# Properties and Characterization of $Al_2O_3$ and $SiO_2$-$TiO_2$ Pillared Saponite

**P. B. Malla[1] and S. Komarneni[*, 2]**

[1] Research and Development, Thiele Kaolin Company, P.O. Box 1056, Sandersville, Georgia 31082
[2] Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

[*] Also with the Department of Agronomy.

**Abstract:** A saponite pillared with a single ($Al_2O_3$) or a mixed ($SiO_2$-$TiO_2$) oxide exhibited basal spacings of 16 – 19 and 30 – 40 Å, respectively. The pillared structures were found to be stable up to 700 ° C. Water, nitrogen, and high resolution argon adsorption were used to study the effect of thermal treatments on surface chemistry, pore structure, and surface area of these pillared clays. The pillared saponites exhibited a hydrophobic behavior at temperatures > 500 ° C, whereas such behavior was observed at ⩾300 ° C for montmorillonite. Most of the micropores in the $Al_2O_3$ pillared clays were < 10 Å, whereas the $SiO_2$-$TiO_2$ pillared clays showed a broad distribution of pores in both micropore and mesopore regions. The $SiO_2$-$TiO_2$ pillared samples possessed higher surface area compared with $Al_2O_3$ pillared clays. The percent decrease in surface area was smaller for pillared saponites compared with pillared montmorillonites when calcined from 300 ° to 700 ° C, indicating a higher thermal stability of the former. The pillared clays were also characterized by solid state $^{27}Al$ and $^{29}Si$ magic-angle spinning nuclear magnetic resonance (MAS/NMR) spectroscopy. There was no direct evidence of cross-linking (covalent bonding between the clay layer and pillar) in montmorillonite irrespective of the types of pillars. In saponite, however, a significant structural modification took place. $^{27}Al$ spectra of $Al_2O_3$ pillared saponite heated at ⩾300 ° C appear to indicate an increase in $Al^{VI}$ as a result, at least in part, of initiation of hydrolytic splitting of Si-O-Al bonds. The actual release of Al from the tetrahedral sheet probably occurred at a temperature > 500 ° C and completed around 700 ° C with the formation of Si-O-Si linkages. The decreased intensity of peak due to Si(1Al) in $^{29}Si$ spectra of the sample heated at 700 ° C corroborates the $^{27}Al$ MAS/NMR results. Additionally, the $^{29}Si$ spectra indicated a cross-linking between $SiO_4$ (clay sheet) with $Al_2O_3$ pillars, which could be achieved by inverting some silica tetrahedra into the interlayer. $^{27}Al$ and $^{29}Si$ spectra of $SiO_2TiO_2$ pillared saponite also showed the trend similar to that exhibited by $Al_2O_3$ pillared saponite, indicating that the crystal chemistry of the host may be more important than the nature of pillars in the structural modification and cross-linking behavior of thermally treated pillared clays.

**Key Words:** Adsorption • Clays • Cross-linking • MASNMR • Montmorillonite • Pillared clay • Saponite • Smectite

*Clays and Clay Minerals*; August 1993 v. 41; no. 4; p. 472-483; DOI: 10.1346/CCMN.1993.0410408

Clay Minerals Society (www.clays.org)