

The Controversy Surrounding the Structure of Zeolite A

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Introduction

Zeolites are crystalline, microporous aluminosilicates consisting of SiO_4 and AlO_4 tetrahedra linked via common oxygen atoms. Enough cations are present to neutralize the anionic framework. There are over 100 structures known for natural and synthetic zeolites. Synthetic zeolites have been used extensively in industry over the past 25 years. The three major uses are: as adsorbents [1,2], in ion exchange [1,3], and in catalysis [2,3].

The first reported synthesis of zeolite A was in 1956. Its basic building block is the sodalite unit, or truncated octahedron. The sodalite unit is a 24-vertex polyhedron, with Si and Al atoms at each vertex, having 14 faces: 6 square and 8 hexagonal. Each sodalite unit is linked to six others through the square faces. This octahedral arrangement of sodalite units leads to three types of cavities in zeolite A: square prisms, the sodalite cavities, and the larger supercages. Access to the supercage, with a diameter of 11.4 Å, is gained through one of the six windows (so called 8-rings) having a diameter of 4.2 Å [1,2].

Zeolite A is normally prepared with Na as the cation, however it can be ion exchanged by treatment with an aqueous solution of a new cation. The three most common forms of zeolite A are: 3A (K form), 4A (Na form), and 5A (Ca form).

The Positions of Exchangeable Cations

The preparation of zeolite 4A was first reported by Breck and his coworkers at Union Carbide [4]. Subsequent x-ray diffraction studies yielded small data sets for hydrated and dehydrated 4A [5,6]. Seff redetermined the crystal structure of dehydrated 4A and assigned eight Na^+ ions to positions near the centers of the 6-rings, three Na^+ ions near the centers of 8-rings and the twelfth Na^+ to a position in the supercage normal to a 4-ring [7]. In other crystal structure studies of various ion exchanged forms of zeolite A Seff reported "zero-coordinate" Rb^+ , K^+ , and Na^+ [8], and near zero-coordinate Cs^+ [9], Tl^+ [10], Ca^{2+} , and Sr^{2+} [11]. A cation was defined as "zero-coordinate" if the distance between the cation and all other atoms exceeded the sum of their ionic radii by more than 1.0 Å [12].

Due to skepticism about the zero-coordinate ions raised by the lack of elemental analysis and the use of the pseudocell (Pm3m) instead of the true unit cell (Fm3c), Smith began to redetermine the structure of dehydrated zeolite A containing supposed zero-coordinate cations. His studies have shown no evidence for zero-coordinate K^+ [13] and Na^+ [14]. He has also found that the near zero-coordinate Ca^{2+} and Sr^{2+} cations are really K^+ ions scavenged during the ion exchange process [15,16].

Ordering of the Aluminosilicate Framework

Smith was able to refine the superstructure and differentiate between Si-O and Al-O bonds. The average Si-O distance of 1.60 Å and Al-O distance of 1.73 Å [13,14] are in excellent agreement with the pure Si-O and Al-O distances of 1.61 and 1.75 Å for feldspar minerals [17]. The Si/Al ratio of 1.0 in zeolite A should lead to a strict alternation of SiO₄ and AlO₄ tetrahedra according to Loewenstein's rule, which forbids Al atoms from sharing neighboring tetrahedral sites [18]. The comparison of ²⁹Si magic angle spinning NMR (MASNMR) spectra for various aluminosilicates seemed to provide evidence for Si bonded to 3 Al and 1 Si via O bridges (the so-called Si(3 Al) or 3:1 model) and vice versa [19], a bonding mode which violates Loewenstein's rule. However, a more recent ²⁹Si MASNMR study of ZK-4, a highly siliceous, synthetic zeolite isostructural with zeolite A, provided evidence for the Si(4 Al) (4:0) model, which is in agreement with Loewenstein's rule [20,21].

References

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