

# MONTMORILLONITE AND PILLARED MONTMORILLONITE - SURFACE CHARACTERISTICS

JOZEF KRAJČOVIČ<sup>1</sup>, FRANTIŠEK GREJTÁK<sup>1</sup>, PETER HLOŽEK<sup>2</sup> and PAVOL HUDEC<sup>2</sup>

<sup>1</sup>Institute of Inorganic Chemistry, Slovak Academy of Science, Dúbravská 9, 842 36 Bratislava, Czecho-Slovakia

<sup>2</sup>Department of Petroleum, Slovak Technical University, 812 37 Bratislava, Czecho-Slovakia

**Abstract:** Hydroxy-aluminium and hydroxy-chromium - pillared montmorillonite were prepared by intercalation and subsequent calcination of Ca montmorillonite (MMT) from Jelšovský Potok (Czecho-Slovakia). The cation exchange capacity (CEC) and thermal stability of these materials have been determined using titration methods, X-ray diffraction and DTA measurements. From adsorption-desorption isotherms of nitrogen, which were measured at nitrogen boiling point, surface characteristics of investigated materials such as specific surface area (BET isotherm), micropore volume and specific mesopore surface (t-curve), pore distribution (desorption isotherm), were determined.

The results confirmed, that a thermally more stable material with higher specific surface area can be obtained by conversion of the original MMT to pillared form. The CEC decreased from 0.99 meq.g<sup>-1</sup> to 0.66 (Al-pillared MMT) and 0.69 meq.g<sup>-1</sup> (Cr-pillared MMT), thus the total amount of cations, which are able to take part in ion exchange, dropped by about one third. The specific surface area was increased by pillaring from 43 m<sup>2</sup>.g<sup>-1</sup> to more than 270 m<sup>2</sup>.g<sup>-1</sup>, the specific mesopore surface increased more than 2.5 times, while the specific micropore volume was increased more than 10 times. The measurements showed that pillaring opens internal surface (increase of specific micropore volume), what may be important from the point of view of catalysis, but the MMT structure itself remains preserved (X-ray diffraction measurements, pores distribution calculation).

**Key words:** montmorillonite, pillared montmorillonite, thermal analysis, adsorption, desorption, X-ray diffraction.

## Introduction

Pillared clays are members of the smectite group of 2 : 1 layered silicates in which the gallery cations are robust species capable of preventing the collapse of the interlayer region upon dehydration. The advantage of these compounds is in the fact, that the pores formed between the cations can be systematically modified by varying the cation size, shape and spacing (Pinnavaia et al. 1985). The preparation of pillared clays consists in ion-exchanging charge-compensating cations with large polyoxocations or with colloidal particles. The compounds of aluminium (Lahav et al. 1978, Suzuki et al. 1988), zirconium (Figueras et al. 1989), chromium (Pinnavaia et al. 1985), iron (Yamanaka et al. 1984), and titanium (Yamanaka et al. 1987) can be used as pillaring agents. Pillared montmorillonite (MMT) is usually prepared using bentonite with a montmorillonite content above 90 %. Typically the surface area and pore volume are in 40-50 m<sup>2</sup>.g<sup>-1</sup> and 0.04 - 0.08 cm<sup>3</sup>.g<sup>-1</sup> range.

Pillared clays exhibit interesting physico-chemical properties, i.e. basal spacing of about 1.8 nm, specific surfaces areas between 150 and 350 m<sup>2</sup>.g<sup>-1</sup>, mean pore diameters of 0.7-0.9 nm, and the ability to adsorb various substances, i.e. hydrocarbons (Schutz et al. 1987). Three properties of pillared clays, acidity, shape selectivity and thermal stability, determine their potential usefulness as catalysts (Bruce & Turney 1988). Pillared interlayer clay compositions are inorganic structures with high thermal stability, but their hydrothermal stability is lower. The hydrothermal stability of these materials may be improved through use of polymeric metal complexes which possess an optimum molecular weight and chemical composition (Vaughan et al. 1981 a). While the interlayer clay products possess some degree of ion-exchange capacity, the ion exchange capability of the cal-

cined interlayer clay products is not equivalent to the ion exchange capacity of the parent clay. It is contemplated that the utility and areas of application of pillared interlayer clay products will be substantially enlarged by increasing the ion exchange capacity thereof (Vaughan et al. 1981 b).

