Synthesis and Catalytic Properties of Silicate-Intercalated Layered Double Hydroxides Formed by Intragallery Hydrolysis of Tetraethylorthosilicate

Sang Kyeong Yun, Vera R. L. Constantino and Thomas J. Pinnavaia

Department of Chemistry and Center for Fundamental Materials Research Michigan State University, East Lansing, Michigan 48824

Abstract: Layered double hydroxides (LDH's) interlayered with silicate anions were prepared by reaction of tetraethylorthosilicate (TEOS) with synthetic meixnerite-like precursors of the type $[Mg_{1-x}Al_x(OH)_2][OH^-]_x \cdot zH_2O$, where $(1 - x)/x \approx 2$, 3, or 4. TEOS hydrolysis at ambient temperature occurred readily in the galleries of the hydroxide precursors with $(1 - x)/x \approx 3$ or 4, but a temperature of ~ 100 ° C was required to achieve silicate intercalation for the LDH composition with $(1 - x)/x \approx 2$. On the basis of the observed gallery heights ($\sim 7.0 - \sim 7.2$ Å) and ^{29}Si MAS NMR spectra that indicated the presence of Q^2, Q^3, and Q^4SiO_4 sites, the intercalated silicate anions, which are formed by condensation reactions of silanol groups and partial neutralization of SiOH groups with gallery hydroxide ions, are assigned short chain structures. Also, some O_3SiOH groups become grafted to the LDH layers by condensation with MOH groups on the gallery surfaces. The LDH-silicates exhibited comparable non-microporous N_2 BET surface areas in the range $59 - 85$ m^2/g, but they differed substantially in acid/base reactivities, as judged by their relative activities for the catalytic dehydration/disproportionation of 2-methyl-3-butyn-2-ol (MBOH). Under reaction conditions where the LDH structure is retained (150 ° C), all the silicate intercalates showed mainly basic reactivities for the disproportionation of MBOH to acetone and acetylene. However, all the LDH silicates were less reactive than the corresponding LDH carbonates. Conversion of the LDH silicates to metal oxides at 450 ° C introduced acidic activity for MBOH dehydration, whereas the metal oxides formed by LDH carbonate decomposition were exclusivity basic under analogous conditions.

Key Words: 2-methyl-3-butyn-2-ol conversion • Acidic and basic properties • Intragallery hydrolysis • Layered double hydroxides • Silicate intercalation • Tetraethylorthosilicate

Clays and Clay Minerals; August 1995 v. 43; no. 4; p. 503-510; DOI: 10.1346/CCMN.1995.0430415
© 1995, The Clay Minerals Society
Clay Minerals Society (www.clays.org)