup>3+</sup>(OH)<sub>6</sub> octahedra sharing edges. According to the Lowenstein rule, the M<sup>3+</sup>(OH)<sub>6</sub> octahedra sharing edges would be quite unstable due to electrical repulsion (Rives, 2002). Additionally, (Shen *et al.*, 1994) stated that the M<sup>2+</sup>/M<sup>3+</sup> molar ratio is normally from 1.5 to 4 in HTlcs.

Prior to the TPR experiments, the adsorbents were calcined in air at a temperature of 450°C for 3 h. The weights of the samples were reduced to about 40% of the initial weight before calcination. The weight reduction agreed with the findings by Rives (2002) since 15% of the total initial weights of carbonate-containing HTlcs consist of interlayer water.

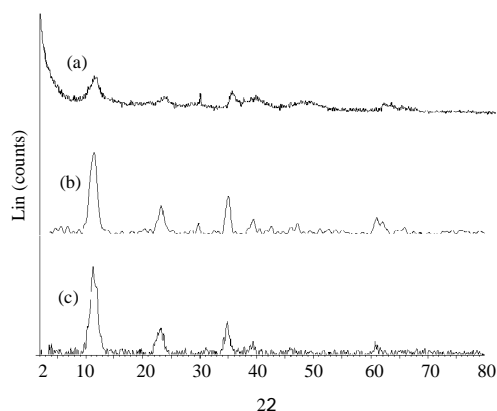


Fig. 2: The XRD pattern for the Mg-Al HTlcs with Mg/Al molar ratio of (a) 2, (b) 3 (b) and (c) 4

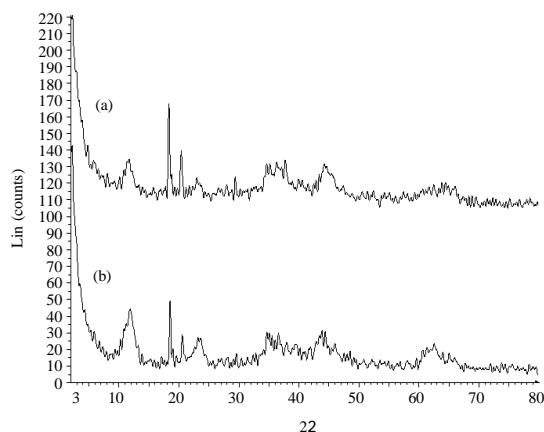


Fig. 4: The XRD pattern for the Mg-Al HTlcs calcined at 600°C, Mg/Al molar ratio (a) 2 and (b) 3

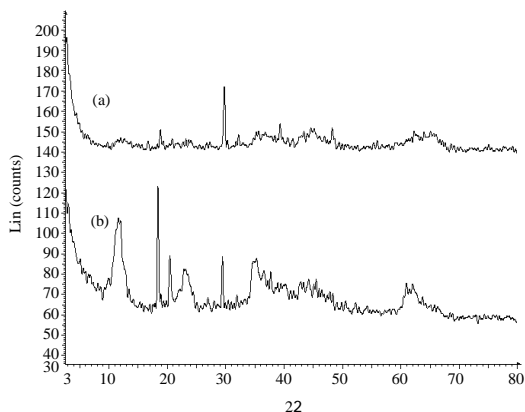


Fig. 3: The XRD pattern for the Mg-Al HTlcs calcined at 450°C with Mg/Al molar ratio of (a) 2 and (b) 3

**XRD analysis of synthesized materials:** The powder XRD patterns of Mg-Al HTlcs are shown in Fig. 2a-c. Meanwhile Fig. 3a, b and 4 show the XRD pattern of calcined Mg-Al HTlcs for temperature of 450 and 600°C respectively. As shown in Fig. 2, the sharp peaks at  $2\theta$  angles of about 11, 22 and 35° corresponds to the (003), (006) and (009) crystal planes indicating crystalline layered structure. Furthermore, the broad and asymmetric peaks at lower  $2\theta$  angles of about 38 and 46° can be attributed to the (015) and (018) crystal planes which are characteristics of hydrotalcites (Yu *et al.*, 2006). Additionally, the values of the d-spacing of the highest peak for all three materials are close to 7.6Å which indicates that the samples have hydrotalcite-like structure with carbonate anions in the interlayer (Rives, 2002).

