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EFFECT OF MAGNESIUM AND CALCIUM ON THE HIGH-TEMPERATURE REACTIONS OF SYNTHETIC MONTMORILLONITE

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ABSTRACT

Three specimens of montmorillonite with different Mg content were synthetized from the SiO_2-Al_2O_3-MgO-CaO-H_2O system /T=300°C, p=8.8 MPa, t=7 days/. They were transfered to monoionic Mg- and Ca-forms. The effect of Mg and Ca amount on high-temperature reactions was studied up to 1250°C.

INTRODUCTION

According to the course of DTA curve near 1000°C and the kind of high-temperature phases of montmorillonite Grim and Kulbicki /1/ divided montmorillonites into two groups. The montmorillonite belongs to the Wyoming type if the first exothermic peak follows immediately the preceding endothermic peak. If there is some delay /100-150°C/ between these two peaks it is that of the Cheto type. These two types differ also in their high-temperature phases. Mullite and cristobalite are typical for the Wyoming type and beta-quartz, cristobalite and cordierite for the Cheto type. Lucas and Trauth /2/ explained the difference between these two types by antagonistic effect of Mg and Fe in structure.

To avoid the influence of Fe on the high-temperature reactions, three specimens of montmorillonite with increasing amount of magnesium but no iron were synthetized. So it was possible to study the effect of the Mg amount on these reactions. The effect of Mg and Ca as exchangeable cations was studied, as well.

EXPERIMENTAL

Montmorillonite was synthetized hydrothermally from silica gel and aluminium, magnesium and calcium hydroxides at 300°C, pressure 8.8 MPa and time of synthesis was 7 days. Then, samples were treated for 1 hour with acetic acid at pH 3.0. Monoionic forms were prepared by multiple treatment with 1M solutions of $MgCl_2$ or $CaCl_2$.

The products of synthesis, as well as high-temperature phases

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were identified by the vertical diffractometer Philips PW 1050. The thermal analysis was performed on Derivatograph MOM, Budapest. Samples were annealed in crucible furnace in which temperature was measured by thermocouple Pt-PtRh.

RESULTS AND DISCUSSION

A purity of all monoionic samples was tested by thermal and X-ray phase analysis. The X-ray analysis shows that all samples are pure dioctahedral montmorillonites. The thermal analysis confirms this for the samples 1,2,4, and 5 but on DTA curves of samples 3 and 6, which have the highest magnesium content there are endothermic peaks near 900°C. TG and DTG curves of these two samples show at this temperature a very small weight loss. This means that in these samples there are small amounts of trioctahedral montmorillonite.

The chemical formulas for unit cell counted on the basis of chemical composition are for the samples 1 and 4, differing only in the exchangeable cation /sample 1 is Ca-form and sample 4 is Mg-form/ as follows:

$$\left[Si_{7.54}Al_{0.46}\right]\left[Al_{3.86}Mg_{0.14}\right](Me^{II}_{0.30})O_{20}(OH)_4,$$

for samples 2 and 5 /2 is Ca-form and 5 is Mg-form/:

$$\left[Si_{7.71}Al_{0.29}\right]\left[Al_{3.63}Mg_{0.37}\right](Me^{II}_{0.33})O_{20}(OH)_4,$$

and for samples 3 and 6 /3 is Ca-form and 6 is Mg-form/:

$$\left[Si_{7.59}Al_{0.41}\right]\left[Al_{3.45}Mg_{0.55}\right](Me^{II}_{0.48})O_{20}(OH)_4.$$

The last formula is only partly correct because it is impossible to take into account a small admixture of trioctahedral montmorillonite.

The DTA curves of samples 1 and 4 are in both cases of Wyoming type /Fig. 1./. The temperature interval between T_{max} of the first exothermic peak and T_{max} of the preceding endothermic peak is 30°C for Ca-form and 15°C for Mg-form. The high-temperature phases are in both cases mullite and cristobalite.

