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GLYCINE AS ALTERNATIVE FUEL IN MAKING HYDROTALCITE COMPOUND BY MEANS OF COMBUSTION METHOD

(Glisin Sebagai Bahanapi Alternatif Dalam Pembuatan Sebatian Hidrotalsit Melalui Kaedah Pembakaran)

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Abstract

Hydrotalcite is anion compound capable of exchanging ions; it has the potential as a catalyst and adsorbent for variety of applications. Hydrotalcite can be prepared through several approaches, depending on the specific need and the characteristics of the compound. In this study, hydrotalcite was prepared through combustion method using glycine as fuel for the first time. Glycine was selected as opposed to urea so that hydrotalcite is safe for use in food processing or health. Hydrotalcite that was successfully obtained via combustion technique using glycine as fuel showed interesting characteristics. The compound demonstrated high thermal endurance and highest alkalinity, which suited the application for biodiesel production from vegetable oil and hydrogenation in the making of fats. However, the surface area was low in comparison with the same compound obtained from co-precipitation and sol-gel techniques.

Keywords: hydrotalcite, catalyst, sol gel technique, combustion method, co-precipitation method, bio-diesel

Abstrak

Hidrotalsit adalah sebatian beranion yang berkebolehan dalam penukaran ion; berprestasi sebagai pemangkin dan bahan penjerap untuk pelbagai kegunaan. Hidrotalsit boleh disediakan melalui beberapa kaedah bergantung kepada keperluan spesifik dan sifat-sifat sebatian. Dalam kajian ini, hidrotalsit telah disediakan melalui kaedah pembakaran dengan menggunakan glisin sebagai bahan api buat kali pertamanya. Glisin dipilih berbanding urea supaya hidrotalsit selamat digunakan untuk pemerosesan makanan atau kesihatan. Hidrotalsit yang telah berjaya dihasilkan melalui teknik pembakaran menggunakan glisin sebagai bahanapi telah menunjukkan ciri-ciri yang menarik. Sebatian ini mempamirkan daya tahan terma tinggi dan alkaliniti yang tertinggi, sesuai digunakan untuk aplikasi pengeluaran biodiesel daripada minyak sayuran dan juga penghidrogenan dalam pembuatan lelemak. Namun, luas permukaannya rendah berbanding sebatian yang sama yang dihasilkan daripada kaedah se-mendakan dan sol-gel.

Kata kunci: hydrotalsit, mangkin, kaedah sol-gel, kaedah pembakaran, kaedah se-mendakan, bio-diesel

Introduction

Hydrotalcite (HT) compounds are double-layered hydroxide that was first found in 1915 [1]. Its structure consists of consecutive layers of brucite, $Mg(OH)_2$ and gibbsite, $Al(OH)_3$ [2]. It was reported that both layers constituted of localized cations [3] where M^{2+} cations are substituted by M^{3+} cations and interlayers containing the charge balancing anions and water molecules. HT is also called layered double hydroxides (LDHs) [4] because it consists of hydroxyl ions held together by van der Waal's force. When a fraction of Mg^{2+} ions in the brucite is substituted by trivalent cations such as Al^{3+}, hydroxide layers exhibit anionic mobility [5], anion exchange and sorption properties [6] in addition to surface basicity. These properties make HT highly potential for base-catalysed reactions [7] such as transesterification of oil into biodiesel. HT materials are also known to exhibit biodegradability and naturally mild materials [8]. Their microstructures and properties have been actively researched and developed over the years. Realizing their reactive behaviour towards certain species and their desirable micro-structural characteristics such as permanent anion exchange, high adsorption capacity, mobility of their interlayer anions and water molecules, large surface areas, stability and homogeneity of the materials; HTs have been exploited for use in a wider range of applications such as adsorbent for liquid ions and gas molecules [9,10,11,12,13, 14].

HTs may occur naturally but are scarcely found. The usual synthetic method for mass production is through co-precipitation [4, 15]. A more recent methods are sol-gel and decomposition-recrystallization, urea method and microwave irradiation [16, 17, 18, 19]. Conventional preparative routes involve oxide precipitation in the presence of alkali hydroxide and carbonates [20, 21, 22, 23]. This presents problem of alkali contaminants in the finished HT [20]. The contaminants were reportedly K [21] or Na [24] residues. This contamination was found to complicate performance comparison [25] of HT.