It can be seen from Fig. 3 that the Mg-Al HTlcs with molar ratio of 2 was completely calcined and it has lost the hydrotalcite structure. On the other hand, the Mg-Al

HTlcs with Mg-Al molar ratio of 3 still showed the peaks which correspond to the hydrotalcite structure indicating that the hydrotalcite structure is retained. This is also the same for Mg-Al HTlcs calcined at 600°C. The preservation of the hydrotalcite structure after calcination has also been reported in earlier study (Labajos *et al.*, 1992) and this may be caused by the rehydration of the materials during testing (Gao *et al.*, 2008). Additionally, it can also be observed from Fig. 3 and 4 that in the calcined Mg-Al HTlcs there is a characteristic diffraction at 43 and 62°. These peaks can be attributed to the mixed Mg-Al oxides (Gao *et al.*, 2008) especially MgO (Yu *et al.*, 2006). This result is obtained as calcination of HTlcs will form mixed oxides (Rives, 2002).

Additionally, the XRD pattern for Mg-Al HTlcs calcined at 450°C showed a new peak at  $2\theta$  angle of 30°. The existence of the additional peak could be due to the formation of spinel phases (Yu *et al.*, 2006). Meanwhile, the Mg-Al HTlcs with Mg-Al molar ratio of 3 showed new peaks at  $2\theta$  angles of 18 and 21°. These peaks can also be observed for both HTlcs calcined at 600°C and they can be attributed to gibbsite ( $Al_2O_3 \cdot 3H_2O$ ).

**Crystal size:** The crystal size of the synthesized materials calculated using the Debye-Scherrer equation and for Mg-Al HTlcs with Mg-Al molar ratio of 2, 3 and 4 were 148, 152 and 125Å, respectively. The crystal sizes obtained were similar to the ones in literature (Kustrowski *et al.*, 2005) where the coprecipitation method was also employed for material synthesis.

**FTIR analysis of materials:** The IR spectrum of the uncalcined samples presented in Fig. 5a-c has an intense broadband between 4000 and 2700  $cm^{-1}$  which represents

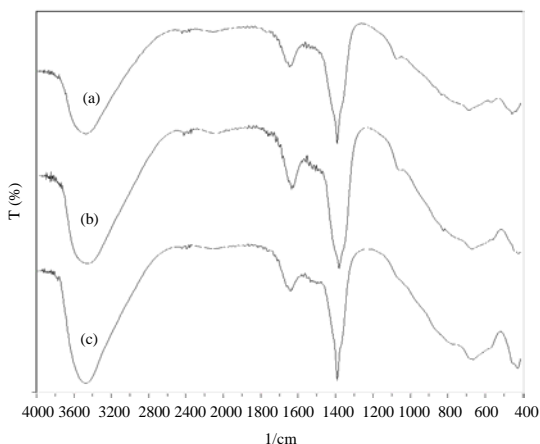


Fig. 5: IR spectrum of the Mg-Al HTlcs with Mg/Al molar ratio of (a) 2, (b) 3 and (c) 4

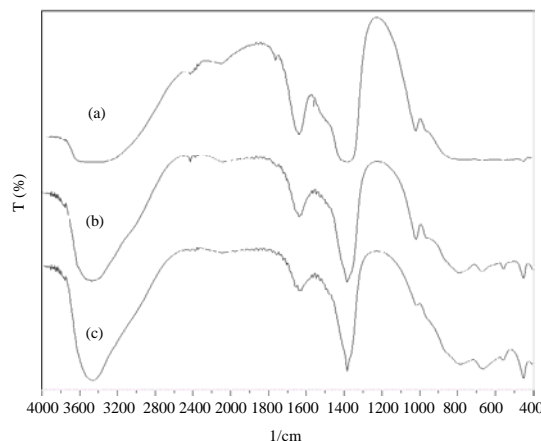


Fig. 6: IR spectrum of the calcined Mg-Al HTlcs with Mg/Al molar ratio of (a) 2, (b) 3 and (c) 4

