PREPARATION AND INVESTIGATION OF PILLARED LAYERED CLAYS

KEY POINTS OF THE PhD THESIS

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INTRODUCTION

Clays such as beidellite and montmorillonite have layer structures. The layers are constructed of vertex and edge-sharing octahedra and tetrahedra. The atoms forming the layers are normally silicon and aluminum together with small mono- and divalent species such as magnesium and lithium. This framework layer has an overall negative charge that is balanced by the incorporation of cations, typically alkali metals, between the layers. It has long been known that these inter-layer cations can be readily ion-exchanged.

In the pillaring of clays the complexes to be exchanged into the inter-lamellar region are selected for size. Pillaring complexes (mainly inorganic cations as polynuclear hydroxy-metal type) may replace the alkali metals. Once a pillaring ion has been incorporated at a certain place between the layers, heating the modified clay results in dehydration and the linking of the ion to the layers. The resulting pillars support the sheets and the galleries thus creating a two-dimensional network of micropores, known as pillared layered clays. Because of the space created these kinds of structures are suitable for a wide variety of applications, e.g. adsorption, catalytic reactions.

Recent research into pillaring has been focussed in two main directions:

- Investigating a wider range or suitable host materials, e.g. metal phosphates,
- Investigating and extending the range of cations to be used in the cation replacement.

At first, the main obstacle to the production of economical pillared layered clays was the fact that they could only be prepared using pillaring suspensions with a very low concentration (less than 1% mass). As recent literature indicates, however, this problem has been overcome, and new processes have been developed which use pillaring suspensions with much higher concentrations.

The aim of present research was to develop and investigate several techniques for the incorporation of robust polycations in the different kinds of clay structures in order to produce cheap and useful new porous materials. Three combinations of host materials and polyoxycations were examined.

Particular emphasis was put on investigating bentonite rocks. There are large deposits of these rocks in Hungary, and the montmorillonite minerals, which they contain, have high cationic exchange capacity. This favourable combination of factors suggested that this bentonite rock could prove to be an economical source for artificially produced pillared layered clays.

KEY POINTS OF THE THESIS

1. Using Hungarian bentonites, namely such as Istenmezeje, Koldu and Mád, the alumina-pillaring was successfully carried out in the case of highly concentrated clay suspensions (10 and 15 wt%) and highly concentrated Al_{13}-keggin-ion solutions with simple stirring engineering at room temperature. The efficiency of the pillaring reaction was better by adding the solutions of pillaring agents to the Hungarian clays suspensions. Both original and sodium-saturated forms were showing pillared layered structures with basal spacing around 19Å, indicating the successful pillaring procedure. Furthermore, the data mentioned about Hungarian pillared structures also demonstrated the well-known fact for overseas (non-Hungarian) clays that the sodium forms have higher tendency or they are more suitable for good pillaring by producing controlled structures than the original forms of montmorillonite. Mád and Koldu pillared layered clay samples absolutely fulfilled the minimum criteria of pillared material using X-ray and thermal analysis. Furthermore, the alumina pillared Na-Mád and Na-Koldu clays have specific surface area around 200 m^2/g that is nicely meets the accepted surface area and porosity requirements.

2. It was found that using higher concentration of Hungarian clay suspensions, the formed pillared layered samples were more stable than in the case of lower clay's concentration both sintered at higher or lower sintering temperature. Pillared samples prepared by higher concentration of clay suspension showed smaller d-spacing loss for all clay than lower concentration at 500ºC sintering temperature. Pillared samples prepared by higher concentration of clay suspension disclosed smaller d-spacing loss for sodium-

clay samples, and larger loss for original forms than in the case of lower concentration of suspension at 350ºc sintering temperature. Mád clay samples had the smallest decrease in d-spacing after sintering at lower or higher temperature that indicated the best pillared form samples both for original and sodium form, such as lower and higher concentration of clay suspension.

3. Iron-oxide-intercalated clays were prepared using two kinds of iron-pillaring agents, namely iron-chloride and iron-benzoate. The stability of the iron-intercalated structures was depended critically on the hydrolysis conditions of iron. in the case of iron-benzoate three kinds of preparation procedures were applied, namely such as reflux, shaking, and stirring, where the stirring was best suitable method for pillaring. In the case of iron-chloride, by increasing the base to metal ration it was detected higher surface area and bigger basal spacing values. The structures of the intercalated clays were collapsed under calcination process at 450 °C with only a few exceptions.

