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COMMUNICATION

Synthesis of Multifunctional Nanocomposite Material: Tungstate-pillared Mg-Al Hydrotalcite-like Compound

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ABSTRAK

Sebatian seperti hidrotalsit dengan nisbah kation (Mg/Al) dan anion pengimbang cas antara lapisan yang berbeza telah disediakan dan dicirikan. Luas permukaan bagi sebatian tersebut didapati bertambah dengan pertambahan nilai nisbah Mg/Al. Sebataian tulen telah didapati bila nisbah Mg/Al kurang daripada 7. Sifat jerapan air menunjukkan ianya adalah mikroporos, sementara luas permukaan (BET) jerapan air dan nitrogen juga bergantung kepada nisbah Mg/Al. Sebatian tersangga tungstat yang disediakan dari Mg/Al=7 telah juga berjaya disediakan dan pencirian sifat fiziknya menunjukkan bahawa ketinggian galeri dan luas permukaan yang lebih besar diperolehi.

ABSTRACT

Hydrotalcite-like compounds (HTLC) with different cationic ratios (Mg/Al) and charge-balancing interlayer anions were prepared and characterized. The surface areas of HTLCs were found to increase with increasing Mg/Al ratio. Pure HTLCs were obtained when the Mg/Al ratio was below 7. Water adsorption properties of HTLCs show that they are microporous. BET surface areas with water and nitrogen are dependent on the Mg/Al ratio of HTLC. Tungstate-pillared HTLC (synthesized from Mg/Al=7) was prepared and characterized, resulting in higher gallery height and surface area.

Keywords: **nano-composite, hydrotalcite-like compound, surface area, layer spacing, tungstate-pillared.**

INTRODUCTION

Over the past ten years or so, an important class of new materials has emerged. This new class of advanced materials, commonly referred to as pillared layered structures (PLS) is synthesized by propping apart the layered structures of the host with nano-structure pillars. Although the main interest has been centred on the molecular sieving and catalytic properties of these materials, the field has now expanded to include additional novel materials. The primary reason for this interest lies in the fact that PLS provide supermesh host structures in which it is possible to tailor the pore structures to the required properties (Mitchell 1990).

Pillared-layered HTLCs are materials in this PLS family. A substantial amount of work has been done on these materials, in terms of synthesis, characterization and pillaring processes (Dredzon. 1988; Demotakis and Pinnavaia 1990), ion exchange and their uses in medicine (Miyata 1980).

The electrical-hydration-related properties of Zn-Al-Cl-HTLC type compounds led to the fabrication of a humidity sensor (Moneyron *et al.* 1991). The use of HTLC in catalysis has been the most-explored area (Jones and Chibwe 1990).

The so-called anionic clays, HTLCs have positively charged metal hydroxide sheets with anions such as carbonates located in the interlayers. The structure is somewhat similar to cationic clays but the charge on the layers is opposite (Reichle 1986).

It has been recently suggested that the organo-anion derivatives of HTLC can be used as precursors to pillared HTLC derivatives (Demotakis and Pinnavaia 1990). In this method the organo-HTLC intercalate was prepared from meixnerite by adding an organic acid in the presence of glycerol as a swelling agent. Subsequent reaction of the organo-HTLC with polyoxometalate (POM) anions affords x-ray crystalline, well-ordered, pure pillared HTLC-POM derivatives.

MATERIALS AND METHODS

HTLC was prepared by the aqueous co-precipitation method (Reichle 1985). A solution containing salts of Mg and Al with selected ratio of Mg/Al (=R) was titrated into a conical flask containing a mixture of concentrated $NaOH/Na_2CO_3$, while stirring with a magnetic stirrer at about 35°C. The resulting slurry was then heated in an oil bath at about 65°C for about 18 hours with continuous agitation. The HTLC that formed was then cooled, centrifuged and washed several times, dried and characterized.

The conversion of HTLC to tungstate-pillared HTLC was carried out using glycerol as a swelling agent and p-toluenesulphonic intercalate as precursor (Demotakis and Pinnavaia 1990). Mg-Al-CO_3^{2-}-HTLC (MACHTLC) with R=7 was prepared and pillared by first calcining the HTLC at 500°C for 3 hours; degassed water was added and stirred for 16 hours, at 25°C (2 wt % solids), under nitrogen atmosphere. Two volumes of glycerol were then added to the resulting slurry, followed by the addition of p-toluenesulphonic acid. Following expansion of the HTLC interlayers, the pillaring agent, tungstate salt, was then added. The pillared product was centrifuged, washed, and dried before further characterization.

RESULTS AND DISCUSSION

Powder XRD results of the different synthetic preparations are shown in *Fig. 1*. The results show that pure MACHTLC was obtained with R values in the range of 2-7 (*Fig. 1a*). Brucite formation above an R value of 7 is evident from *Fig. 1b*.

The water and nitrogen-sorption properties of MACHTLC were probed by measuring water absorption isotherms at 25°C. *Fig. 2* shows the surface area (N_2 BET) to R relationship, obtained by multipoint measurements.