The present paper reports the preparation of aluminium - and chromium - pillared montmorillonite, and compares their thermal and surface properties.

For each class of pillared clay, the pore size and its distribution and the thermal stability of the clay have been found to depend on the method of preparation (Malla & Komarneni 1990). Pinnavaia et al. (1984) demonstrated that the pore-size distribution of alumina-pillared clay can be changed by varying the method of drying, e.g. the freeze drying of pillared clay gives wider pore-size distributions, compared with air drying, as evidenced by the sorption of large molecule organic adsorbates.

## Experimental

### Materials

Natural montmorillonite obtained from Jelšovský Potok bentonite (Czechoslovakia) was used in these studies. It was purified by conversion to the calcium form by suspension in 1 M CaCl<sub>2</sub> solution. 1 % w.t. suspension was used in pillared montmorillonite preparation. The cation-exchange capacity (CEC) of Ca montmorillonite was measured to be 0.99 meq.g<sup>-1</sup>.

Aluminium pillared agent was prepared by reaction of AlCl<sub>3</sub> solution with solution of NaOH (Krajčovič & Horváth 1992). The solution of chromium ions was obtained by partial neutralization of Cr(NO<sub>3</sub>)<sub>3</sub> solution by Na<sub>2</sub>CO<sub>3</sub> (Pinnavaia et al. 1985). The resulting solution was aged at 97 °C for 40 hours.

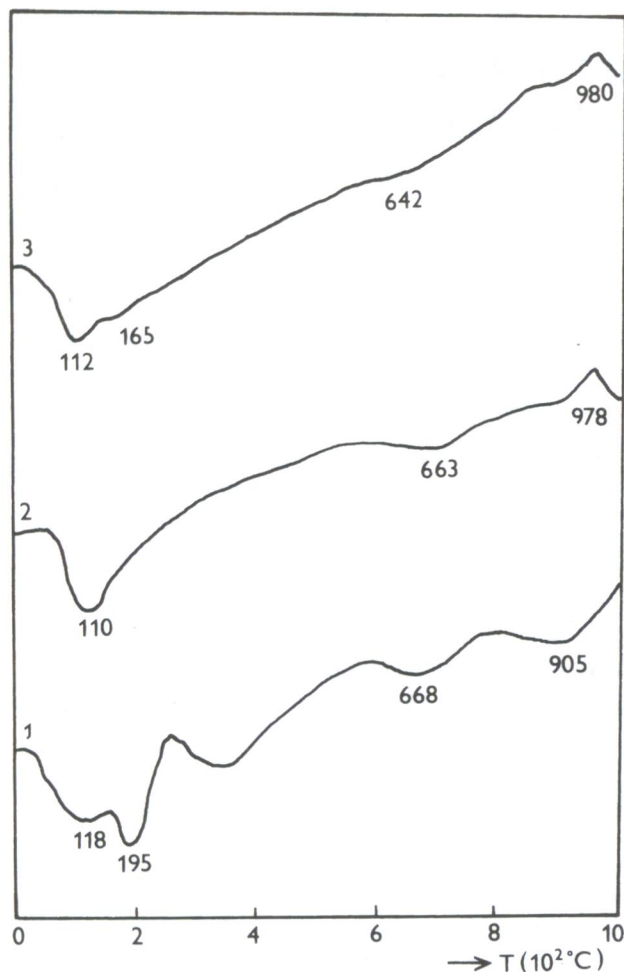


Fig. 1. DTA curve; 1 - Ca MMT; 2 - hydroxy-Al precursor; 3 - hydroxy-Cr precursor.