4. Smectite clays had the high tendency to insert into their surfaces three-dimensional organosilicon oligomers in amounts exceeding the CEC of the mineral, the excess was being in the form of physically adsorbed ion-pairs. The presence of ion-paired silsesquioxanes in the clay galleries influenced the free distance between the layers and the surface area and porosity of the silica-pillared compositions. Removal of the ion-paired cubes by water treatment reduced the d_{001} spacing from 18 Å to 16 Å. Lower surface areas were found for the unwashed samples indicating stuffing of the galleries by the ion-paired cubes. Water treatment of the intercalated samples bringed a gradual decrease in the interlayer distance. The performed cubic silsesquioxanes were introduced as intact units into the clay layers, the cubes were first fixed at the exchanged sites of the mineral and then occupied the between space in the form of ion-pairs. Calcination of the washed or unwashed phases gived silica-pillared structures with d_{001} spacings near 16 Å, with the washed phase showing the higher surface area. the repeated washing of the material caused the evacuation of micropores from the ion-paired intercalated species that otherwise stuff the empty space of the clay galleries.

PUBLICATIONS

Vassányi, I., **Szabó, A.** : Thermic dehydroxylation of muscovite-2M1, *Materials Science Forum*, 1993. v133/136 p2, page:655-658.

Szabó, A., D. Gournis, M.A. Karakassides, and D. Petridis: Clay-Aminopropylsiloxane Compositions, *Chemistry of Materials*, 1998., 10, 639-645.

Szabó, Anikó, Zsuzsanna Hartyáni, Ernő Nemecz: Investigation of Hungarian montmorillonites and preparation of alumina-pillared montmorillonites (is submitted to *Clays and Clay minerals*)

Szabó Anikó, Hartyáni Zsuzsanna, Nemecz Ernő: Aluminium-oxid pillérezett magyarországi montmorillonitok vizsgálata röntgendiffrakcióval (is prepared)

PRESENTATIONS

Vassányi, I., **A. Szabó**: Thermic dehidroxylation of muscovite-$2M_1$, *2nd European powder Diffraction Conference*, July 30-August 1,1992., Enschede, The Nederlands

Szabó, A. et al.: Examination of bore-hole samples from South-Hungary, *12th Conference on clay Mineralogy and Petrology*, August 31-September 4,1992., Bratislava, Slovakia

Vassányi, I., **A. Szabó**, Zs. Csikós-Hartyáni: Examination of soil Weathering Processes Through a New Method, *12th Conference on clay Mineralogy and Petrology*, August 31-September 4,1992., Bratislava, Slovakia

Szabó, A., I. Varsányi, I. Vassányi: Mineralogical examination of bore-hole samples of Mindszent, South-Hungary, *General Assembly of Hungarian Clay Minearls Society*, December 7, 1992., ELTE University, Budapest, Hungary

Szabó, A.: Investigation of pillared smectites by X-ray diffraction, *Symposium about application possibilities of X-ray diffraction in material science*, Prof. I. Vassanyi Memorial Meeting, April 20, 1995., Veszprém, Hungary

Szabó, A., D. Petridis, A. Simopoulos, Preparation of Iron Mesoporous materials, *Vegyészkonferencia'96 (Conference of Chemists'96)*, July 2-4, 1996., Eger, Hungary

Szabó, A., Z. Pilter, I. Vassányi, E. Nemecz: Alumina Pillared hungarian Montmorillonites, *EUROFORUM'96 Conference*, 4-6 September 1996., Veszprém, Hungary

Szabó, Anikó: Pillaring of Hungarian Bentonites, *Symposium of Clay Minerals Section of the Hungarian Geological Society*, November 25, 1996., Institute of Earth Science, Budapest, Hungary

Szabó, Anikó: Preparation and investigation of pillared montmorillonites, *Board Meeting of Geochemical- and Mineralogical Section of Hungarian Academy of Sciences*, December 2, 1996., Budapest, Hungary

Szabó, A., Z. Pilter, E. Nemecz: Alumina Pillared Hungarian Montmorillonites, *The 4th IUMRS International Conference in Asia*, September 16-18, 1997., Makuhari, Chiba, Japan

Szabó, A., Zs. Hartyáni, E. Nemecz: Investigation of Hungarian montmorillonites and preparation of alumina pillared montmorillonites, *2nd MID-EUROPEAN CLAY CONFERENCE*, 20-24 September 2004., Miskolc, Hungary