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Laporan Akhir Projek Penyelidikan Jangka Pendek

Crystallization of Hydrotalcite from a Combustion Method

by
Assoc. Prof. Mohd Roslee Othman
Assoc. Prof. Dr. Ridzuan Zakaria

2011

UNIVERSITI SAINS MALAYSIA

LAPORAN AKHIR PROJEK PENYELIDIKAN JANGKA *PENDEK*

FINAL REPORT OF SHORT TERM RESEARCH PROJECT

Sila kemukakan laporan akhir ini melalui Jawatankuasa Penyelidikan di Pusat Pengajian dan Dekan/Pengarah/Ketua Jabatan kepada Pejabat Pelantar Penyelidikan

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1. **Nama Ketua Penyelidik:** *Mohd Roslee Othman*
Name of Research Leader

■ Profesor Madya/ *Assoc. Prof.* ☐ Dr./ *Dr.* ☐ Encik/Puan/Cik *Mr/Mrs/Ms*

2. **Pusat Tanggungjawab (PTJ):** *Chemical Engineering*
School/Department

3. **Nama Penyelidik Bersama:** *Assoc. Prof. Dr. Ridzuan Zakaria*
Name of Co-Researcher

4. **Tajuk Projek:** *Crystallization of hydrotalcite from a combustion method*
Title of Project

6035297.

5. **Ringkasan Penilaian**/*Summary of Assessment*:	Tidak Mencukupi *Inadequate*		Boleh Diterima *Acceptable*	Sangat Baik *Very Good*	
	1	2	3	4	5
i) **Pencapaian objektif projek:** *Achievement of project objectives*	☐	☐	☐	☐	■
ii) **Kualiti output:** *Quality of outputs*	☐	☐	☐	☐	■
iii) **Kualiti impak:** *Quality of impacts*	☐	☐	☐	☐	■
iv) **Pemindahan teknologi/potensi pengkomersialan:** *Technology transfer/commercialization potential*	☐	☐	☐	☐	■
v) **Kualiti dan usahasama :** *Quality and intensity of collaboration*	☐	☐	☐	☐	■
vi) **Penilaian kepentingan secara keseluruhan:** *Overall assessment of benefits*	☐	☐	☐	☐	■

6. Abstrak Penyelidikan

(Perlu disediakan di antara 100 - 200 perkataan di dalam **Bahasa Malaysia dan juga Bahasa Inggeris**. Abstrak ini akan dimuatkan dalam Laporan Tahunan Bahagian Penyelidikan & Inovasi sebagai satu cara untuk menyampaikan dapatan projek tuan/puan kepada pihak Universiti & masyarakat luar).

Abstract of Research

(An abstract of between 100 and 200 words must be prepared in Bahasa Malaysia and in English). This abstract will be included in the Annual Report of the Research and Innovation Section at a later date as a means of presenting the project findings of the researcher/s to the University and the community at large)

Hydrotalcites were successfully synthesized using modified combustion method from aluminum and magnesium nitrates and potassium carbonate precursors. Glucose was used as fuel to facilitate oxide formation. The synthesis temperatures were systematically varied. The resulting hydrotalcites were calcined until lattice destruction and recrystallization in the presence of a carbonate aqueous solution was achieved. The structural modifications were evaluated using X-ray diffraction, SEM, EDX and FTIR.

Hidrotalsit telah disentisis dengan jayanya menggunakan pembakaran terubahsuai daripada bahan awalan sebatian magnesium dan nitrat dan sebatian kalium dan karbonat. Glukosa telah digunakan sebagai bahanapi untuk memudahkan pembentukan oksida. Suhu sintesis telah diubah secara sistematik. Hidrotalsit yang dihasilkan telah dikalsin sehingga kemusnahan kekisi dan penghabluran semula di dalam larutan akuas karbonat dicapai. Pengubahsuaian struktur telah dinilai menggunakan pembelaun sinar X, SEM, EDX dan FTIR.

Sila sediakan laporan teknikal lengkap yang menerangkan keseluruhan projek ini.
[Sila gunakan kertas berasingan]
Applicant are required to prepare a Comprehensive Technical Report explaning the project.
(This report must be appended separately)

Senaraikan kata kunci yang mencerminkan penyelidikan anda:
List the key words that reflects your research:

Bahasa Malaysia	*Bahasa Inggeris*
Hidrotalsit	Hydrotalcite
Pembakaran	Combustion
Penjerap	Adsorbent

8. Output dan Faedah Projek

Output and Benefits of Project

(a) * **Penerbitan Jurnal**
Publication of Journals
(Sila nyatakan jenis, tajuk, pengarang/editor, tahun terbitan dan di mana telah diterbit/diserahkan)
(State type, title, author/editor, publication year and where it has been published/submitted)

1. *Othman, M.R., Martunus, Femando, W.J.N. Hydrotalcite from Modified Combustion Method. International Conference on X-Rays & Related Techniques in Research & Industry 2010, Langkawi, Malaysia.*
2. *Martunus, Othman, M.R., Femando, W.J.N. Elevated temperature carbon dioxide capture via reinforced metal hydrotalcite. Microporous and Mesoporous Materials. 138 (2011) 110–117*
3. *Results from this project will be published in the international journals after patent is successfully filed.*

(b) **Faedah-faedah lain seperti perkembangan produk, pengkomersialan produk/pendaftaran paten atau impak kepada dasar dan masyarakat.**
State other benefits such as product development, product commercialisation/patent registration or impact on source and society.

Patent filing has been applied for this project.

* Sila berikan salinan/*Kindly provide copies*

(c) **Latihan Sumber Manusia**
Training in Human Resources

i) Pelajar Sarjana: PhD
Graduates Students
(Perincikan nama, ijazah dan status)
(Provide names, degrees and status)

1. Martunus, PhD, Deceased.

ii) Lain-lain:
Others

1. Mohd Razaely Bin Anuar, BSc., graduated.

9. **Peralatan yang Telah Dibeli:**
Equipment that has been purchased

7.10.2010

Tandatangan Penyelidik
Signature of Researcher

Tarikh
Date

Komen Jawatankuasa Penyelidikan Pusat Pengajian/Pusat
Comments by the Research Committees of Schools/Centres

The findings from this research has resulted to a filing of a patent. This is ~~[illegible]~~ indeed a very good effort for possible commercialisation of this invention.

PROFESOR AZLINA HARUN @ KAMARUDDIN
Dekan
Pusat Pengajian Kejuruteraan Kimia
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Universiti Sains Malaysia, Seri Ampangan
14300 Nibong Tebal, Seberang Perai Selatan
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TANDATANGAN PENGERUSI
JAWATANKUASA PENYELIDIKAN
PUSAT PENGAJIAN/PUSAT
Signature of Chairman
[Research Committee of School/Centre]

10/10/11
Tarikh
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Microporous and Mesoporous Materials 138 (2011) 110–117

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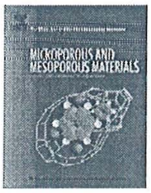

Elevated temperature carbon dioxide capture via reinforced metal hydrotalcite

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ABSTRACT

Hydrotalcite-like compounds (HT) were synthesized following a combustion-recrystallization-impregnation procedure using aluminum, magnesium nitrates precursors and carbonate solutions. Different types and amount of fuels, different amount of carbonate and different synthesis temperature were used during HT synthesis in order to understand their roles in forming HT structure and CO_2 adsorption level. It was discovered that the addition of fuels to facilitate the reaction into mixed oxides and later HT influenced the capacity of CO_2 adsorption. Beside type and amount of fuels, the carbonate amount and synthesis temperature also played important roles in forming the HT structure and thus, the CO_2 adsorption level. The highest adsorption capacity was observed at 1.21 mmol/g by K–Na HT (K of 18.5% and Na of 1.5%) at operating temperature of 300 °C and 0.4 bar of CO_2 partial pressure in the presence of N_2 (equivalent to total pressure of 1.34 bar). The HT exhibited Type IV isotherm, a typical mesoporous and slit shape pore material with pore size of 5.4 Å and BET surface area of 124 m^2/g.

1. Introduction

Coal-based electricity is well-established and highly reliable since coal is abundant and comparatively cheap energy source. However, burning of coal to generate electricity in coal-fired power plants emit billion tons of CO_2 per year globally [1]. CO_2 emission will continuously increase from this source with the construction of new coal-fired power plants and the increase on the capacity of existing coal-fired power plants as demand for electricity grows.

Several options are available to curb carbon dioxide emissions, including substitution of fossil fuels with sustainable and renewable energy resources, reduction of fossil fuel consumption, increased efficiency of fossil plants, improved energy efficiency and capturing the carbon dioxide prior to emission into the environment. While these techniques are attractive, they may present unique economic, technical, or/and societal challenges.