Combustion method is preferred prior due to the short period of heating required whilst saving significant amount of energy and time. This method involves very rapid chemical process as it is based on the explosive decomposition of organic fuels. The fuels typically used were urea [19. 26] and sugar [27]. The combusted mixed oxides were recrystallized as layered double HT by contacting with sodium carbonate solution. The reaction was initiated with heat. A network of Mg^{2+}-O^{2-} was initially formed while the aluminium was progressively incorporated into a mixed oxide with a periclase-like structure [27]. The combusted HT prepared in this manner was reportedly able to adsorb and desorb CO_2 in pressure swing adsorption (PSA) over 50 times with insignificant capacity loss [28].

The present work is dedicated to preparing of HT from 3 different methods. Their observed properties were compared in order to identify relevant applications.

Materials and Methods

Samples from co-precipitation were purchased from Tomita Pharmaceutical. The samples were pretreated by heating it up in a furnace at 450°C, 650°C and 850°C, respectively.

Samples prepared from sol-gel method started by mixing aluminium tri-sec-butylate ($C_{12}H_{27}AlO_3$) and magnesium methoxide $(CH_3O)_2Mg$ at 3:1 atomic ratio with deionized water. The alkoxides were hydrolyzed under vigorous stirring at 70-90 °C to form sol. Then, 9.5ml 1M potassium carbonate (K_2CO_3) was added to the mixture, followed by peptization of the sol using molar composition of the alkoxide, acid and water at 1:0.07:100. Polyvinyl alcohol (PVA) (4g PVA/100ml H_2O) was added to increase sol's strength. The peptized sol was allowed to cool steadily for hydroxylation, alkoxilation or condensation. A small amount of the resulting mixture was poured onto a polypropylene petri dish, dried under ambient and highly humid conditions to obtain a hardened dried gel. The resulting paste was later placed into furnace and heated at 450°C, 650°C and 850°C, respectively to obtain mixed oxides.

Sample prepared from combustion method started by mixing magnesium nitrate and aluminum nitrate with deionized water at Mg/Al atomic ratio of 3:1. The nitrates were hydrolyzed separately for approximately 30 minutes under vigorous stirring at 70°C. Then, the sodium carbonate (Na_2CO_3) of 0.10 to 0.20 per gram of solid mixture was added. 10% of glycine per gram of mixture was added and the mixture was allowed to be suspended in water. The solution was heated at 80 °C. About 5ml of polyvinyl alcohol (PVA) (4g PVA/100ml H_2O) was added to the heating mixture until water was evaporated. The resulting paste was heated at 450 °C, 650 °C and 850 °C, respectively.

Results and Discussion

Figure 1a shows XRD pattern of a mixed oxide of hydrotalcite and Fig. 1b to 1d, show the XRD patterns of the mixed oxides after they were contacted with the carbonate solution. It is obvious that the mixed oxides were disordered in nature but they returned to the more ordered state after being in contact with carbonate solution to form HT. The peaks that correspond to hydrotalcite are 11.4, 22.9, 34.6, 38.9, 45.9, 60.2, and 61.7. The intercalated structure with at least a mono-molecular layer is described by the distinguished peak at 2θ of less than 20° [8]. The heat released per mole of burned glycine, $C_2H_5O_2N$ was reportedly 528 kJ/mol [28]. Although it is low when compared to other fuels such as saccharose (5646.7kJ/mol), fructose (2826.7 kJ/mol) and glucose (2815.8 kJ/mol) [28], the energy from glycine was found to be sufficient to form complexes with the metal ions to form mixed oxides and later HT upon contact with carbonate solution. The enthalpy required to form Mg-O and Al-O bonds is 363.2 and 511 kJ/mol, respectively, lower than the energy provided by glycine.

