

E0006

Crystal Structures of Excessively Ca²⁺-exchanged Zeolite X Containing Ca₈O₄⁸⁺, Ca²⁺, and H⁺ Cations. Karl Seff^a, Yijia Wang^a, and Charles J. Simmons^b, ^aDept. of Chemistry, Univ. of Hawaii at Manoa, Honolulu HI 96822, ^bDept. of Chemistry, Univ. of Hawaii at Hilo, Hilo HI 96720

Ca(OH)₂ was imbibed into zeolite X (FAU) when ion exchange of single crystals was attempted using a mixed Ca(NO₃)₂/Ca(OH)₂ aqueous solution, pH 11.5, and aqueous Ca(OH)₂, pH 12.0. After vacuum dehydration at 350 °C, both crystal structures, **1** and **2**, respectively, were determined by X-ray diffraction in the cubic space group $Fd\bar{3}$ at 23 °C. In both crystals, Ca₄O₄ clusters (interpenetrating tetrahedra, symmetry $2\bar{3}(T_d)$) are seen in the sodalite cavities. In crystal **1**, 2.40(4) of the 8 sodalite cavities per unit cell contain Ca₄O₄ clusters; in crystal **2**, 4.95(4) sodalite cavities are so occupied. The Ca-O bond lengths in these Ca₄O₄ clusters are relatively long, 2.545(8) and 2.581(5) Å, respectively. Each Ca₄O₄ unit coordinates further via its oxygen atoms to four more Ca²⁺ ions (Ca-O = 2.376(21) and 2.328(13) Å, respectively) in the 6-rings (site II) to give the larger cationic Ca₈O₄⁸⁺ clusters (symmetry $2\bar{3}(T_d)$). As oxide ions were taken from H₂O and OH⁻ to form Ca₈O₄⁸⁺, H⁺ ions formed in both crystals. In this way, stable acid forms of low-silica FAU can be prepared.