Adsorption has been proposed for CO_2 separation and capture from high temperature flue gases of fossil fueled power plants and other stationary sources prior to emission into the atmosphere [1]. Many researchers have explored the adsorbent for CO_2 adsorption [2–9]. Several studies have focused on developing zeolite for the CO_2 adsorption [2–5]. Activated carbon would also be attractive CO_2 adsorbent materials [5–9]. While these materials are excellent for CO_2 adsorption, they may suffer low adsorption capacity at elevated temperatures and are thus limited to operation at lower temperature (<100 °C). For example, ASRT-5A zeolites demonstrated very high CO_2 adsorption potential equivalent to 15.8% by weight at 25 °C, but subsequently decreased to 1.43% at 250 °C [5]. In addition, zeolites are effective for CO_2 separation from the gas mixtures containing species that are less polar than CO_2 but less effective in the presence of water and SO_2.

For an application operating at high temperature such as removing CO_2 from flue gases of coal-fired power plant (the temperature is in the range of 400–600 °C), the adsorbents should exhibit (i) high selectivity and adsorption capacity in this temperature domain, (ii) adequate adsorption/desorption kinetics, (iii) stable CO_2 capacity after repeated adsorption/desorption cycles, and (iv) good hydrothermal and mechanical stability [5,10,11]. The potential CO_2 adsorbents that would meet these criteria are reportedly metal oxides (e.g., CaO, MgO, etc.) [12–14], lithium metal oxides (e.g., Li_2ZrO_3, Li_4SiO_4, etc.) [15–17], hydrotalcites [10,18–25] and double salts [25]. Of these materials, metal oxides and lithium metal oxides compounds are preferably regenerated by temperature swing since they react with CO_2 in a strongly exothermic reaction ($\Delta H = 170$ kJ/mol for CaO at 800 °C, $\Delta H = 170$ kJ/mol for Li_4SiO_4 at 700 °C). The desorption process of the two materials may pose bigger technical challenge than hydrotalcites and double salts material because the latter can be regenerated by pressure swing at relatively low energy (17 kJ/mol) [18]. On the other hand, the stability of double salts has not been investigated very well since a good recipe for a binder to produce pellets from the precipitates has not been found yet [26]. Moreover double salts show a very unusual adsorption isotherm [27].

While hydrotalcite adsorbs CO_2 poorly to a certain extent and exhibits low adsorption kinetics, it is structurally stable at high

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Table 1
Sample coding and the preparation method.

Sample	Mg/Al ratio	Carbonate source	Temperature synthesis (°C)	Preparation
HT oxide-K @450	3	K_2CO_3	450	Mixed oxide
HT-K @450	3	K_2CO_3	450	Recrystallization
HT-K @650	3	K_2CO_3	650	Recrystallization
HT-K @850	3	K_2CO_3	850	Recrystallization
HT oxide-Na @450	3	Na_2CO_3	450	Mixed oxide
HT-K @450	3	Na_2CO_3	450	Recrystallization
HT-Na @650	3	Na_2CO_3	650	Recrystallization
HT-Na @850	3	Na_2CO_3	850	Recrystallization

temperatures as reported previously [5,10–11]. When a specific metal element is incorporated into hydrotalcite, the stability of the material is sustained and adsorption is improved as a result of the acid base interaction between acidic CO_2 and the basic sites of the adsorbent material which promotes CO_2 separation [18,19]. For example, the adsorption capacity of CO_2 for hydrotalcite coated/doped on zeolites was almost quadruply higher than that of the uncoated/doped zeolites at 200 °C [29].

In separate experiments [19,23,24], the CO_2 adsorption capacity of commercially purchased pure hydrotalcites was ca. 0.10 mol/kg. However, when the pure hydrotalcite was doped with cesium, the adsorption capacity was improved to 0.35–0.44 mol/kg. Incorporation of potassium into the hydrotalcite micro-structural network also increased the adsorption capacity of up to 0.76 mol/kg.

Hydrotalcite is a natural occurring anionic clay. The most common formula Hydrotalcite-like compounds or layered double hydroxides is $[(M^{2+}{}_{(1-x)}M^{3+}{}_{x}(OH)_2)^{x+}.(A^{n-}{}_{x/n}\ nH_2O)^{x-}]$ where M^{2+} is a di-valent cation (Mg^{+}, Ca^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, or Mn^{2+}), M^{3+} is a three-valent cation (Al^{3+}, Fe^{3+}, or Cr^{3+}). The layer are positively charged as M^{3+} cations substitute M^{2+} cations. This charge is balanced by A anions with charge n- such as OH^-, Cl^-, $NO_3{}^-$, CO_3^{2-} or SO_4^{2-} , among others and x is normally between 0.17 and 0.33. Carbonates (CO_3^{2-}) are generally the preferred anion [21,29,30] and they have been described in the literature [21–34] for potential use as adsorbents, catalysts, anion exchangers, hosts of electro-active and flame retardant in polymers [21,31].

The layered double hydroxides that occur naturally are scarcely found. They are usually synthesized. Two common methods of synthesis are: co-precipitation and sol–gel [30–32,34–36]. Other methods such as decomposition-recrystallization, urea method, microwave irradiation and solvothermal may also be employed [37–39].

In this work, a hydrotalcite-like compound (HT) was selected for CO_2 adsorption at elevated temperature due to its reportedly high stability and good CO_2 adsorption capacity when a specific metal element was incorporated into it [21]. The preparation of HT by combustion method was employed because it reportedly saves energy and time as it involves a very rapid chemical process [21]. In this study, saccharose, glucose, fructose or glycine was selected as organic fuel to facilitate the combustion. The fuel also serves as a source of C and H in order to form complexes with the metal ions [21]. Different types and amount of fuels, different amount of carbonate and different synthesis temperature were used during HT synthesis in order to understand their roles in forming HT structure and CO_2 adsorption level.

2. Materials and method

20 g of magnesium nitrate and 6.67 g of aluminum nitrate (Mg/Al mole ratio of 3) were placed into a 100 ml beaker followed by addition of 6.67 g of potassium carbonate and 1.67 to 8.34 g of fuel (saccharose, glucose, fructose or glycine). The mixture was stirred and heated to a temperature of 80 °C for 5 min. A 2 ml hot water at 90 °C was added and the mixture was maintained at 80 °C. The solution was stirred at a constant speed for 10 min. Two drops of 4 wt.% of poly-vinyl alcohol was added. When water evaporated for 8 min, it produced slurry and later, paste. The resulting paste was transferred into a 50 ml crucible and heated in a furnace at 450° C for slightly over 5 min to produce a mixture of oxides. The resulting sample was designated as HT oxide-K @450.

The sample was ground into powder and placed into a 100 ml beaker, followed by the addition of 50 ml 0.1 M K_2CO_3 solution. The product was stirred for 5 min and the solid filtered, washed with de-ionized water and dried at 120 °C for 20 min to produce re-crystallized HT sample. The re-crystallized HT was designated as HT-K @450. Sample re-crystallized by contacting with sodium carbonate was designated as HT-Na @450. The procedure was repeated for different calcination temperature and fuel types. The experimental conditions for the samples preparation are shown in Table 1.

It was found from this study that by reinforcing the re-crystallized sample with proper mixture of K and Na, the CO_2 adsorption was improved significantly. Prior to the impregnation of the metal elements into HT sample, 100 g of re-crystallized HT was calcined

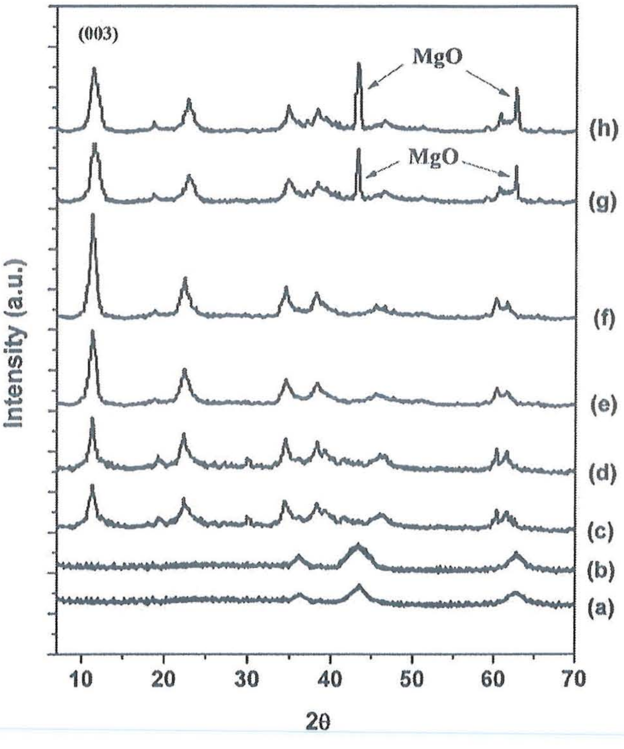


Fig. 1. XRD pattern of mixed oxide and hydrotalcite-like compounds using saccharose as fuel, (a) HT oxide-Na @450, (b) HT oxide-K @450, (c) HT-Na @450, (d) HT-K @450, (e) HT-Na @650, (f) HT-K @650, (g) HT-Na @850, (h) HT-K @850.

