THERMAL STABLE POROUS CRYSTALS FROM MONTMORILLONITE

II. PREPARATION AND THE PROPERTIES OF CR PILLARED MONTMORILLONITES

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Chromium pillared montmorillonites were prepared by cation exchange reaction of Na and Ca Jelšový Potok montmorillonite with hydroxy-chromium solution and by subsequent calcination, when oxide pillars in interlayer space were formed. Solution of Cr polymer cations was obtained by aging of $Cr(NO_3)_3$ solution titrated by Na_2CO_3 with final molar ratio (OH) / (Cr) = 2. thermal, XRD and IR spectroscopy methods were used to investigate prepared materials. A higher oxidation ability of Cr pillared sample in comparison with Na- and Al pillared-montmorillonite was shown in thermal measurements after p-xylene adsorption.

INTRODUCTION

There are several methods for pillaring of the expanding layer silicates [1]. With respect to possible precipitate formation, two methods can be distinguished: a) a direct cation exchange method and b) titration method. In method a) a solid phase dispersed in water interacts with solution containing the hydrolyzed cations. In method b) a solution of cations is added to clay dispersion and resulting mixture is treated by hydrolysis. The method a) is used more frequently to the preparation of Al, Zr and Cr-pillared clays, respectively. The pioneer work regarding the preparation of the Cr-pillared clays was made by Brindley and Yamanaka [2]. They used the solutions of $Cr(NO_3)_3$ - NaOH as the pillaring agent and investigated the Cr_xO_y pillars formation in montmorillonite interlayers in dependence on the basicity of the pillaring agent. They found, that intercalated Cr species are in the form of $[Cr(OH)(H_2O)_5]^{2+}$ cations.

In a similar way, Carr [3] defined the pillaring Cr cations in the form of $[Cr_2(H_2O)_8(OH)_2]^{4+}$. Chromium exists in water as hexaaquachromium cation. In this medium is submitted to hydrolysis and dimerization with equation

$[Cr(H_2O_6)]^{3+} + H_2O = [Cr(H_2O)_5OH]^{2+} + H_3O^+$

$2\ [Cr(H_2O)_5]^{3+} = [Cr_2(H_2O)_8(OH)_2]^{4+} + 2\ H_2O$

It becames oligomerization

$$5\ [Cr(H_2O)_6]^{3+} \longrightarrow [Cr(H_2O)_8(OH)_2]^{4+} + \\ + [Cr(H_2O)_9(OH)_4]^{5+} + \\ + 6H_3O^+ + H_2O.$$

It is verified, that cations created by the hydrolysis at 95°C are bigger than the cations formed after room temperature (RT) hydrolysis. The influence of temperature on the formation of Cr polymers is reported by Laswick and Plane [4]. Shaptai et al. [5] prepared cross-linked montmorillonites using $CrK(SO_4)_2$ solution titrated with NaOH. Hopkins et al. [6] have used nitrate solution. It was found later, that the utilization of less basic Na_2CO_3 for the titration, the formation of $Cr(OH)_3$ precipitate is avoided due to the prevention of the local extremely high concentration in the solution.

Recently, the investigation of the preparation and the properties of chromium pillared clays was accomplished by Pinnavaia et al. [7, 8]. They studied the Cr-oligomers formation at higher temperatures. Tzou and Pinnavaia [9] applied the chromium pillared clays in the study of benzene formation from cyclohexane. Chromium catalysts in the form of pillared clays are utilized as oxidation agents in various kinds of the organic synthesis [10], as well as the cracking catalysts [13]. Zielke and Pinnavaia [11] studied the adsorption of the chlorine substituted phenols on the chromium pillared clays prepared according to [12]. They found that adsorption of chlorinated phenols in slightly basic environment increases with increasing of the hydrophobicity.

In present work the hydroxy-chromium montmorillonites have been prepared by direct cation-exchanged method using Na_2CO_3 as base. The aim of the study was to evaluate the data obtained from thermal analysis, IR spectroscopic and X-ray diffraction measurements.