a superimposition of deformational vibrations of physically adsorbed water, vibrations of structural OH- groups, characteristic valent vibrations of OH...OH and/or CO<sub>3</sub><sup>2-</sup>-OH<sup>-</sup> in hydrotalcite. Besides that, this broadband may also represent characteristics stretching vibration of the Mg<sup>2+</sup>-OH bond in Mg, Al-hydroxycarbonate as suggested in (Parida and Das, 2000). Additionally, the band at around 1632 cm<sup>-1</sup> may be assigned to the adsorbed interlayer water since this is the bending vibration for δ HOH. Meanwhile, the absorption band at 1383 cm<sup>-1</sup> is attributed to the CO<sub>3</sub><sup>2-</sup> absorption and the impurities of NO<sub>3</sub><sup>-</sup> which is probably due to the synthesis solution. Finally, the broadband at around 663 cm<sup>-1</sup> was implied by Parida and Das (2000) as a superposition of the characteristic bonds of boehmite and hydrotalcite in this frequency interval.

On the other hand, upon calcination, there is a decrease in the intensity of water and carbonate characteristic peaks for Mg-Al HTlcs with Mg-Al molar ratio of 2 as shown in Fig. 6a-c. This is due to the removal of water and CO<sub>2</sub> vapours during calcination at low temperature (Parida and Das, 2000). Besides that, it can be seen for Mg-Al HTlcs with Mg/Al molar ratio of 2 that the broadband at 663 cm<sup>-1</sup> has disappeared confirming the disappearance of the hydrotalcite structure. However, the bands for NO<sub>3</sub><sup>-</sup> is still present in the calcined samples as temperatures higher than 450°C are required to remove the interlayer nitrates (Kustrowski *et al.*, 2005). The IR spectra of Mg-Al HTlcs with Mg-Al molar ratio of 3 and 4 showed that some weak bands exists in the 700-600 cm<sup>-1</sup> wavenumber range which means that the hydrotalcite structure is still preserved.

**Temperature-programmed reduction:** The reduction profiles for the calcined Mg-Al HTlcs are shown in the

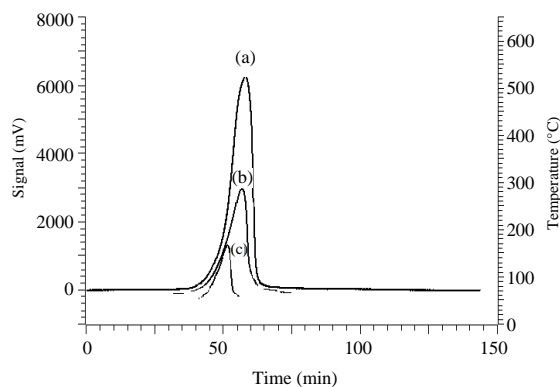


Fig. 7: Reduction profile for Mg-Al HTlc with Mg/Al molar ratio of (a) 2, (b) 3 and (c) 4

Fig. 7a-c. The peak shifted towards lower time when the Mg content is higher. However, the amounts of consumed H<sub>2</sub> decreased with increase in Mg content which are 3175.91765, 1395.65979 and 277.55466 mol g<sup>-1</sup>, respectively. The amount of gas uptake were very little as MgO is difficult to be reduced. Yu *et al.* (2006) reported that for calcined Mg-Al HTlcs or MgO, no reduction peaks were detected until 900°C.

## CONCLUSION

The powder XRD analysis showed the presence of the hydrotalcite structure in the synthesized Mg-Al HTlcs. Additionally, the FTIR analysis gave IR spectrum which showed the characteristics of HTlcs. Besides that, it was also evident from the IR spectrum that calcination caused the removal of water and CO<sub>2</sub> gas. The TPR experiments conducted on the materials showed that at 600°C only a small amount of gas is consumed.

The future work for this project will include modification of the synthesis steps with the addition of metals (eg: Li or Ni) into the adsorbent and also use of other calcination temperatures. This approach is going to be taken since addition of metal can make the material reducible (Yu *et al.*, 2006) and it is anticipated that after prolonged exposure of the material to H<sub>2</sub>, the desired H<sub>2</sub> uptake will occur. Subsequently, it is expected that the investigation of H<sub>2</sub> adsorption of the adsorbents by using TGA can be conducted in the near future.

#### ACKNOWLEDGMENTS

The authors gratefully acknowledge the support from Universiti Teknologi PETRONAS in carrying out this research.

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