### Syntheses

Pillared montmorillonites were made by adding a known amount of aluminium polycation or chromium polycation to a dilute suspension of clay and stirring until the clay coagulated. The solution was centrifuged to recover the clay and then washed to free it from calcium chloride and other soluble materials. It was dried at 60 °C and finally calcined in a furnace at 500 °C for 2 hours either in air (aluminium-pillared MMT), or in nitrogen (chromium-pillared MMT).

### Analyses

Thermal analysis of the montmorillonites was made using Derivatograph Q-1500 D (MOM Budapest), in static air, at a heating rate 10 °C min<sup>-1</sup>. DTA curves of investigated materials are shown in Fig. 1.

XRD measurements of the powdered textureless samples by means of a Philips diffractometer PW 1050 (CuK $\alpha$  radiation filtered by Ni) provided the values of  $d_{001}$  parameter. The results of these measurements are presented in Fig. 2.

The CEC of the clays was determined by the titration method, used in natural zeolites investigation (Hudec et al. 1988). The

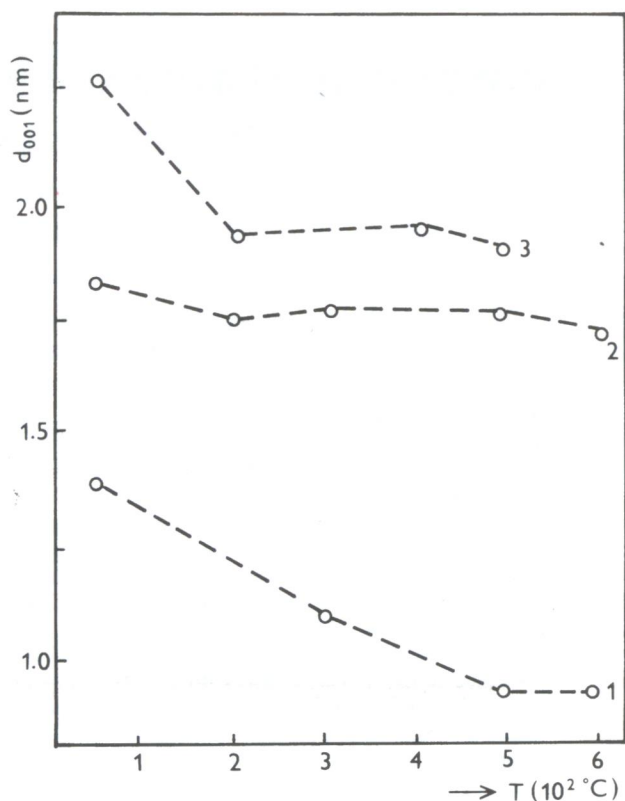


Fig. 2. Basal spacing,  $d(001)$  in nm.

1 - Ca MMT; 2 - Al<sub>2</sub>O<sub>3</sub> pillared MMT; 3 - Cr<sub>2</sub>O<sub>3</sub> pillared MMT.

adsorption-desorption measurements were performed using a Sorptomatic 1800 instrument. The measured data were treated by the standard BET-method and by t-plot method for calculation of micropore volumes, external surface areas and approximate pore size (Hudec et al. 1986). The adsorption - desorption isotherms of the investigated materials are shown in Figs. 3 - 5.

## Results and discussion

### Thermal measurements

MMT (Fig. 1, curve 1) corresponds to the dehydration of montmorillonite interlayer space, which contains two-valent cations. The next endothermic peak - at 668 °C indicates dehydroxylation of montmorillonite structure. The third endothermic peak (at 905 °C) represents the montmorillonite structure decomposition, after which the high-temperature phases are formed (Grim & Kulbicky 1961).

There is just one endothermic peak - at 110 °C in the DTA curve of hydroxy-Al precursor (Fig. 1, curve 2). Hydroxy-Cr precursor possesses two endothermic peaks (112, 165 °C). These peaks correspond to dehydration of hydroxy-metal precursors.