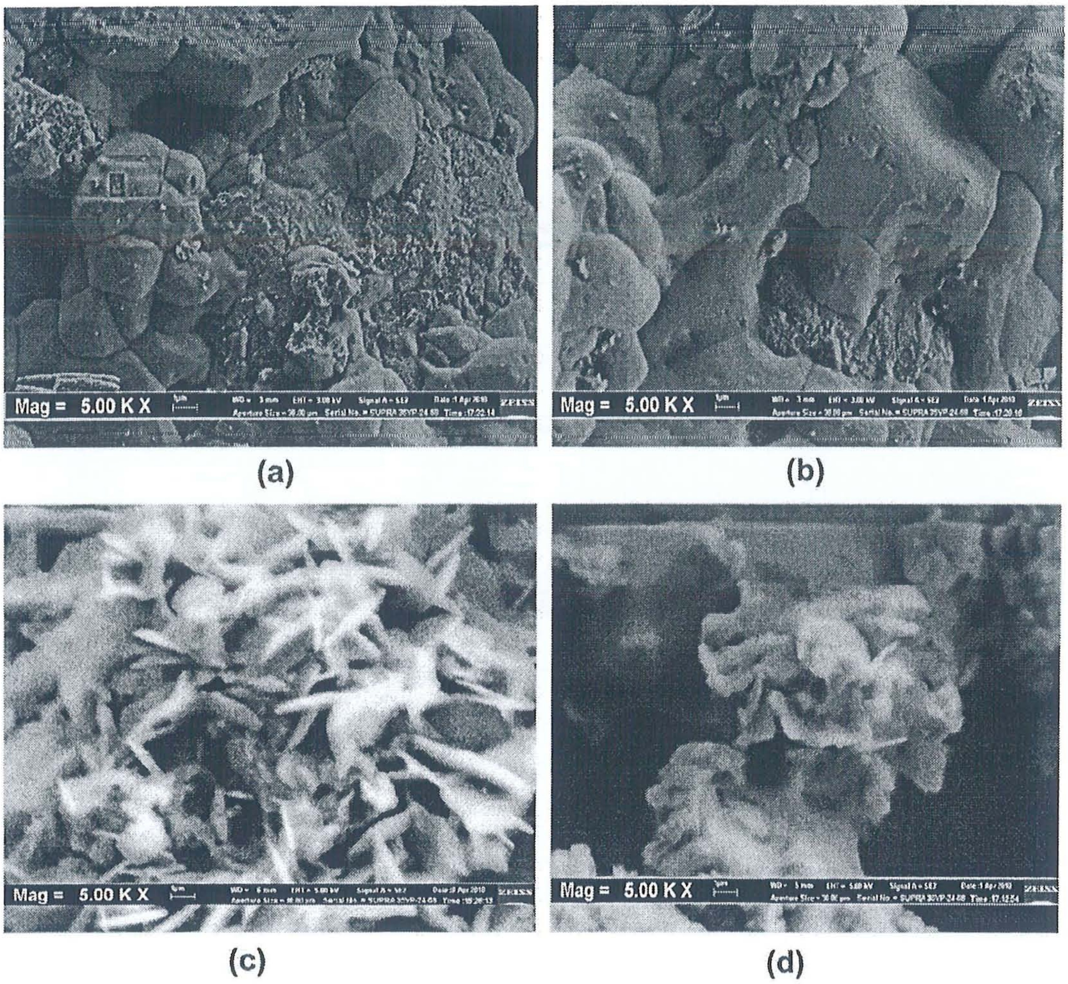


Fig. 2. SEM images of (a) HT oxide-Na @650, (b) HT oxide-K @650, (c) HT-Na @650, (d) HT-K @650.

at 650 °C for 4 h in the air. The calcined solid was contacted with 112 ml of carbonate solution containing proper amount of potassium and sodium to achieve K and Na loading of up to 20%. After 1 h of contact, the remaining liquid was decanted. The solid was either washed or unwashed with de-ionized water prior to the solid being dried at 120° C for 16 h. The resulting sample was designated as HTI-K-Na for sample containing reinforced K and Na. Sample without Na reinforcement was designated as HTI-K.

3. Characterization

The crystallization phases were studied using XRD. The analysis was carried out using Philips Goniometer PW 1820 diffractometer, PW 1710 diffraction controller and X-ray generator PW 1729. The diffractometer was used with monochromatized CuK_{α} radiation and taken in the range of 10–70° (2θ). The X-ray tube was operated at 40 kV and 120 mA.

The surface morphology was analyzed using SEM from Germany, model Leo Supra 50 VP Field Emission. Samples were placed in the sample grid for electron reflection and vacuumed (5–10 min) before analysis. SEM equipped with Oxford INCA 400 EDX microanalysis system with an operating voltage in the range of 0.1–30 kV was used in the present work. EDX was used to determine elemental composition of the sample by analyzing the microscopic image under EDX instrument. The EDX analysis used MnK_{α} as the energy source operated at 15 kV of accelerating voltage, 155 eV resolution 22.4° takeoff angle.

An infrared (IR) spectrum of the samples was obtained using FTIR spectrophotometer (Perkin Elmer FTIR 2000, USA). Samples were prepared by mixing with KBr (the blank) in a 15:85 ratio to get transparent pellet auto supported on the different solids at 8 ton pressure. The infrared spectra were recorded both over the wave number range from 400 to 4000 cm^{-1}.

Autosorb I (Quantachrome Autosorb Automated Gas Sorption System) supplied by Quantachrome Corporation, USA, was used to calculate the pore size and BET surface area of a sample. The sample was outgassed at 573 K under nitrogen flow for 3 h. The adsorption multi-point data were obtained at 77 K and relative pressure of 760 mm Hg. The above procedure was carried out automatically by the software controller pre-installed with the Autosorb I unit.

4. CO_2 adsorption

The CO_2 adsorption of the adsorbent material was measured using a digital Thermal Gravimetric Analyzer (TGA) by placing 60 mg of sample into the TGA sample holder. The temperature was increased from room temperature at a rate of 5 °C/min in an N_2 atmosphere (flow rate of 30 ml/min) to the preset point (e.g., 300, 350 °C, etc.), and maintained at this temperature until the sample weight became constant. Subsequently, the cyclic adsorption experiments were initiated via temperature swing. Multiple adsorption/desorption cycles were then carried out at selected temperatures; 350 °C for samples without impregnation and 300, 400, and 500 °C for samples with impregnation. Upon reaching the desired temperature, the feed was switched to pure carbon dioxide and N_2/CO_2 binary mixture (20 ml/min, N_2 of 70%) for samples with and without impregnation, respectively, and maintained for 3 h. Then, the sample was evacuated for 1 h, switched back to binary mode for 3 h until the sample weight became constant.

