I-3 14:30~15:10 Invited Talk III

Structures and Chemical Bonds of Dehydrated Ca^{2+}-Exchanged Zeolite X and of Its Sorption Complexes

Yang Kim

Chemistry Department, Pusan National University, Pusan 609-735, Korea

Crystal structures of dehydrated fully Ca^{2+}-exchanged zeolite X, and its sorption complexes of NH_3, H_2S, C_2H_2, C_2H_4, C_3H_6, C_6H_6, and C_9H_{12} have been determined by single-crystal X-ray diffraction techniques in the cubic space group *Fd*3. All the crystals were prepared by ion exchange in the flowing stream of 0.05M aqueous $Ca(NO_3)_2$ for four days, followed by dehydration at 380℃ and 2 x 10^{-6} Torr for two days. For the structures of sorption complexes, the dehydrated crystals were exposed to guest molecules. In the dehydrated structure,[1] Ca^{2+} ions are located at two crystallographic sites. Sixteen Ca^{2+} ions fill the octahedral sites I at the centers of the hexagonal prisms (Ca-O = 2.429(8) Å). The remaining 30 Ca^{2+} ions are at sites II; each extends 0.30 Å into the supercage where it coordinates to three trigonally arranged framework oxygens at 2.276(5) Å. For the structures of the sorption complexes, thirty cyclopropane,[2] thirty acetylene or thirty ethylene molecules[3] are sorbed, all in the supercages, one coordinating laternally to each site II Ca^{2+} ions. For the structures of H_2S or NH_3 sorption complexes,[4,5] 16 Ca^{2+} ions at site I and 30 Ca^{2+} ions at site II are found. Each Ca^{2+} ion at site II coordinately octahedrally to three framework oxygens and to three ammonia or to hydrogen sulfide molecules. Each of remaining 45 NH_3 molecules hydrogen bonds via its lone pair to two coordinating NH_3 molecules and is in position to associate weakly with two or more framework oxygens. For hydrogen sulfide sorption complexes, Each of the remaining ca. 59 H_2S hydrogen bonds to two 12-ring oxygens. For the benzene sorption complexes,[6] 16 octahedrally coordinated Ca2+ at site I and 30 Ca^{2+} ions at two differnet site IIs, with occupancies of 8 and 22 ions, are found per unit cell: There are two kinds of benzene molecules: 22 coordinate to six-ring Ca^{2+} ions in the supercage; six fit remarkably well in 12-ring windows. In the structure of a mesitylene sorption complex, one mesitylene molecule per supercage lies on a threefold axis where it interacts facially with a Ca^{2+} ion (Ca^{2+}-mesitylene center = 2.98 Å). One hydrogen atom of each methyl group and all three hydrogen atoms of the central ring are near framework oxygens: altogether each mesitylene molecule has six H··· O interactions (H··· O = 2.50 and 2.66 Å, respectively) with the zeolite framework.

References

1. Yeom Y. H.; Jang, S. B.; Song, S. H.; Kim, Y.; Seff, K. *J. Phys. Chem.. B* 1997, *101,* 6914-6920.

2. Jang, S. B.; Jeong M. S.; Kim, Y.; Seff, K. *J. Phys. Chem., B* 1997, *101,*

3091-3096.
3. Jang, S. B.; Jeong M. S.; Kim, Y.; Seff, K. *Micro. Meso. Mat.* 1998, *23*, 33-44
4. Jang S. B.; Jeong, M. S.; Kim, Y.; Song, S. H.; Seff, K. *Micro. Meso. Mat.* 1999, *28* 173-183,
5. Yeom, Y. H.; Kim, A. N.; Kim, Y.; Song, S. H.; Seff, K, *J. Phys. Chem. B* 1998 *102*, 6071-6077.
6. Choi, E. Y.; Kim, Y.; Seff, K. accepted to *J. Phys. Chem. B* 2001.