SYNTHESIS AND PHYSICOCHEMICAL CHARACTERIZATION OF PAMOATE-INTERCALATED ZINC-ALUMINIUM LAYERED DOUBLE HYDROXIDE HYBRID NANOCOMPOSITE

By

ZAEMAH BINTI JUBRI @ MOHD ZUFRI

Thesis Submitted to the School of Graduates Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Doctor of Philosophy

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Chairman: Professor Mohd. Zobir bin Hussein, PhD

Faculty: Science

Layered organic-inorganic hybrid nanocomposites were prepared by using pamoate ion (PA) as a guest into Zn-Al layered double hydroxide (Zn-Al-LDH) inorganic host by co-precipitation technique. Two methods of aging used in the synthesis process were conventional oil bath and microwave-assisted methods. The Zn to Al molar ratio of the mother liquor was kept constant at 4 at the beginning of the synthesis with concentration of PA, 0.02 M. As the result of successful intercalation of pamoate ion into the interlayer structure of Zn-Al-LDH, an expansion of the interlayer spacing from 8.9 Å in the layered double hydroxide (ZAL) to 18.1 Å in the nanocomposite (ZAP) could be observed in the powder X-ray diffractogram. The advantage of using microwave-assisted method is that the time for aging process is shortened to only 15 to 30 minutes to achieve a well-ordered layered nanocomposite materials compared to 18 hours to age the sample if conventional oil bath method

is used to synthesis the nanocomposite. Nanocomposite prepared using various Zn to Al molar ratios 2, 3, 4, 5, 6, 7 and 8 gave a well-ordered nanolayered structure. The effect of various Zn to Al ratios on the properties of layered organic-inorganic hybrid nanocomposite materials show that the BET surface area increases as the Zn to Al molar ratio increases. Nanocomposite prepared from various Zn to Al molar ratios using ion-exchange method, resulted in less ordered nanocomposite materials, with BET surface area in the range of (20.6 - 27.4) m^2/g. Thermal decomposition of the nanocomposite was studied by heating the sample at 100-1000 °C under atmospheric condition. The layered structure of the nanocomposite collapsed when the sample was heated at 350 °C or higher and the formation of ZnO phase was observed at 400 °C or higher. Further heating at 1000 °C, resulted in the formation of $ZnAl_2O_4$ phase. It was also found that the release of PA anions from the interlamellae of the nanocomposite was controlled by the first order kinetics at least at the beginning of the reaction up to 7 hours. At the end of rapid release rate, the amount of PA released into the aqueous solution at various initial pH values was 16%, 20% and 30% for pH 2, pH 11 and pH 12, respectively.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTESIS DAN PENCIRIAN SIFAT KIMIA DAN FIZIKAL NANOKOMPOSIT HIBRID PAMOAT TERSISIP DALAM HIDROKSIDA BERLAPIS GANDA ZINK-ALUMINIUM

Oleh

ZAEMAH BINTI JUBRI @ MOHD ZUFRI

November 2006

Pengerusi: Profesor Mohd. Zobir bin Hussein, PhD

Fakulti: Sains

Bahan nanokomposit hibrid organik-inorganik berlapis telah disediakan dengan menyisipkan ion pamoat (PA) sebagai tetamu ke dalam perumah hidroksida berlapis ganda Zn-Al (Zn-Al-LDH) dengan kaedah pemendakan bersama. Proses penuaan dilakukan dengan menggunakan dua kaedah berbeza iaitu kaedah konvensional dalam kukus minyak dan bantuan gelombang mikro. Nisbah molar Zn terhadap Al dalam larutan pada peringkat awal sintesis dikekalkan pada 4 dan kepekatan PA adalah 0.02 M. Hasil daripada pamoat yang berjaya disisipkan di antara lapisan Zn-Al-LDH, corak pembelauan sinar-X menunjukkan pengembangan jarak lapisan berlaku daripada 8.9 Å dalam hidroksida berlapis ganda (ZAL) kepada 18.1 Å bagi nanokomposit (ZAP). Kelebihan penggunaan kaedah bantuan gelombang mikro adalah kerana ia dapat menghasilkan bahan nanokomposit dengan masa proses penuaan yang lebih pendek iaitu antara 15 hingga 30 minit berbanding

dengan 18 jam dengan kaedah konvensional. Bahan nanokomposit yang disediakan menggunakan pelbagai nisbah molar Zn terhadap Al iaitu 2, 3, 4, 5, 6, 7 dan 8 juga memberikan struktur hablur nanokomposit yang baik. Penggunaan pelbagai nisbah molar Zn terhadap Al dalam penyediaan nanokomposit menunjukkan bahawa luas permukaan BET bertambah dengan pertambahan nisbah molar Zn terhadap Al yang digunakan semasa sintesis. Kaedah penukar ion yang digunakan untuk menyediakan nanokomposit dengan pelbagai nisbah molar Zn terhadap Al menunjukkan kaedah penukar ion memberikan bahan nanokomposit yang kurang teratur. Luas permukaan BET bagi nanokomposit yang terhasil adalah di antara 20.6 - 27.4 m^2/g. Penguraian terma dilakukan dengan memanaskan bahan nanokomposit pada suhu 100-1000 °C dibawah tekanan atmosfera. Struktur nanokomposit yang berlapis runtuh apabila sampel dipanaskan pada suhu 350 °C atau lebih tinggi dan pembentukan fasa ZnO berlaku pada suhu lebih tinggi daripada 400 °C. Pemanasan nanokomposit pada suhu 1000 °C telah menyebabkan berlakunya pembentukan fasa $ZnAl_2O_4$. Perlepasan terkawal anion PA daripada antara lapisan hidroksida berlapis ganda adalah mematuhi tindak balas tertib pertama diawal tindak balas sehingga 7 jam berikutnya. Di akhir perlepasan yang cepat, jumlah PA yang terbebas ke dalam larutan akueous adalah masing-masing 16%, 20% dan 30% pada pH 2, pH 11 dan pH 12.

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I certify that an Examination Committee met on 30th November 2006 to conduct the final examination of Zaemah binti Jubri @ Mohd Zufri on her Doctor of Philosophy thesis entitled "Synthesis and Physicochemical Characterization of Pamoate-Intercalated Zinc-Aluminium Layered Double Hydroxide Hybrid Nanocomposite" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidates be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

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