5. Result and discussion

5.1. Combusted and recrystallized samples

The samples that emerged from the combustion before treating with carbonate solution, exhibit the XRD patterns typical of Mg(Al)O mixed oxides with a periclase-like structure such as shown in Fig. 1(a–b). The sharp peak indicates that the sample obtained was ordered, while broad asymmetric peaks indicate that the sample was disordered. It is clear that HT oxide-Na @450 and HT oxide-K @450 are disordered in nature but they return to the more ordered state after being in contact with carbonate solution such as shown in Fig. 1(c–h). It was reportedly shown that these mixed oxides have a chemical composition close to $Mg_6Al_2O_{9-(x+y)}$-$(OH)_{2x}(CO_3)_y$ and they could recrystallize into hydrotalcite-like compounds after contacting with carbonate solution [33]. All the samples prepared in this work exhibit the same attribute that the literature described. They recrystalized (returned to ordered state) and formed layered double HT on contact with either $NaCO_3$ or K_2CO_3 solution. The intercalated structure with at least a monomolecular layer is described by the distinguished peak at 2θ of less

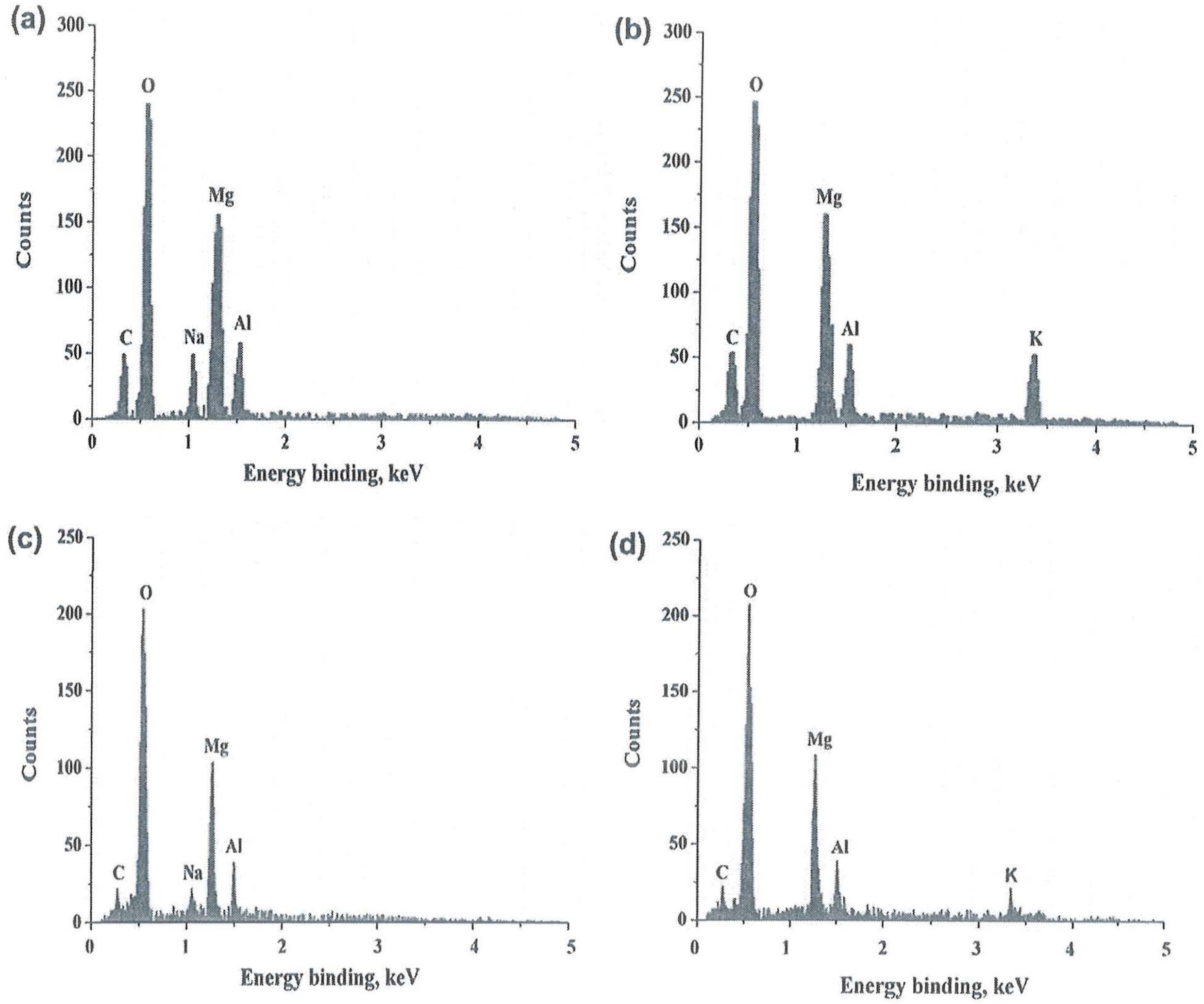


Fig. 3. The binding energy from EDX analysis at 500 X of (a) HT oxide-Na @650, (b) HT oxide-K @650, (c) HT-Na @650, (d) HT-K @650.

Table 2
Chemical composition of samples from EDX analysis.

Sample	Weight(g)	Mg/Al in analysis	Chemical composition, %wt					
			Mg	Al	O	C	K	Na
HT oxide-Na @650	28	2.67	28.05	10.49	43.40	9.04	0.00	9.04
HT oxide-K @650	27	2.66	28.02	10.51	42.91	9.28	9.28	0.00
HT-Na @650	13	2.77	27.53	9.93	51.12	5.71	0.00	5.71
HT-K @650	12	2.91	29.14	10.02	50.12	5.36	5.36	0.00

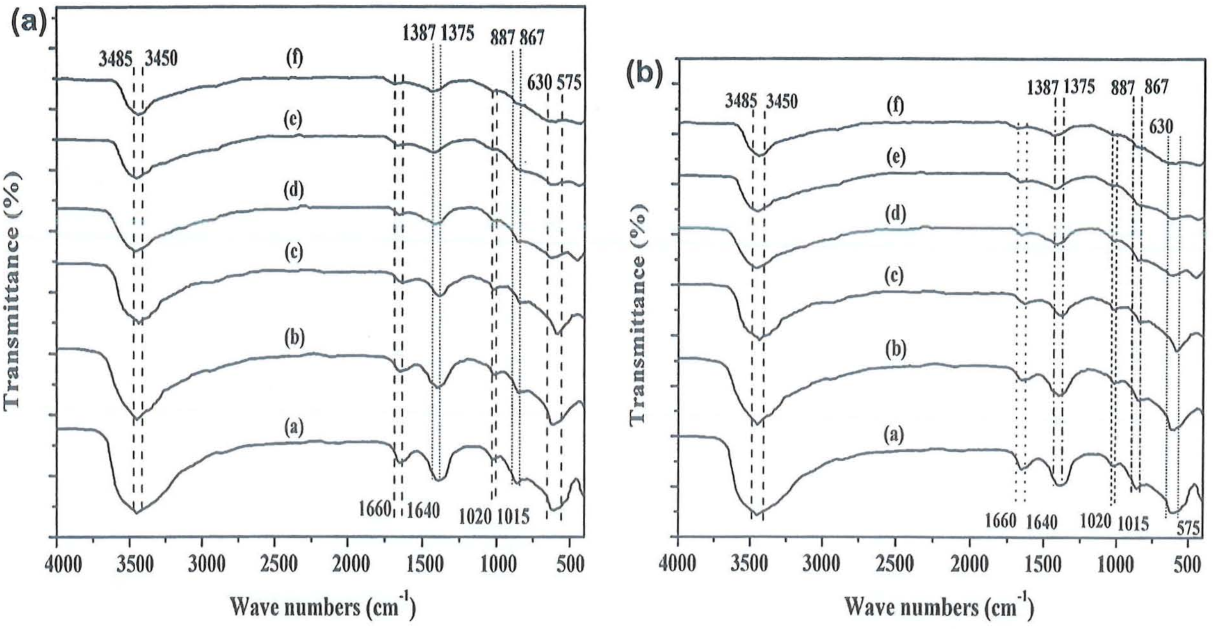


Fig. 4. FTIR spectra of (A) HT-Na: (a) HT-Na @450, (b) HT-Na @650, (c) HT-Na @850, (d) HT oxide-Na @450, (e) HT oxide-Na @650, (f) HT oxide-Na @850 and (B) HT-K: (a) HT-K @450, (b) HT-K @650, (c) HT-K @850, (d) HT oxide-K @450, (e) HT oxide-K @650, (f) HT oxide-K @850.

than 20° [34]. The existence of lamellar structures was barely detectable for the samples not contacted with the solution. Another salient feature is shown by HT-K @850 and HT-Na @850 samples by the XRD peaks at 42° and 62.5°. These peaks, which correspond to magnesium oxide specifically emerged at the highest calcination temperature, were not observed in the other samples calcined at lower temperatures. The other peaks (11.4, 22.9, 34.6, 38.9, 45.9, 60.2, and 61.7) correspond to hydrotalcite structure that match with JCPDS file (220700) and previously reported literatures [39–40].

The $d_{(003)}$ spacing values obtained for the synthetic hydrotalcites are 7.87, 7.89, 7.86, 7.85,7.94 and 7.92 Å for HT-Na @450, HT-K @450, HT-Na @650, HT-K @650, HT-Na @850 and HT-K @850, respectively. These values appear to be in good agreement with the previously reported literature [41]. The $d_{(003)}$ spacing value represents the distance between hydrotalcite layers, and therefore changes in this value indicate the effect of anions on the hydrotalcite structure.