Comparison with original montmorillonite shows that the top of dehydration occurs at lower temperatures for hydroxy-metal precursors. This is caused by different binding of water with interlayer cations in Ca-montmorillonite as compared to the inorganic polyoxo-cations in precursors. The DTA curve of precursors shows an exothermic peak at 978 °C (hydroxy-Al precursor) or at 980 °C (for hydroxy-Cr precursor) reflecting the formation of high temperature phases.

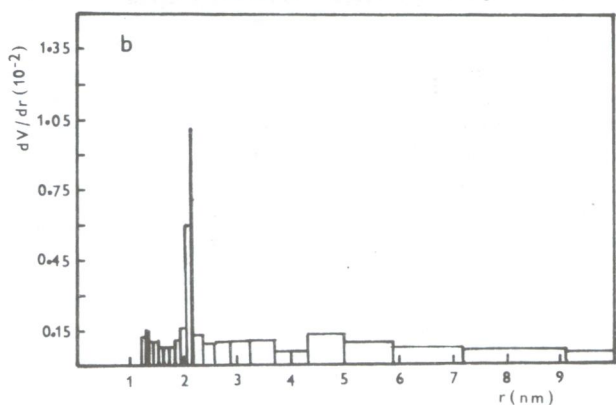
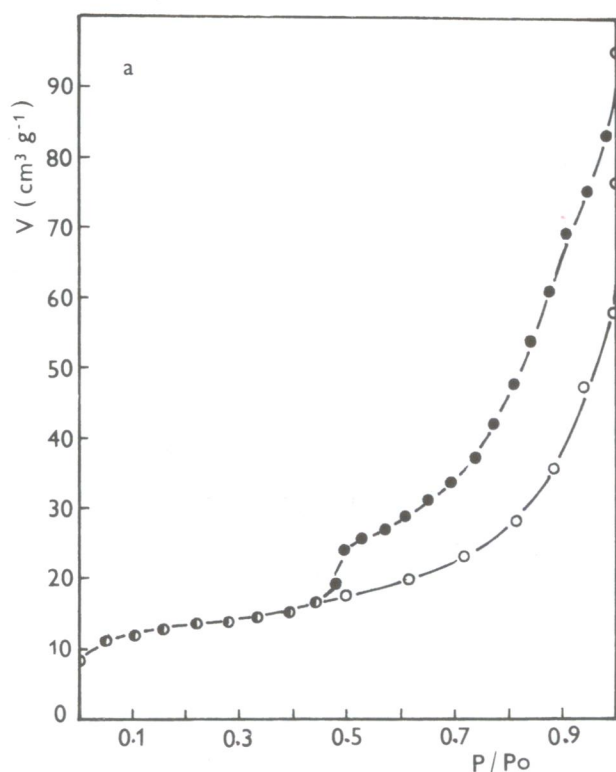


Fig. 3. Nitrogen adsorption (o) - desorption (●) isotherm (a) and pore size distribution (b) of Ca MMT heated at 60 °C in air.

#### XR-diffraction measurements

The temperature dependence of the  $d_{001}$  spacing for Ca-MMT, hydroxy-Al precursor and hydroxy-Cr precursor is shown in Fig. 2. While the Ca-MMT lattice already collapses after heating at low temperatures, the Al-pillared and Cr-pillared MMT, with strongly bonded oxide clusters in their structures, are stable to higher temperatures.

#### CEC measurements

CEC of Ca-MMT was 0.99 meq.g<sup>-1</sup>; it was decreased after pillaring and calcination to 0.66 meq.g<sup>-1</sup> in Al-pillared montmorillonite case or 0.69 meq.g<sup>-1</sup> for Cr-pillared MMT. This was caused by the fact, that part of the charge-compensating protons released by calcination of hydroxy-metal precursor were no longer available for the exchange.