EXPERIMENTAL

Starting material

Jelšový Potok (Slovakia) bentonite was used in this study. After separation and calcification, resp. natrification, the calcium and sodium montmorillonite was obtained from this material. The chemical analysis (wt. %) of both montmorillonites are as follow: SiO_2 (Ca MMT 61.9, Na MMT 63.1), Al_2O_3 (20.8 resp. 20.6), Fe_2O_3 (3.19, 3.11), CaO (2.86, 0.16), MgO (2.98, 3.12), Na_2O (0.14, 2.83), K_2O (under 0.1), loss on ignition (6.26, 6.24).

Pillaring hydroxy-chromium solution

The chromium pillaring agent was prepared by a method [12]. A 0.1 M chromium nitrate was hydrolyzed by the addition of 0.2 M sodium carbonate

Table 1

pH and UV absorption maxima of Cr solutions prepared by hydrolysis with Na_2CO_3

Ratio	Fresh Cr solution at RT		Solution after 40 hours at 97°C	
OH/Cr	pH	abs. max. (nm)	pH	abs. max. (nm)
0.0	2.15	572.4	–	–
2.0	3.63	574.0	2.10	587.4

to achieve a final (OH)/(Cr) ratio of 2.0. The resulting solution was then aged for 40 hours at 97°C in steel block. The effect of aging at 97°C on d-d transitions of chromium nitrate in aqueous solution is shown in Table I. and Fig. 1. The data obtained by this measurement were similar as in [9]. The changes of these properties and time of aging indicate that the hydrolysis of chromium to higher polymers is slower process than the formation of hydroxy-aluminium polymer species.

Precursor preparation

Montmorillonite suspension (1% wt. of solid) was added in small amount at constant stirring to Cr pillaring solution at 80°C. Resulting chromium to montmorillonite ratio was 80 mmol. of Cr / meq. of montmorillonite. After adding of the all suspension the mixture was stirred for 2 hours. Solid product was then collected by centrifugation and washed free of excess salt using distilled water and dried at 60°C. The intercalated Cr is expressed empirically as $[Cr(OH)_{3-q}]^{q+}$, where q is the apparent net charge per chromium [7].

Precursor calcination

The dried sample was heated for 2 hours at 500°C in nitrogen. The inert atmosphere prevents the chromium oxidation and following formation of Cr_xO_y outside of pillared structure as was demonstrated by DSC measurements in [8]. The chemical analysis of Cr pillared sample prepared from Ca MMT showed that this materials contains 21.5 wt. % of Cr_2O_3 and approximately 1 wt. % of CrO_3.

Characterization of the samples

Montmorillonites and prepared materials were studied by thermal analysis, IR spectroscopy, X-ray diffraction analysis and B.E.T. adsorption method, as described previously [1]. The results are shown in Figs. 2–5. Moreover, the adsorption of p-xylene probe molecules on Na montmorillonite, Al- and Cr-pillared sample was performed and studied using thermal methods (Fig. 6). The effect of aging was checked by

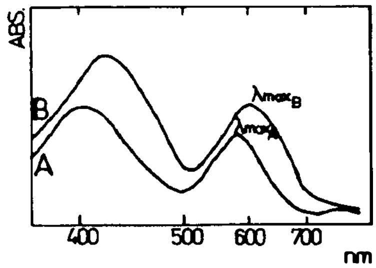

Fig. 1. UV-visible spectra of chromium nitrate solution with (OH)/(Cr) = 2.0 at room temperature (A) and after 40 hours-aging at 97°C (B).

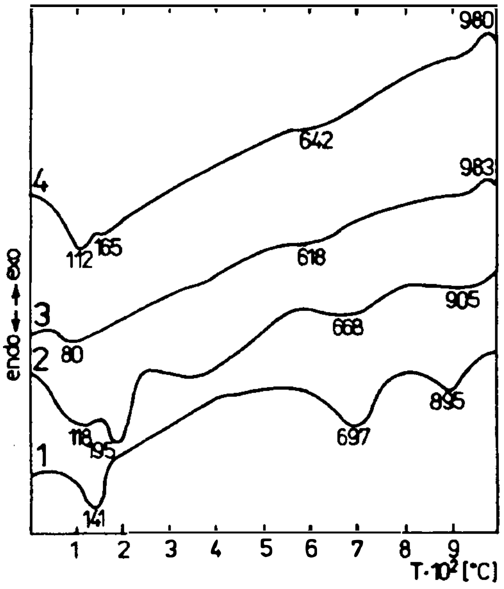

Fig. 2. DTA curve of Na MMT (1), Ca MMT (2), Cr precursor from Na MMT (3) and Cr precursor from Ca MMT (4).