Fig. 2 shows SEM images for mixed oxide and recrystalized samples at 650 °C. The former samples show agglomeration of micro-particles in less orderly manner, while the later samples show more orderly packed microstructure and are more crystalline on the same carbonate source which is in good agreement with the XRD results discussed earlier. Both mixed oxide and recrystalized samples containing Na appear less granular and more refined, respectively.

Fig. 3 shows the energy binding of mixed oxide and recrystalized samples. Both of the samples were calcined at 650 °C. The elemental potassium has the strongest energy binding in the hydrotalcite network despite its insignificant amount. The energy for all the elements remained the same regardless of whether the samples were treated with the carbonate solution or not. Table 2 shows the elemental components from the samples from EDX analysis. The actual Mg/Al ratios from EDX analysis for HT oxide-Na @650 and HT oxide-K @650 were 2.67 and 2.66, respectively. Whereas, the actual Mg/Al ratios for re-crystallized HT-Na @650 and HT-K @650 were 2.91 and 2.77, respectively. The slightly higher Mg/Al ratio in the re-crystallized samples was possibly due to reduction of the metal oxide after contact with either K_2CO_3 or Na_2CO_3 solution. The possibility of Al reduction due to lower sample weight may also contribute to the higher Mg/Al ratio. However, all the metal elements (including carbon) were reduced in quantity after recrystallization as observed from Table 2, perhaps due to additional washing. The oxygen content, on the other hand, was higher after recrystallization possibly due to partial hydrolysis and condensation during contact with the carbonate solution and then syneresis on drying [33].

The FTIR spectra of hydrotalcite with and without impregnation are shown in Fig. 4. The first spectrum at 3450–3485 cm^{-1} corresponds to the OH mode, caused by the interlayer water molecules and hydroxyls groups in the brucite-like layers. These values appear to be in good agreement with the previously reported literature [29]. The band as observed in the 1640–1660 cm^{-1} region was due to the H_2O from the interlayer water. The peak appears weaker for sample that was treated at high temperature, indicating that water molecule still exists in the interstices of the mixed oxide sample in order to hold the hydrotalcite structure. The 1375–1387 cm^{-1} peak corresponds to stretching vibrations of carbonate anions. The peaks at 1015–1020 and 877–867 cm^{-1} correspond to covalent carbonate. Bands at around 575–630 cm^{-1} corresponds to the characteristic vibration of the metal oxides (Mg-O and Al-O) [39].

Fig. 5 shows the adsorption of carbon dioxide in pure CO_2 gas system at 350 °C and 1.34 using HT-Na @650 and HT-K @650 samples synthesized from fours types of fuels (sucrose or saccharose, fructose, glucose and glycine). The adsorption of CO_2 was the highest when sucrose was used as fuel. The adsorption capacity follows the order of saccharose > fructose = glucose > glycine. The highest adsorption by saccharose was possibly due to the higher content of C and H in order to form complexes with the metal ions [21]. Saccharose is a disaccharide molecule containing the highest energy to fuel the combustion. It is derived from glucose ($C_6H_{12}O_6$) and fructose ($C_6H_{12}O_6$) with molecular formula of $C_{12}H_{22}O_{11}$. The entalphies of these fuels are: 5646.7 kJ/mol for saccharose, 2826.7 kJ/mol for fructose, 2815.8 kJ/mol for glucose and 528 kJ/mol for glycine.

It was also discovered that the CO_2 adsorption increased with the increase in the amount of the fuel used. Fig. 6 shows the effect of the saccharose amount on the CO_2 adsorption capacity. The CO_2

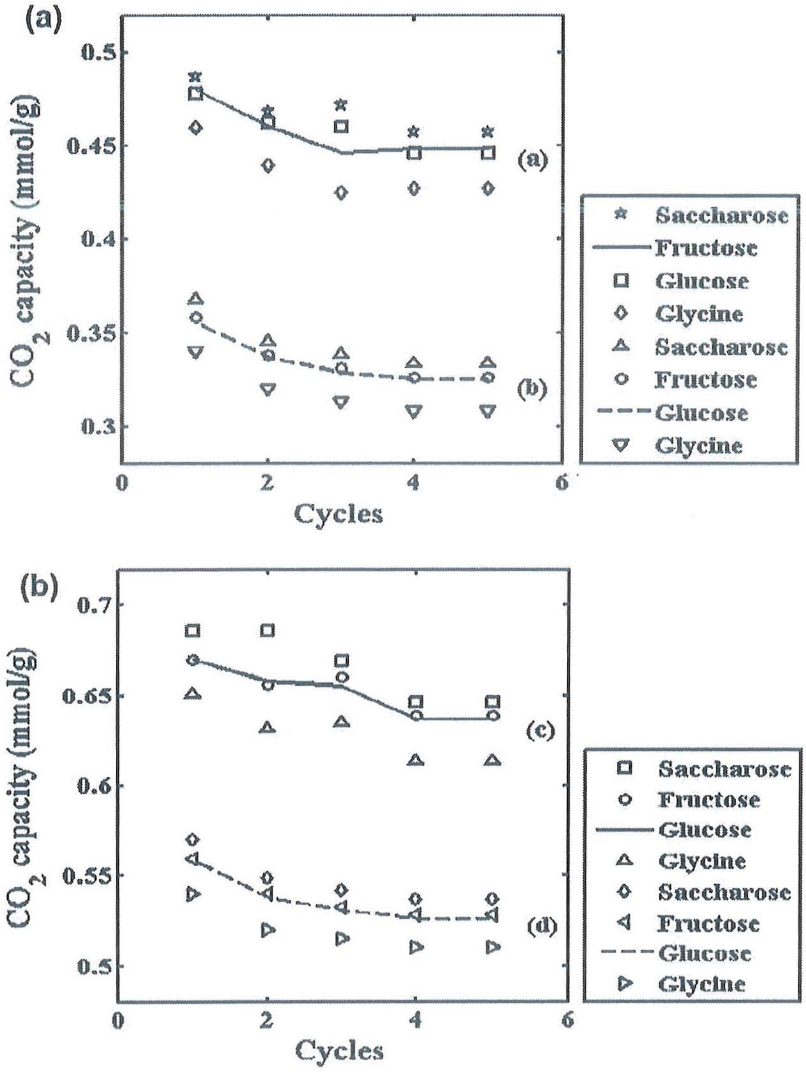


Fig. 5. The CO_2 adsorption capacity of (A) 5% fuel in preparation of (a) HT-Na @650 and (b) HT-K@650; (B) 20% fuel in preparation of (c) HT-Na @650 and (d) HT-K @650 at 350 °C and 1.34 bar.

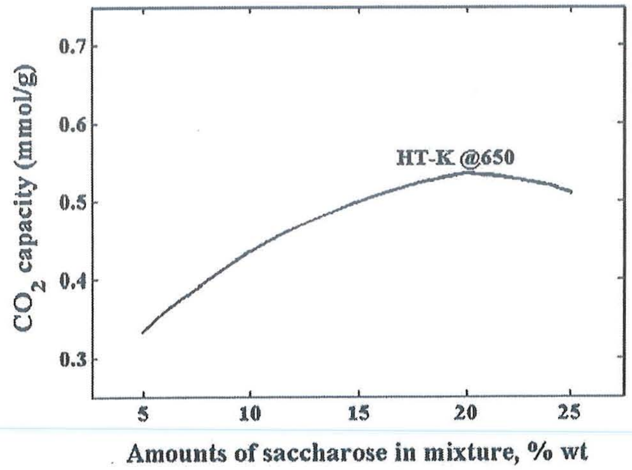


Fig. 6. The CO_2 adsorption capacity as a function saccharose amount. The adsorption was measured at 350 °C and 1.34 bar.

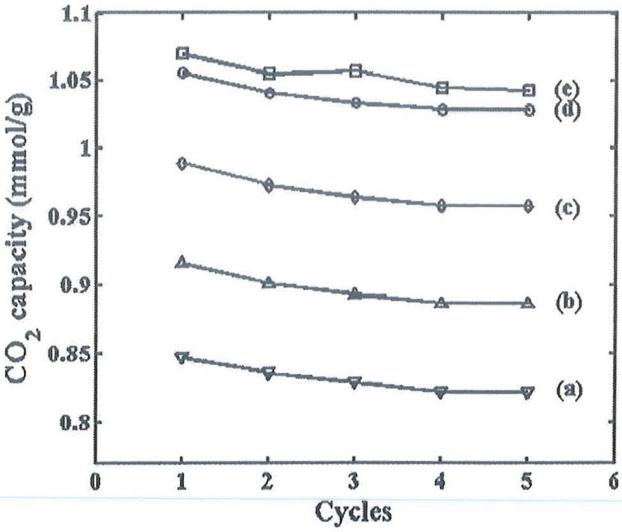


Fig. 7. The CO_2 adsorption capacity at 400 °C of unwashed: (a) HTl-K 20%, (b) HTl-K 19.5%-Na 0.5%, (c) HTl-K 19%-Na 1%, (d) HTl-K 18.5%-Na 1.5%, (e) HTl-K 18.4%-Na 1.6%.

