UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND PHYSICO-CHEMICAL PROPERTIES OF ZINC ALUMINIUM-LAYERED DOUBLE HYDROXIDE AND ITS NANOCOMPOSITES

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By

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Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of requirement for the Degree of Doctor of Philosophy

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January 2008

Chairman: Associate Professor Asmah Hj. Yahaya, PhD

Faculty : Science

In this study, zinc-aluminium-nitrate-LDH (ZANO) at different Zn/Al molar ratios of 1, 2, 3 and 4 were successfully synthesised via co-precipitation method. Studies on intercalation of various anions namely dodecylsulphate (DS), acetate (AC), anthranilate (AN), salicylate (SAL) acetylsalicylate (ASAL), 2,4-dichlorophenoxy acetate (24D), naphthalene acetate (NAA) and anthraquinone-2-sulfonate (AQ2) for the formation of the nanocomposites had been carried out.

The anions of DS (having 12 C) and AC (having 2 C) were chosen to study the effect of the alkyl length on the formation of the nanocomposites and it was revealed that the basal spacing values were varied depending on the size of the anion. The nanocomposites of AN, SAL and ASAL with different *ortho* benzoate substitution

groups were prepared via co-precipitation method. The basal spacing expansions of the nanocomposites: ZAA (ca. 1.3 nm), ZAS (ca. 1.6 nm) and ZAAS (1.6 nm) compared to that of the LDH (0.9 nm) are evidence of the successful intercalation process.

Anion exchange study of various anions having different number of benzene rings (24D, NAA, AQ2) and different *ortho* benzoate substitution groups (AN, SAL, ASAL) were carried out. ZADS was chosen as a starting material where DS (interlayer anion), was expected to exchange with the newly introduced anions. Only AQ2 and AN were successfully exchanged with DS in between the layers. Thermal decomposition of the nanocomposites (ZAA, ZAS, ZAAS) at the heating temperature of 100-1000 ºC showed that the nanocomposites were thermally stable up to 300 ºC.

The release profile of the ASAL anion from ZAAS in different solutions (pH 2, 6.5, 10) revealed that the ASAL anion was rapidly released into the medium at pH 2. The interlayer spacing of ZAAS slightly reduced at pH 6.5 and at pH 10 the basal spacing shrinks due to the replacing the ASAL anion by the carbonate anion. Kinetic models of pseudo-second order could be used to describe the release of the ASAL from ZAAS.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia bagi memenuhi keperluan untuk Ijazah Doktor Falsafah

SINTESIS DAN PENCIRIAN SIFAT KIMIA DAN FIZIKAL ZINK ALUMINIUM-HIDROKSIDA BERLAPIS GANDA DAN BEBERAPA NANOKOMPOSITNYA

Oleh

MAZIDAH BINTI MAMAT

Januari 2008

Pengerusi: Professor Madya Asmah Hj. Yahaya, PhD

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Dalam kajian ini, hidroksida berlapis ganda HBG zink-aluminium-nitrat (ZANO) telah berjaya disintesis pada nisbah logam Zn/Al yang berbeza iaitu 1, 2, 3 dan 4 melalui kaedah ko-mendakan. Kajian penyisipan terhadap pelbagai anion iaitu dodesilsulfat (DS), asetat (AC), anthranilat (AN), salisilat (SAL), asetilsalisilat (ASAL), (2,4-diklorofenoksi asetat (24D), naftalina asetat (NAA) dan anthraquinon-2-sulfonat (AQ2), bagi menghasilkan nanokomposit telah dijalankan.

Anion DS (mempunyai 12 C) dan AC (mempunyai 2 C) telah dipilih untuk mengkaji kesan panjang alkil terhadap penghasilan nanokomposit dan ia menunjukkan nilai jarak asas adalah berbeza bergantung kepada saiz anion. Nanokomposit bagi AN, SAL dan

ASAL yang mempunyai kumpulan penukarganti *orto* benzoat yang berbeza telah disediakan melalui kaedah ko-mendakan. Pengembangan jarak asas nanokomposit: ZAA (1.3 nm), ZAS (1.6 nm) dan ZAAS (1.6 nm) bila dibandingkan dengan HBG (0.9 nm) membuktikan proses penyisipan telah berjaya.

Kajian penukargantian ion ke atas pelbagai anion yang mempunyai bilangan gelang yang berbeza (24D, NAA, AQ2) dan kumpulan penukarganti *orto* benzoat yang berbeza (AN, SAL, ASAL) telah dilakukan. ZADS telah dipilih sebagai bahan pemula di mana DS (anion yang berada di antara lapisan), dijangkakan akan digantikan dengan anion yang baru diperkenalkan. Hanya AQ2 dan AN yang berjaya menggantikan DS di antara lapisan. Penguraian terma nanokomposit (ZAA, ZAS, ZAAS) pada suhu pemanasan 100-1000 ºC menunjukkan nanokomposit stabil secara terma sehingga suhu mencapai 300 ºC.

Profil pengeluaran anion ASAL dari ZAAS dalam larutan yang berlainan (pH 2, 6.5, 10) menunjukkan bahawa anion ASAL telah keluar dengan cepat ke dalam medium pada pH 2. Jarak antara lapisan ZAAS berkurang sedikit pada pH 6.5 dan pada pH 10 jarak antara lapisan mengecut disebabkan oleh penggantian anion ASAL oleh anion karbonat. Model kinetik pseudo-kedua boleh digunakan untuk menjelaskan pengeluaran ASAL dari ZAAS.

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I certify that an Examination Committee met on 21st July 2008 to conduct the final examination of Mazidah binti Mamat on her Doctor of Philosophy thesis entitled "Synthesis And Physico-Chemical Properties Of Zinc Aluminium-Layered Double Hydroxide And its Nanocomposites" In accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the students be awarded the degree of Doctor of Philosophy.

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This thesis was submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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DECLARATION

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

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MAZIDAH BINTI MAMAT

DATE: 03 January 2008

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