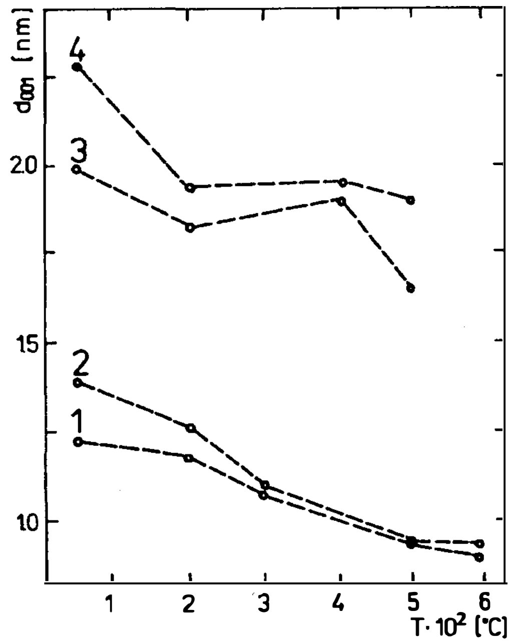

Fig. 3. d_{001} values for Na MMT (1), Ca MMT (2), Cr precursor from Na MMT (3) and Cr precursor from Ca MMT (4).

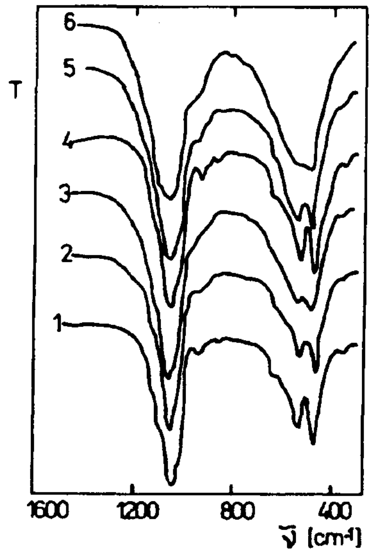

Fig. 5. IR spectra of Cr precursor from Na MMT (1, 2, 3) and Cr precursor from Ca MMT (4, 5, 6) at RT (1, 4), 400 (2, 5) and 500°C (3, 6).

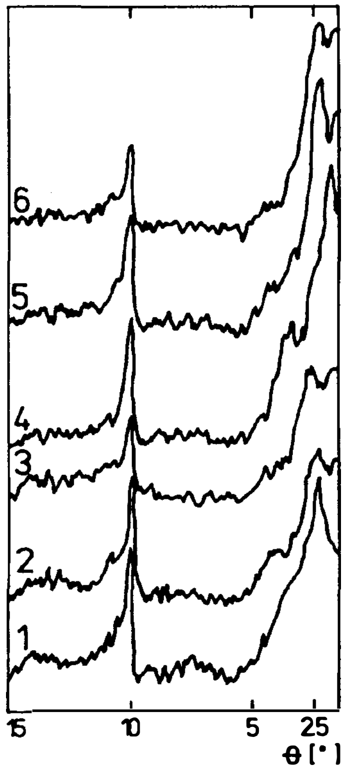

Fig. 4. XRD pattern of Cr precursor from Na MMT (1, 2, 3), Cr precursor from Ca MMT (4, 5, 6) heated 2 hours at 50°C (1, 4), 400°C (2, 5), 500°C (3, 6).

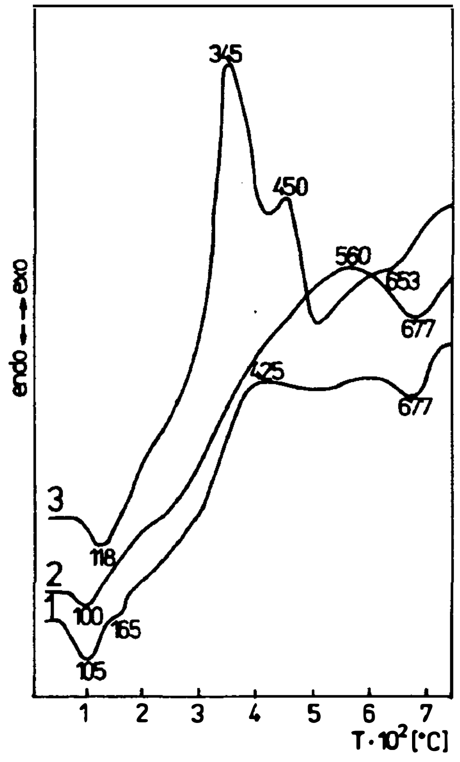

Fig. 6. DTA curve of Na MMT (1), Al pillared MMT (2) and Cr pillared MMT (3) after p-xylene adsorption.