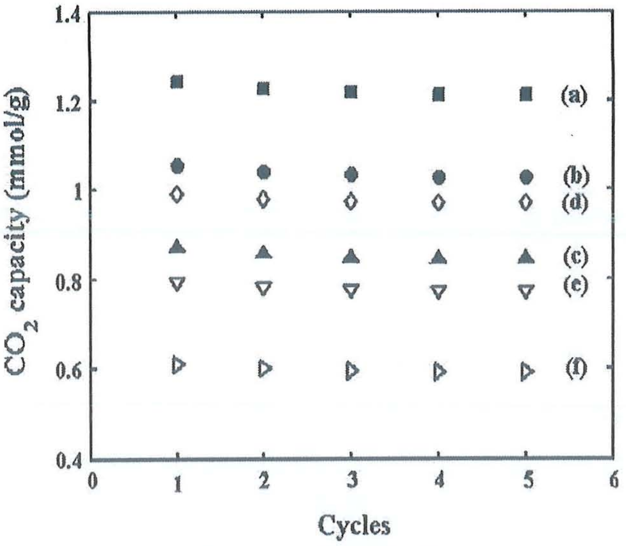
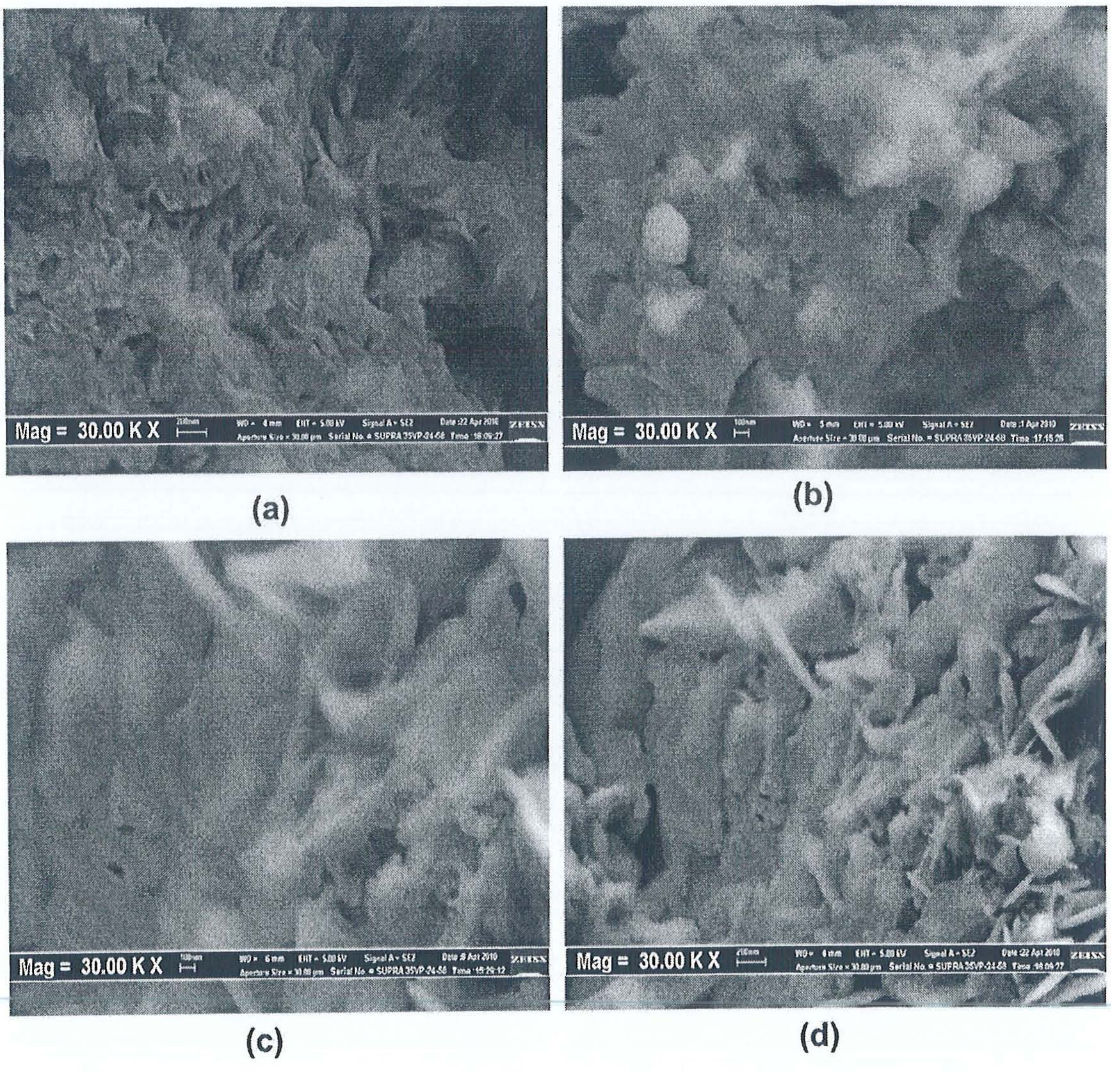


Fig. 8. The CO_2 adsorption capacity of (a-c) unwashed HTI-K 18.5%-Na 1.5%: (a) at 300 °C, (b) at 400 °C, (c) at 500 °C and (d-f) washed HTI-K 18.5%-Na 1.5%: (d) at 300 °C, (e) at 400 °C, (f) at 500 °C.

adsorption increased almost logarithmically and the maximum CO_2 adsorption was obtained when 20% (by weight) of saccharose was used, beyond which, the adsorption capacity started to decline.

5.2. Impregnated samples

Fig. 7 shows the adsorption capacity of the impregnated samples in carbon dioxide in CO_2/N_2 gas mixture containing different loading of K and Na. The CO_2 adsorption capacity of the metal reinforced HT increased with increasing Na loading. The adsorption capacity of the HT with K and Na was also found to be higher than HT without Na. Fig. 8 shows the effect of washing on the CO_2 adsorption capacity. It is clear that washing the sample with deionized water prior to drying reduced the adsorption capacity by about 17–30% due to the lower content of all the metal elements (including carbon) in the washed samples as described earlier. The HT sample with the highest and most stable CO_2 adsorption capacity of 1.21 mmol/g after five cycles was obtained using unwashed HTI-K-Na (K of 18.5% and Na of 1.5%). Although sample containing higher than 1.5% Na loading appears to give higher adsorption as suggested by Fig. 7, its adsorption is highly erratic at varying pressure. The adsorption isotherm shows a very unusual



(a) (b) (c) (d)

Fig. 9. SEM images of (a) unwashed HTI-K 20%, (b) unwashed HTI-K 18.5%-Na 1.5%, (c) washed HTI-K 20%, (d) washed HTI-K 18.5%-Na 1.5%.

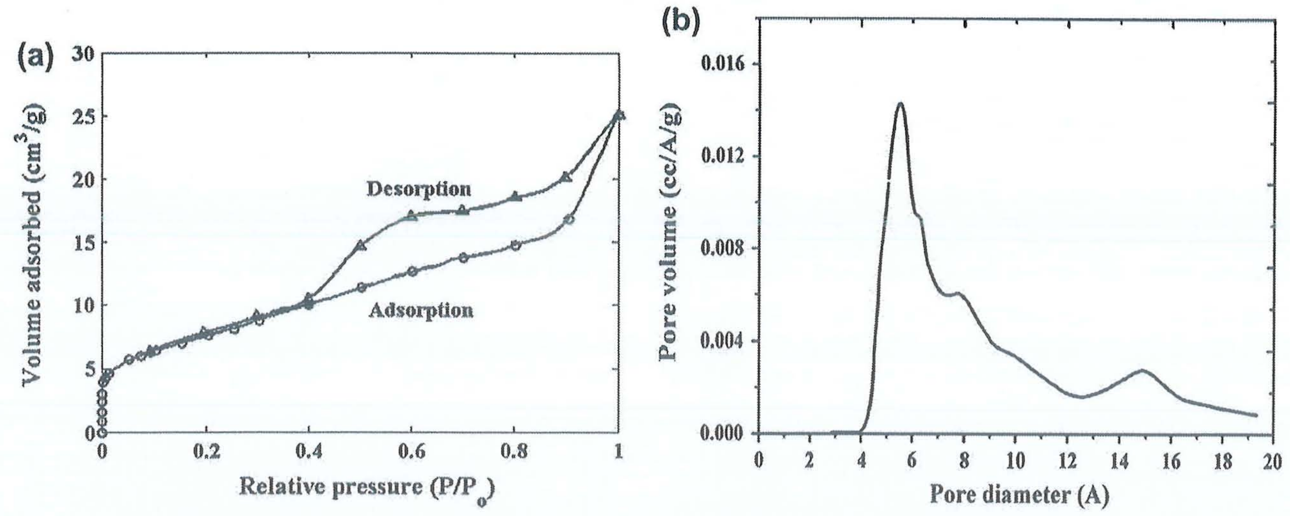


Fig. 10. (a) N_2 adsorption isotherms at 77 °K and (b) micro-pore size distribution (H-K plot) of unwashed HTI-K 18.5%-Na 1.5%.

adsorption isotherm pattern and therefore not conducive for pressure swing adsorption.