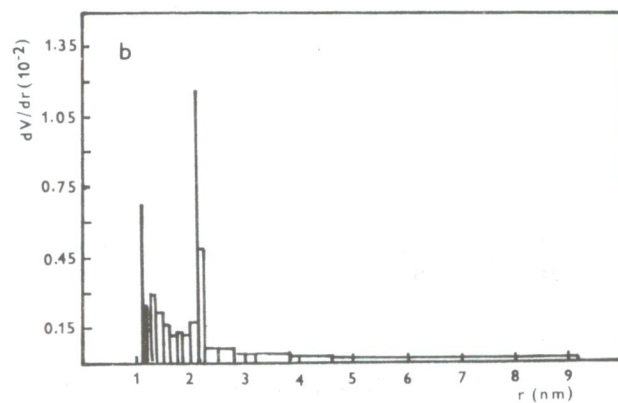
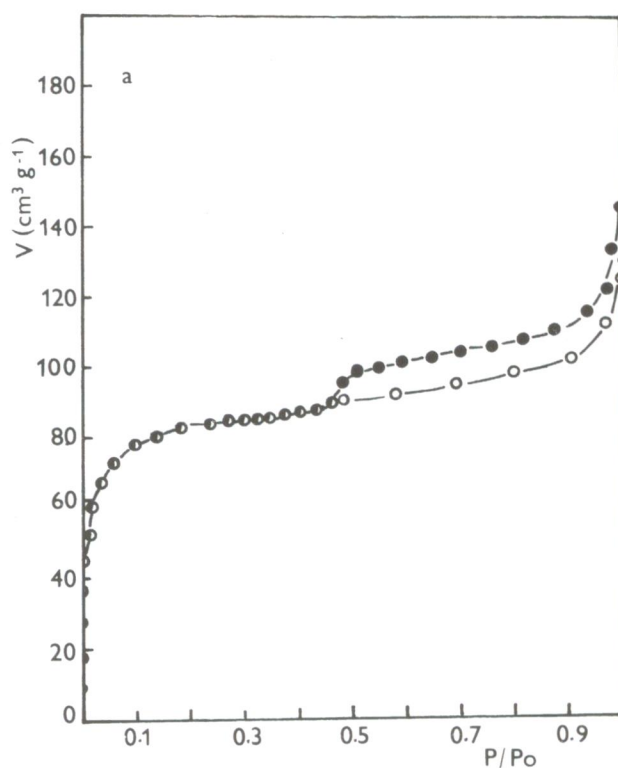


Fig. 4. Nitrogen adsorption (o) - desorption (●) isotherm (a) and pore size distribution (b) of Al<sub>2</sub>O<sub>3</sub> pillared MMT heated at 500 °C in air.

#### Adsorption-desorption measurements

The adsorption-desorption isotherms of Ca MMT and Al- and Cr-pillared MMT show hysteresis due to the presence of mesopores in montmorillonite structure. Al- and Cr-pillared MMT exhibit type I isotherms (Langmuir) with nitrogen (Malla & Komarneni 1990). From the shape of the adsorption isotherms it can be seen that nitrogen adsorption for Al- and Cr-pillared MMT is considerably higher than for Ca-MMT at lower  $p/p_0$  ratio, i. e. pillared MMT structure contains substantially more zeolitic pores.

From the shape of the adsorption isotherm of Ca-MMT one can expect a wider pore distribution for original MMT. This is confirmed by the pore size distribution diagram (Fig. 3). Diagrams of pore distribution show that for all three investigated materials the majority mesopores are from 2.2 nm area, what agrees well with the behaviour of other clay materials.