The DTA curves of samples 2 and 5 depend on the nature of exchangeable cation /Fig. 1./. The temperature interval between the endotherm and the exotherm is 75°C for sample 2 and the high-temperature phases are mullite, anorthite and cristobalite. The temperature interval for the same peaks for the sample 5 is 35°C and the high-temperature phases are mullite, cristobalite and cordierite.

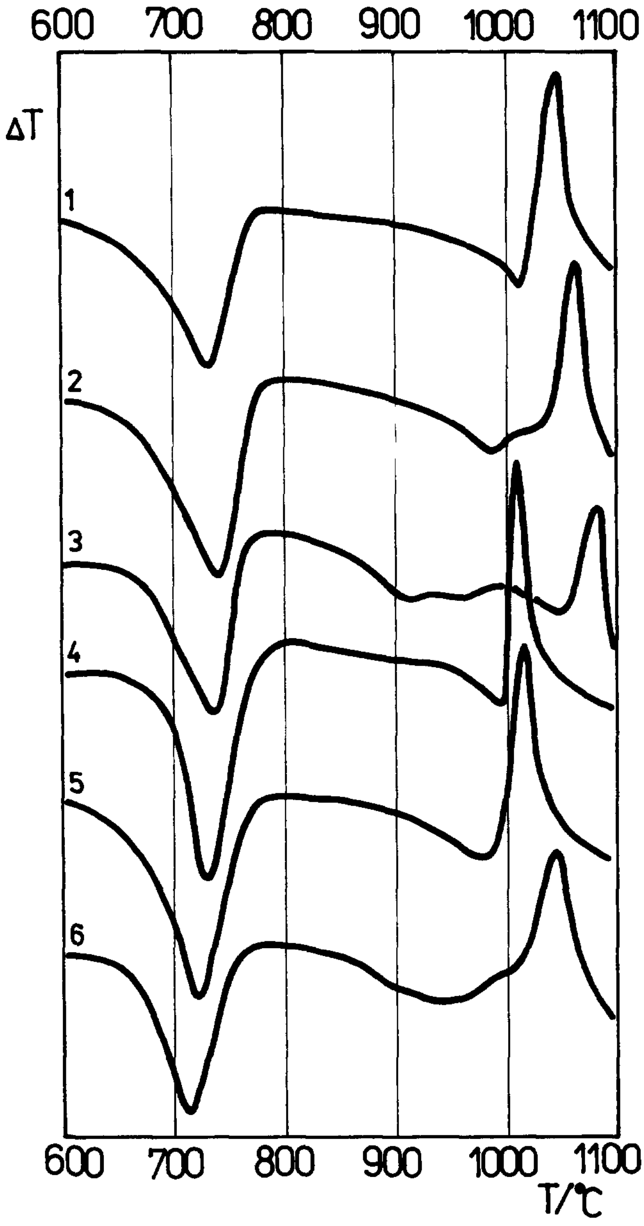

Fig. 1. DTA curves of synthetic montmorillonites (explanation in text)

The same intervals for the samples 3 and 6 are 115° and 100°C, respectively. The high-temperature phases are in case of sample 3 mullite, beta-quartz, cristobalite, anorthite and cordierite, and for the sample 6 mullite, cristobalite and cordierite.

CONCLUSIONS

If there is no iron in the structure, the montmorillonite with low Mg content in octahedral layer /below 0.5 Mg in unit cell/ belongs to the Wyoming type and to the Cheto type if the Mg content is higher.

The presence of Ca in exchangeable positions in montmorillonite causes:

a. the inhibition of the first high-temperature phase crystallization /spinel, mullite/,

b. shifting of T_{max} of the first exothermic peak on DTA curve towards higher temperature /Δ 40°C/,

c. easier formation of the beta-quartz-similar phase in case of the Cheto type montmorillonite and crystallization of cristobalite in case of the Wyoming type montmorillonite,

d. formation of anorthite in case of montmorillonite with higher cation exchange capacity / over 100 meq./100g/.

REFERENCES

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