Fig. 9 shows SEM images of the washed and unwashed impregnated samples. Typical fragmented platelet-like structure of hydrotalcite can be observed, and it became 'cleaner' after washing. Fig. 10 shows N_2 adsorption isotherm at 77 K and micro-pore distribution of unwashed K and Na impregnated HT at 18.5% and 1.5% loading, respectively. The adsorption isotherm was Type IV according to IUPAC classification, indicating that the sample exhibited the characteristic of a mesoporous solid. The hysteresis indicates the presence of slit pores. The micro-pore size when the sample was measured following the Horváth-Kawazoe method [42] was in the range of 0.4–2.0 nm with a predominance of 0.54 nm pore width. The BET surface area of the sample from this analysis was found to be 124 m^2/g.

6. Conclusion

Mg–Al hydrotalcite-like compounds were synthesized following combustion method using saccharose, fructose, glucose and glycine as fuel. The samples were mostly metal oxide on combustion and they returned to a more ordered hydrotalcite-like structure after contacting with carbonate solution. The re-crystallized hydrotalcite adsorbed the highest CO_2 when 20 wt.% of saccharose was used as fuel to facilitate chemical reaction on combustion at 650 °C. However, when the sample was reinforced with additional K and Na at 18.5% and 1.5%, respectively, the adsorption capacity surged from 0.688 to 1.21 mmol/g, even after five cyclic adsorption and desorption. This was achievable despite the relatively low BET surface area of 124 m^2/g.

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Hydrotalcite from Modified Combustion Method

M. R. Othman, Martunus, and W. J. N. Fernando

Abstract—Hydrotalcite-like compounds were successfully synthesized using the modified combustion method from aluminum and magnesium nitrates and potassium carbonate. Glucose was used as fuel. The synthesis temperatures were systematically varied. The resulting hydrotalcites were calcined until lattice destruction and recrystallization in the presence of a carbonate aqueous solution was achieved. The structural modifications were evaluated using X-ray diffraction, SEM, EDX and FTIR.

Keywords: hydrotalcite, combustion modified, Mg , Al, K_2CO_3

I. INTRODUCTION

HYDROTALCITE (HT) is a natural occurring anionic clay. The most common formula Hydrotalcite-like compounds or layered double hydroxides is $[(M^{2+}_{(1-x)}M^{3+}_x(OH)_2)^{x+}.(A^{n-}_{x/n}\ nH_2O)^{x-}]$ where M^{2+} is a di-valent cation (Mg^+, Ca^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+} or Mn^{2+}), M^{3+} is a three-valent cation (Al^{3+}, Fe^{3+} or Cr^{3+}). The layer are positively charged as M^{3+} cations substitute M^{2+} cations. This charge is balanced by A anions with charge n-, for instance OH^-, Cl^-, NO_3^-, CO_3^{2-} or SO_4^{2-}, among others and x is normally between 0.17 and 0.33. Carbonates (CO_3^{2-}) are generally the preferred anion [1-2] and they have been widely described in the literature [2-3]. Hydrotalcite-like compounds are used as adsorbents, catalysts, anion exchangers, hosts of electro-active and flame retardant in polymers [4].

The layered double hydroxides that occur naturally are scarcely found. They are usually synthesized. Two common methods of synthesis are: co-precipitation and sol-gel. Other methods such as decomposition-recrystallization, urea method and microwave irradiation may also be used but they are time consuming and require high amounts of water [5]-[6].

A relatively new method to produce HT in shorter period of time is through combustion. This method is based on the explosive decomposition of some organic fuels such as urea or glycine among others, initiated with heat [4]. In this work, HT from combustion method with modification from the previous method [4] was successfully synthesized and characterized using XRD, SEM, EDX and FTIR.

II. MATERIALS AND METHOD

II.1. MODIFIED COMBUSTION METHOD

To prepare the Mg-Al-O mixed oxides; the precursors of layered double hydroxides; a solid mixture was prepared from magnesium nitrate hexahydrate, aluminum nitrate nonahydrate and potassium carbonate. The amount of Al and Mg nitrates was maintained constant (Mg/Al ratio of 3) and the amount of potassium carbonate of 8 g (20% g/g of mixture) was used. 4 g of glucose (as fuel) was added and, the mixture was heated at 80°C and stirred for 5 minutes. 2 ml of hot water at 90°C was added, until the mixture formed a solution at 80°C for 10 minutes under continuous stirring. Two drops of 4% wt Poly-Vinyl Alcohol (PVA) were added until water evaporated for 10-15 minutes. The resulting paste was transferred into a crucible before calcination took place in a furnace at 450-850° C. The combustion process was over in 5 min producing mainly a mixture of oxides.

The mixed oxides were placed in contact with 50 ml 1 M of K_2CO_3 solution at room temperature. The obtained products were stirred for 5 min and the solid was separated by filtration, washed with deionized water and dried at 120° C for 20 minutes for recrystallization.

II.2. CHARACTERIZATION

The crystallization phases were studied using XRD. The analysis was carried out using Philips Goniometer PW 1820 diffractometer, PW 1710 diffraction controller and X-ray generator PW 1729. The diffractometer was used with monochromatized CuK_α radiation and taken in the range of 10-70° (2θ). The X-ray tube was operated at 40 kV and 120 mA.

The surface morphology of the hydrotalcite powder was analyzed by SEM from Germany, model Leo Supra 50 VP Field Emission. Samples were placed in the sample grid for electron reflection and vacuumed (5 min) before analysis. SEM equipped with Oxford INCA 400 EDX microanalysis system with an operating voltage in the range of 0.1-30 kV

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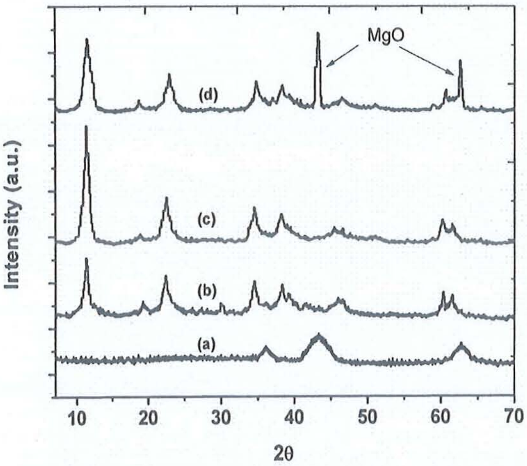
was used in the present work. EDX was used to determine elemental composition of hydrotalcite by analyzing the microscopic image under EDX instrument. The EDX analysis used MnK_α as the energy source operated at 15 kV of accelerating voltage, 155 eV resolution 22.4° takeoff angle.

An infrared (IR) spectrum of hydrotalcites was obtained using FTIR spectrophotometer (Perkin Elmer FTIR 2000, USA). Samples were prepared by mixing the powdered solids with potassium bromide, KBr (the blank) in a 15:85 ratio to get transparent pellet auto supported on the different solids at 8 ton pressure. The infrared spectra were recorded both over the wave number range from 400 to 4000 cm^{-1}.