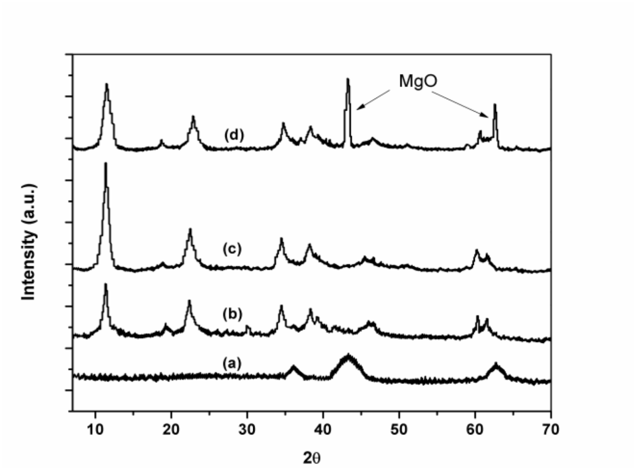

Figure 1. XRD pattern of (a) mixed oxide of hydrotalcite at 450°C, (b) hydrotalcite at 450°C (c) hydrotalcite at 650°C and (d) hydrotalcite at 850°C.

Table 1 compares the results of the characterization that describe the most desirable properties (smallest pores, highest BET surface area, etc). The results suggest that HT from co-precipitation is suitable for application such as in filtration that requires extremely small pores. HT from sol-gel method is suitable as catalyst for biodiesel production from oil due to its highest BET surface area. Whereas, HT from combustion is suitable for application requiring thermal endurance such as adsorption of CO_2 from hot flue gas. However, due to high crsytallinity level and the highest alkalinity, HT from combustion is also suitable for use as base catalyst in biodiesel production via transesterification of vegetable oils and hydrogenation to convert liquid vegetable oils to solid or semi-solid fats, such as margarine and shortening.

Table 1. Comparisons of as-synthesized HT from different approaches

	Characteristics	HTcp	HTcomb	HTsg
1.	Minimum pore size (nm)	1.5	1.9	4.1
2.	Maximum BET surface area (m^2/g)	58.86	22.21	273.8
3.	Particle size (µm)	15.81	28.22	20.91
4.	Specific surface area (m^2/g)	0.77	1.10	1.49
5.	Crystallinity*	Moderate	High	High
6.	Stability temperature (^oC)	600	624	550
7.	pH of HT	9.02	13.6	9.35

*Low - below 100Å; Moderate - 100-300Å; High - 301Å and above

Conclusion

The results suggest that HT from co-precipitation using glycine as fuel is suitable for application requiring thermal endurance such as adsorption of CO_2 from hot flue gas. HT from combustion is also suitable for use as base catalyst in biodiesel production via transesterification of oil and hydrogenation to convert liquid vegetable oils to solid or semi-solid fats, such as margarine and shortening due to its high crsytallinity level and the highest alkalinity.