UV spectroscopic measurements using Spectrometer Specord M 40 fy Carl Zeiss Jena.

DISCUSSION

Thermoanalytical measurements

The thermal behaviour of Cr-precursors prepared from the both Ca- or Na-montmorillonite was studied using DTA method (Fig. 2). The kind of originally present exchangeable cation influenced the shape and intensity of DTA peaks in dehydration and dehydroxidation region after chromium treating (curves No. 3 and4). It indicates, that part of the Ca- and Na-exchangeable cations remained in the interlayer space of the Cr-precursor. Dehydroxidation of Cr-precursors occured at lower temperatures as compared with the starting materials. It is due to corridor space formation by means of chromium oxide pillars (easier water molecules diffusion through the permanent porous system of the Cr-pillared clay). The striking high temperature peak at 980°C present in DTA curves of chromium treated samples (curves No. 3 and 4) indicates the catalytic action of Cr atoms on the formation of high temperatures phases.

XRD measurements

The alteration of d_{001} values on heating show in Fig. 3 illustrates the thermal stability of the Cr-pillared materials. The sample of Cr-precursors were heated in inert atmosphere to prevent the release of chromium atoms outside of the pillared region [8]. There are some differencies in behaviour of Cr-precursors prepared from Ca- and Na-montmorillonite (d_{001} values 3 and 4). Cr-precursor prepared from calcium montmorillonite seems to produce more stable pillared structure (d_{001} values 4). XRD patterns in the range of 3.5–15° 2θ are shown in Fig. 4. Aside of d_{001} diffractions the XRD spectra contain the significant diffraction at 0.443 nm belonging to (hk) reflection of montmorillonite structure. There is possible to observe a slight decreasing in intensity of this reflection on heating at 500°C.

IR spectroscopic measurements

The absorption maxima typical for the montmorillonite structure were evaluated according [15, 16]. The were no any differencies found between the IR spectra of precursors prepared from Ca- and sodium montmorillonite (Fig. 5). The strong absorption band at 1040 cm^{-1} in spectra belongs to the stretching Si-O vibration and another one at 920 cm^{-1} represents the bending vibrations of Al-Al-OH groups. bending vibrations of Al-Mg-OH groups occurs at 845 cm^{-1}. Absorption band at 800 cm^{-1} can be ascribed to the Si-O vibration in free SiO_2 compound present as the impurity in montmorillonite. On the heating, the absorption bands attributed to OH bending vibration as well as for R-O-R-vibrations at 625 cm^{-1} and Si-O-Al vibrations at 520 cm^{-1} have been dimishing gradually. Moreover, two bending vibrations at 520 and 470 cm^{-1} become less distinguishable with higher temperatures of chromium pillared precursors.

P-xylene adsorption measurementt

Thermal stability of p-xylene adsorbed on Na-montmorillonite, Al- and Cr-montmorillonite was studied using DTA method (Fig. 6). The DTA curve of chromium pillared species (curve No. 3) shows the striking oxidation action of chromium atoms (strong exothermal maxima at 345 and 450°C) in decomposition of p-xylene molecules in the porous system of the adsorbent. The additional study is needed to explain the technological importance of this observation.

The characteristics of the porous system of the Cr-pillared montmorillonite

Aside of XRD measurements BET adsorption experiments were accomplished to characterize the sterical properties of the studied materials. The details are described elsewhere [14]. The adsorption measurements showed, that the specific area was 270 $m^2.g^{-1}$ for chromium precursor heated at 500°C for 2 hrs. The mesopores surface increased after pillaring aproximately 2.5 times, while the micropores volume increased more than 10 times.