III. RESULTS

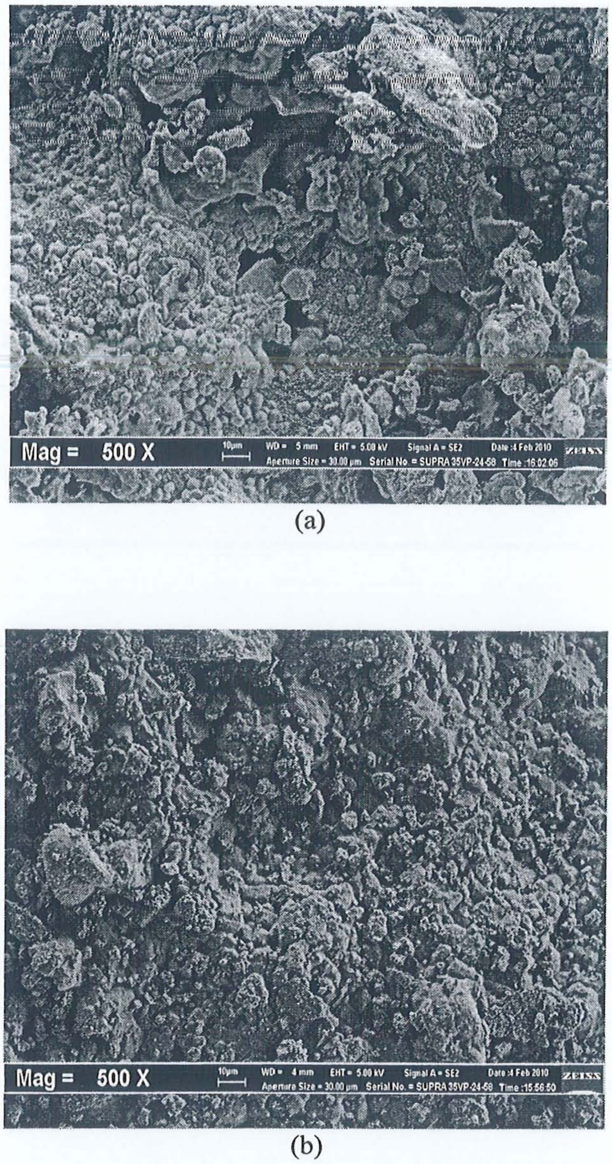
'Figure 1' shows XRD pattern of a mixed oxide of hydrotalcite at 450° C (a) and the XRD patterns of hydrotalcite at 450 to 850 ° C (b) to (d). The samples of a mixed oxide of hydrotalcite and the hydrotalcite at the highest temperature (d) contains amount of magnesium oxide shown by the X-ray diffraction peaks at 42 and 62.5 degrees (2θ) [4]. All other peaks correspond to hydrotalcite =11.4, 22.9, 34.6, 38.9, 45.9, 60.2, and 61.7, the result is in good agreement with that reported previously [3].

Hydrotalcite at 650° C was more crystalline than the others because aluminum was progressively incorporated into the MgO network. As temperature was increased, more aluminum was included. In contrast, at low synthesis temperature, aluminum diffused slowly and did not reach the crystallite core [4].



'Figure 1' XRD pattern of (a) mixed oxide of hydrotalcite at 450°C, (b) hydrotalcite at 450 °C (c) hydrotalcite at 650°C and (d) hydrotalcite at 850 °C.

'Figure 2' shows SEM images taken at 500 magnification for mixed oxide hydrotalcite and hydrotalcite samples at 650° C. 'Figure 2b' shows more closely packed microstructure than 'Figure 2a'. Hydrotalcite sample after recrystlalization shown in 'Figure 2b' became more compact due to particles that reduced oxide elements and agglomerated after contact with K_2CO_3 solution and washing.



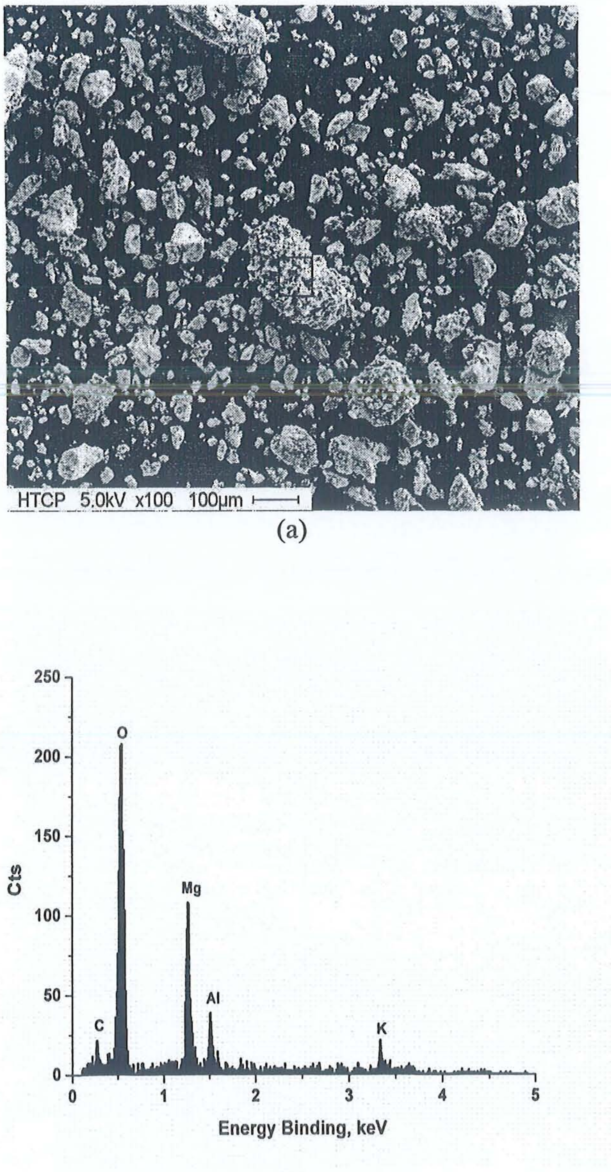
(a)

(b)

'Figure 2' SEM images of (a) mixed oxide of hydrotalcite, (b) hydrotalcite at 650° C.

'Figure 3' shows the typical EDX analysis of hydrotalcite at 650° C. The EDX shows that the 32 g hydotalcite sample was constituted of Mg (27.32%), Al (9.52%), C (5.85%), O (51.46%) and K (5.85%).

The EDX shows that the sample contained Mg/Al at ratio of 2.87 and K_2CO_3/mixture at 5.85%. The high oxygen content in the sample was probably attributed to the presence of magnesium nitrate hexahydrate, aluminum nitrate nonahydrate and potassium carbonate.

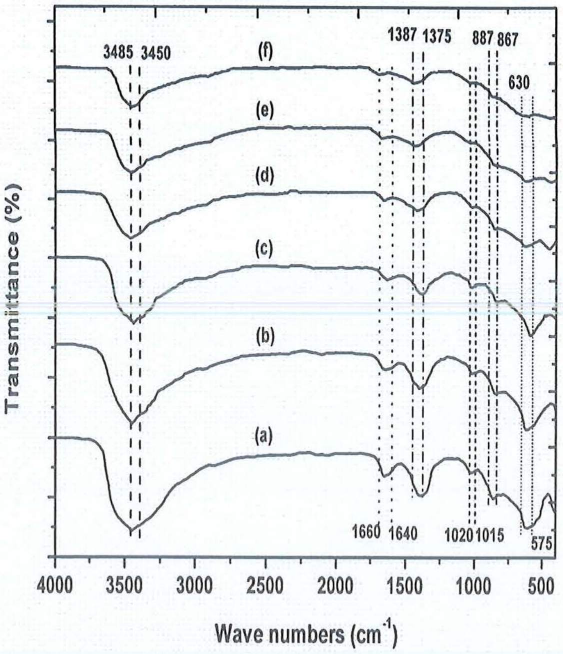


(a)

(b)

'Figure 3'(a) SEM of the hydrotalcite at 650° C sample at 100x magnification; (b) EDX analysis to the area: box

The FTIR spectra of mixed oxide hidrotalcite and the hydrotalcite samples is shown in 'Figure 4'. The first band at 3450-3485 cm^{-1} corresponds to the OH mode, caused by the interlayer water molecules and hydroxyls groups in the brucite-like layers [6]. The weak band as observed in the 1640-1660 cm^{-1} region was due to the H_2O from the interlayer water. The 1375-1387 cm^{-1} peak corresponds to stretching vibrations of carbonate anions. The peaks at 1015-1020 and 877-867 cm^{-1} correspond to covalent carbonate. Bands at around 575-630 cm^{-1} corresponds to the characteristic vibration of the metal oxides (Mg-O and Al-O) [4].



'Figure 4' FTIR spectra of (a-c) hydrotalcite: (a) at 450° C, (b) at 650° C, (c) at 850° C and (d-f) mixed oxide of hydrotalcite: (d) at 450° C, (e) at 650° C, (f) at 850° C.

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Attn: En. Khairul Anuar Che Azmi

Dear Sir,

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IN THE NAME OF UNIVERSITI SAINS MALAYSIA

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