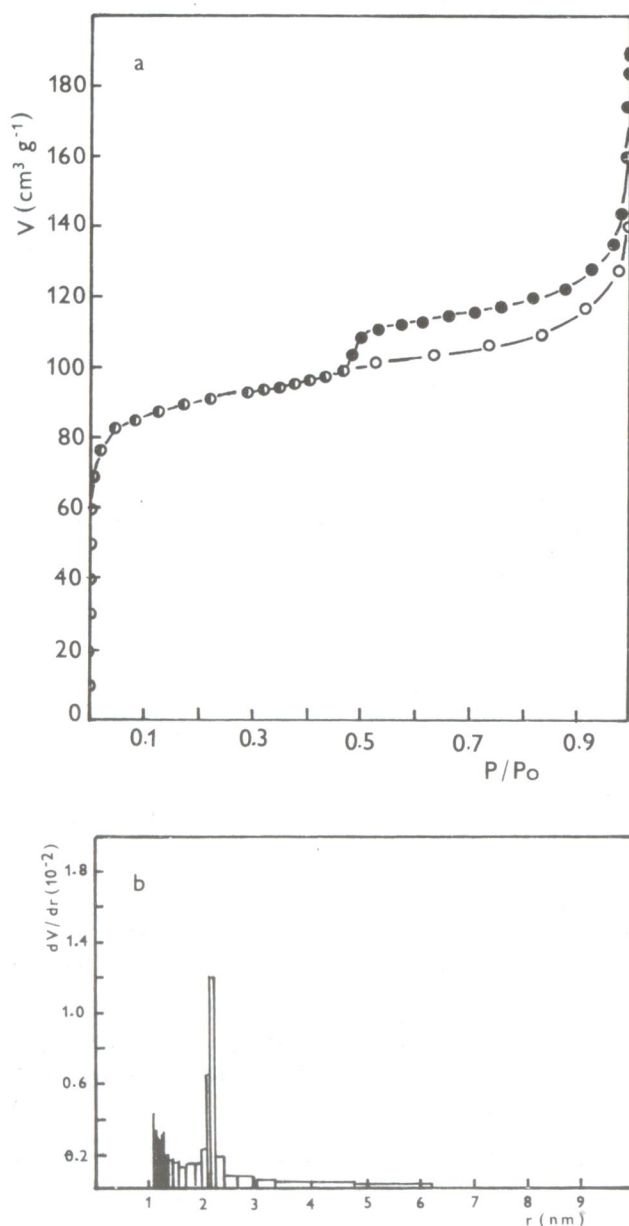


Fig. 5. Nitrogen adsorption (○) - desorption (●) isotherm (a) and pore size distribution (b) of  $\text{Cr}_2\text{O}_3$  pillared MMT heated at  $500^\circ\text{C}$  in nitrogen.

The surface characteristics of the investigated materials are shown in Tab. 1. The specific surface area of calcium montmorillonite increased from  $43 \text{ m}^2 \cdot \text{g}^{-1}$  to about  $275 \text{ m}^2 \cdot \text{g}^{-1}$  for both pillared montmorillonites. From analysis of surface properties (t-plot) it was found that the increase in the specific surface area was due to the increase of micropore volume, which after pillaring was more than 10 times larger, while the mesopores surface increased approximately 2.5 times. It can be said that prevalent part of pores volume of pillared materials is from micropores area of pores sizes. The specific mesopores volume of Ca-MMT presents about 70 % of specific surface area, while the specific mesopores surface of pillared montmorillonites presents less than 30 %.

Table 1: Surface characteristics of investigated materials

Property	Material		
	Ca-MMT	Al-MMT	Cr-MMT
CEC ( $\text{meq} \cdot \text{g}^{-1}$ )	0.99	0.66	0.69
specif. surface area ( $\text{m}^2 \cdot \text{g}^{-1}$ )	43	281	274
specif. micropor. volume ( $\text{cm}^3 \cdot \text{g}^{-1}$ )	0.0074	0.1070	0.0934
specif. mesop. surface ( $\text{m}^2 \cdot \text{g}^{-1}$ )	29.9	75.3	77.5

## Conclusion

The reaction of Ca - montmorillonite with Al-, Cr- polyoxocations and subsequent calcination generate microporous materials, which are thermally stable up to  $500^\circ\text{C}$ . The prepared pillared montmorillonites present more advantageous surface and thermal properties than unpillared material. The testing of their molecular-sieve properties and catalytic activity is important from the point of view of possible exploitation.

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