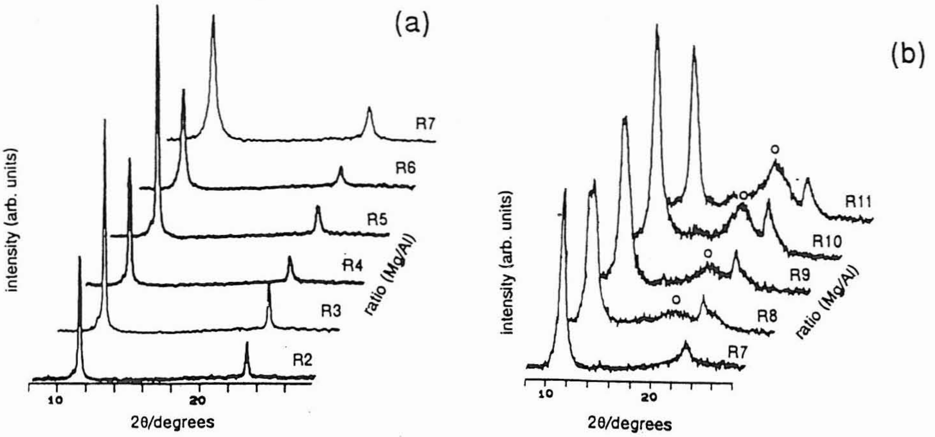

Fig. 1. X-ray powder diffraction patterns of (a) MACHTLCs at lower values of R (R=2 to R=7) (b) MACHTLCs at higher values of R (R=7 to R=11). The peak labelled (o) belongs to brucite and its intensity increases as R increases

Generally speaking, the surface area increased with an increase in R as can be expected from an increase in the basal spacing. The large increase in surface area at R=4 is an exception and this increase appears to be related to the formation of uniform micropores as can be deduced from moderated Type 1 water adsorption isotherm of this sample. The microporous nature of all the samples was also apparent from the high surface areas of all samples, as estimated from the BET monolayer capacity for water.

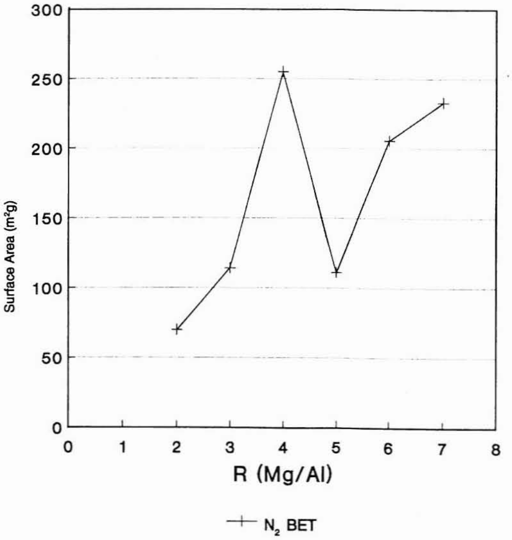

Fig. 2. R versus surface areas (N_2 BET) for MACHTLC

X-ray diffraction data of the starting material and the tungstate-pillared HTLC are shown in *Fig. 3*. This pillared HTLC had a layer spacing of 15.35 Å. This value indicated the presence of tungstate-pillared species of about 7.32 Å in diameter between layers; this was calculated by subtracting the thickness of the basal HTLC layer which is 8.03 Å.

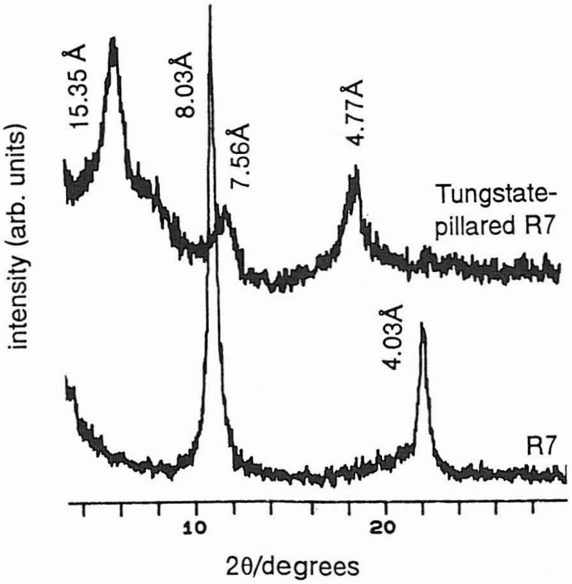

Fig. 3. X-ray powder diffraction pattern and basal spacing d(003) of MACHTLC, (a) Starting material, MACHTLC (R=7) (b) Tungstate-pillared material obtained from (a)

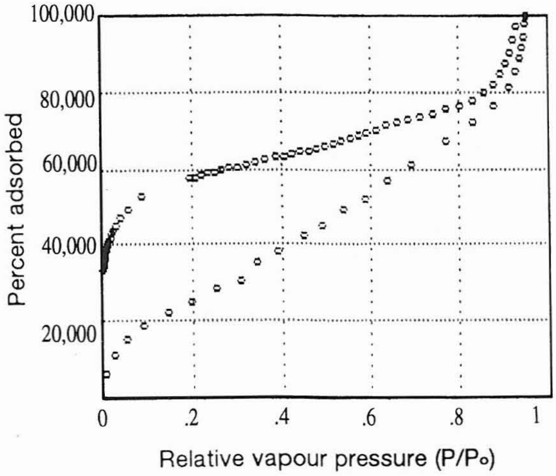

Fig. 4. Nitrogen adsorption and desorption isotherms of tungstate-pillared MACHTLC (R=7)

The pore structure of tungstate-pillared MACHTLC (R=7) was probed by measuring the N_2 adsorption isotherm at liquid nitrogen temperature. This pillared MACHTLC exhibited a type 1 N_2 adsorption isotherm (*Fig. 4*) which indicated it also to be microporous in nature with high surface area.

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