Cross-linked Smectites. V. Synthesis and Properties of Hydroxy-Silicoaluminum Montmorillonites and Fluorhectorites

Johan Sterte[1] and Joseph Shabtai

Department of Fuels Engineering, University of Utah Salt Lake City, Utah 84112

[1] Research associate on leave from Chalmers University of Technology, Gothenburg, Sweden.

Abstract: Solutions containing hydroxy-SiAl (HSA) oligocations were prepared by two procedures: (1) treatment of a mixture of orthosilicic acid and $AlCl_3$ with aqueous NaOH, followed by aging of the product; and (2) preliminary preparation and aging of hydroxy-Al_{13} oligocations followed by reaction of the latter with orthosilicic acid. Ion exchange of Na,Ca-montmorillonite with HSA oligocations yielded pillared, cross-linked montmorillonites (designated as HSA-CLM) showing a maximum d(001) value of 19.5 Å for air-dried samples, and maximum surface areas of ~500 m^2/g after outgassing at 250 °C/10^{-3} torr. Corresponding ion exchange of Li-fluorhectorite yielded HSA fluorhectorites (HSA-CLFH) showing a maximum d(001) value of 19.0 Å and a surface area of 355 m^2/g. Calculated structural formulae for the HSA-CLM and HSA-CLFH products, based on elemental analysis, showed a gradual increase in the Si/Al ratio in the intercalated HSA oligocations with increasing Si/Al ratio in the pillaring solution. Optimum d(001) values and surface areas of HSA-CLM and HSA-CLFH products were obtained using method 2 and applying a ratio of 1.6 – 2.5 mmole (Si)Al/g smectite.

The thermal stabilities of HSA-CLM and HSA-CLFH products were determined by heat treatment between 250 ° and 700 ° C and subsequent measurement of the d(001) values and surface areas. HSA-CLFH products showed the unusual behavior of increase of d(001) with increase in temperature from 400 ° to 500 ° C, and essential constancy of d(001) from 500 ° to 600 ° C. The HSA-CLM products showed a gradual decrease in surface area, whereas the HSA-CLFH products prepared with a Si/Al ratio of 1.04 – 2.18 in the pillaring solution showed constant surface areas with increasing temperature from 250 ° to 600 ° C. HSA-CLM and HSA-CLFH show sharply higher acidities compared with those of reference Al-CLM and Al-CLFH samples obtained by pillaring with hydroxy-Al_{13} oligocations. This increased acidity is probably due to the presence of acidic, surface silanol groups in the HSA oligocations.

Key Words: Cross-linked smectite • Fluorhectorite • Hydroxy-SiAl oligocations • Pillared montmorillonite • Thermal stability

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