CONCLUSIONS

The presented data show that montmorillonite Jelšový Potok (Central Slovakia) is suitable for the preparation of chromium pillared porous crystals. The properties of these compounds seems to be better compared with aluminium or zirconium analogous derivatives describes previously [1]. It results in higher specific area as well as larger d_{001} values. Additionally, the specific properties of Cr atoms intercalated in montmorillonite interlayer in Cr_xO_y clusters can play an importand role in technical utilization of these materials.

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TERMICKY STABILNÉ PÓROVITÉ KRYŠTÁLY NA BÁZE MONTMORILLONITU

II. PRÍPRAVA A VLASTNOSTI CR PILIEROVANÝCH MONTMORILLONITOV

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Cr-pilierované montmorillonity boli pripravené katiónovýmennou reakciou Ca- a Na-montmorillonitu Jelšový Potok (Slovensko) s hydroxy – Cr roztokom, a následnou kalcináciou. Roztok Cr – polymérnych katiónov sa pripravil titráciou $Cr(NO_3)_3$ roztokom $NaCO_3$. Výsledný pomer (OH)/(Cr) bol rovný dvom. Získané materiály boli študované termickými, RTG difrakčnými, IČ spektroskopickými a adsorpčnými metódami. Termické merania po adsorpcii p-xylénu na Na montmorillonit, Al- a Cr-pilierovaný montmorillonit demonštrovali najvyššiu oxidačnú schopnosť v prípade Cr-pilierovaného montmorillonitu.

Obr. 1. UV-viditeľné spektrum roztoku $Cr(NO_3)_3$ s $(OH)/(Cr) = 2{,}0$ pri izbovej teplote (A) a po státí 40 hod. pri 97°C (B).

Obr. 2. DTA krivka Na MMT (1), Ca MMT (2), Cr prekurzora pripraveného z Na MMT (3) a Cr prekurzora z Ca MMT (4).

Obr. 3. Hodnoty parametra d_{001} pre Na MMT (1), Ca MMT (2), Cr prekurzora z Na MMT (3) a Cr prekurzora z Ca MMT (4).

Obr. 4. RTG-difrakčný záznam Cr prekurzora z Na MMT (1, 2, 3), Cr prekurzora z Ca MMT (4, 5, 6) zahrievaného 2 hod. pri 50 (1, 4), 400 (2, 5) 500°C (3, 6).

Obr. 5. IČ spektrum Cr prekurzora z Na MMT (1, 2, 3) a Cr prekurzora z Ca MMT (4, 5, 6) pri RT (1, 4), 400 (2, 5) a 500°C (3, 6).

Obr. 6. DTA krivka Na MMT (1), Al pilierovaného MMT (2) a Cr pilierovaného MMT (3) po adsorpcii p-xylénu.

Book Review

CERAMIC TRANSACTIONS, VOL. 19. ed. M.D. Sacks. Advanced Composite Materials: Processing, Microstructures, Bulk and Interfacial Properties, Characterization Methods, and Applications. The American Chemical Society, Inc., Westerville, Ohio 1991, 1117 pages.

The book contains the proceedings of the "Symposium on Composites: Processing, Microstructures and Properties", held in November 12–15, 1990 in Orlando in Florida as a part of the Second International Ceramic Science and Technology Congress of the American Ceramic Society. From 196 presentations, 115 manuscripts were selected for the book.

Composite materials represent a progressive trend in the preparation of new materials. Combinations of various types of matrices with various types of reinforcement allow extraordinary properties to be achieved. Attainment of synergic effects, and the resulting quite unthought-of possibilities, are the decisive factors.

The proceedings comprise the following sections:

Section I. Synthesis and Processing
Section II. Surface and Interfaces: Structure, Absorption Behaviour, Wetting, Chemical Reactions, and Related Phenomena
Section III. Processing, Microstructures, Properties, and Applications of Optical, Electrical and Magnetic Composites
Section IV. Fracture Behaviour and Mechanical Properties
Section V. Interface-Mechanical Property Relations
Section VI. Processing-Microstructure-Mechanical Property Relations
Section VII. Oxidation, Corrosion and Environmental Effects
Section VIII. Characterization Methods
Section IX. Applications for Wear-Resistant and Tough Composites.

The book is suitable for scientists and engineers dealing with the development of new types of materials, in particular composites ones, their properties and applications. However, it should also be useful for research and development departments of some industrial establishments.

J. Kutzendörfer