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References

1. Manasse, E. (1915). Rocce eritree e di aden della collezione issel. Atti Soc. oscana. Sc. Nat., Proc. Verb. 24: 92
2. Feitknecht, W. (1942). The Formation of Double Hydroxide between Bivalent and Trivalent Metals Helv. *Chim.Acta* 25: 131 and 555.
3. Almann, R. (1968).The crystal structure of pyroaurite, *Acta Cryst.* 24: 972
4. Cavani, F., Trifiro, F., Vaccari A. (1991). Hydrotalcite-type anionic clays: preparation, properties and applications. *Catal. Today* 11: 173.
5. Oesten, R. and Bohm, H. (1993). Ionic mobility in basic double salts. Part 1: Hydrotalcites.*Solid State Ionics* 62: 199.
6. Ookubo A, Ooi H, Hayashi K. (1993). Preparation and phosphate ion-exchange properties of a hydrotalcite-like compound. *Langmuir* 9:1418.
7. Reichle, W.T. (1986). Synthesis of anionic clay minerals (mixed metal hydroxides, hydrotalcite). *Solid State Ionics*. **22**: 135 – 141.
8. Lee, W.F., Chen Y.C. (2006). Effects of intercalated hydrotalcite on drug release behaviour for poly(acrylic acid-co-N-isopropyl acrylamide)/intercalated hydrotalcite hydrogels. *Eur Polymer J* 42:1634.
9. Aramendia, M.A., Aviles, Y., Benitez, J.A., Borau, V., Jimenez, C., Marinas, J.M.,Ruiz, J.R. and Urbano, F.J. (1999). Comparative study of Mg/Al and Mg/Ga layered double hydroxides. *Microporous and Mesoporous Materials* 29: 319 – 328.
10. Yong, Z. and Rodrigues, A. E. (2002). Hydrotalcite – like compounds as adsorbents for carbon dioxide. *Energy Conversion and Management* 43 :1865 – 1874.
11. Yamamoto, T., Kodama, T., Hasegawa, N., Tsuji, M. and Tamaura, T. (1995). Synthesis of hydrotalcite with high layer charge for CO_2 adsorbent. *Energy Conversion Management* 36 : 637 – 640.
12. Ding, Y. and Alpay, E. (2000). Equilibria and kinetics of CO_2 adsorption on hydrotalcite adsorbent. *Chemical Engineering Science* 55: 3461 – 3474.
13. Othman, M.R., Rasid, N.M., Fernando, W.J.N. (2006). Effects of thermal treatment on the micro-structures of co-precipitated and sol-gel synthesized (Mg-Al) hydrotalcites. *Microporous and Mesoporous Materials* 93: 23-28.
14. Othman M.R., Fernando W.J.N, Kim, J. (2009). The conversion of an organometallic compound into an intercalated thin-layer amorphous structure. *Appl. Organometal Chem*. 23: 403-408.
15. Lopez – Salinas, E., Torres – Garcia, E. and Garcia – Sanchez, M.(1997). Thermal behavior of hydrotalcite – like $[Mg_{1-x} Ga_x (OH)_2] (CO_3)_{x/2} \cdot mH_2O$ as a function of Galium content. *Journal Physical Chemistry Solids*. 58(6): 919 – 925.
16. Fetter, G., Hernandez, F., Maubert, A.M., Lara, V.H., Bosch, P. (1997). Microwave irradiation effect on hydrotalcites synthesis, *J. Porous Mater*. 4:27
17. Yang, W., Kim, Y., Liu Paul, K.T., Tsotsis, T.T. and Sahimi, M. (2002). A study by in situ techniques of the thermal evolution of the structure of a Mg – Al – CO_3 layered double hydroxide. *Chemical Engineering Science* 57 : 2945 – 2953.
18. Patil, K.C., Aruna, S.T., Ekambaram, S. (1997). Combustion synthesis, *Solid State Mater. Sci.* 2: 158.
19. Cruz, D., Bulbulian, S. (2003). Synthesis of lithium silicate tritium breeder powders by a modified combustion method, *J. Nucl. Mater*. 312: 262.
20. Constantino, U., Mamottini, F., Nocchetti, M., Vivani, R. (1998). New synthetic routes to hydrotalcite-like compounds-characterisation and properties of obtained materials, *Eur. J. Inorg. Chem*. 10:1439.

21. Diez, V.K., Apesteguia, C.R., and J.I. Di Cosimo (2003). Effect of the chemical composition on the catalytic performance of MgyAlOx catalysts for alcohol elimination reactions. *J. Catal.* 215: 220-233.
22. Mistra, C., Perrotta, A. (1992). Composition and properties of synthetic hydrotalcites, *Clays Clay Miner*. 40: 145.
23. Kagunya, W., Hassan, Z., Jones, W. (1996). Catalytic Properties Of Layered Double Hydroxides and Their Calcined Derivatives, *Inorg. Chem* 35: 5970.
24. Prinetto, F., Ghiotti, G., Graffin, P. and Tichit, D. (2000). Synthesis and characterization of sol gel Mg/Al and Ni/Al layered double hydroxides and comparison with co-precipitated samples. *Microporous and Mesoporous Materials* 39 : 229 – 247.
25. Cantrell, D.G., Gillie, L.J., Lee, A.F., Wilson, K. (2005). Structure-reactivity correlations in MgAl hydrotalcite catalyst for biodiesel synthesis, *Applied Catalysis A*: Gen. 287, 183-190.
26. Erickson, K.L., T.E. Bostrom, and R.L. Frost (2004). A study of structural memory effects in synthetic hydrotalcites using environmental SEM. *Materials Letters*, 59(2-3): 226-229.
27. Davila, V., Lima, E., Bulbulian, S., Bosch, P. (2008). Mixed Mg(Al)O oxides synthesized by the combustion method and their recrystallization to hydrotalcites, *Microporous and Mesoporous Materials* 107: 240-246.
28. Martunus, Othman, M.R., Fernando, W.J.N. (2011). Elevated temperature CO_2 capture via reinforced metal hydroxide, *Microporous and Mesoporous Materials*, 138:110-117.