Poster

Direct quantification of Aluminum content in zeolites by Three-Dimensional Electron Diffraction

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Zeolites are microporous aluminosilicate materials that are widely utilized as industrial catalysts or sorbents since the micropore confinement along with the presence of acid sites enables the shape-selective catalysis and adsorption of various guest entities [1]. The high commercial demand for zeolites has fuelled extensive efforts to develop innovative synthetic variations, surpassing the diversity of naturally occurring solids [2]. To date, the International Zeolite Association's Structure Commission (IZA-SC) has documented over 256 unique types of zeolitic structures.

Along with their micropore architecture, a particularly relevant aspect of the zeolite structure is associated with the partial substitution of silicon (Si^{IV}) with aluminum (Al^{III}) T sites which can be significantly influenced using organic structure-directing agents (OSDAs) [3]. This substitution creates a negative charge on the oxygen atoms surrounding the (Al^{III}) sites that must be balanced by a nearby cation. When balanced by a proton, this creates the Brønsted acid site, which is the central active site in catalysis by zeolites [3]. The strength of the Brønsted acid site is primarily influenced by the concentration and local environment of the AlO^4 tetrahedron, which, in turn, is affected by the distribution of aluminum within the framework and the Si:Al ratio. The ratio and distribution are crucial factors that impact selectivity, activity, and stability in various applications of zeolites [1]. Distinguishing between aluminum and silicon T-sites in zeolite structures is of paramount relevance for obtaining precise structural information that can be correlated with the catalytic absorption performances. However, this task poses technical challenges. Methods that are sensitive to differentiate Si from Al often do not provide spatial information. X-ray diffraction provides spatial information, but the grain size of industrially relevant zeolites is too small for single crystal structure determination.

The 3D Electron Diffraction (3D ED) technique is recognized as a pioneering method, and its capability to analyse individual particles of micro-sized crystalline materials has been a subject of intense development over the past one or two decades. In our study, we applied 3D ED to determine the aluminum distribution in two aluminosilicate structures, albite, and FER, with clearly defined silicon and aluminum crystallographic sites, alongside one ZSM-5 zeolite with unknown aluminum T sites. The fraction of aluminum is determined by expressing the electron atom scattering factor as the linear combination between silicon and aluminum at $fe(\mathrm{T}) = occ_{\mathrm{Al}} \cdot fe(\mathrm{Al}) + (1 - occ_{\mathrm{Al}}) \cdot fe(\mathrm{Si})$. This is common practice in crystallography to determine substitutional disorder, in which different types of atoms occupy the same site in two unit cells. Such disorder is commonly observed in minerals and salt-like crystals like Albite, FER, and MFI, where both Al and Si atoms share the same site [4].

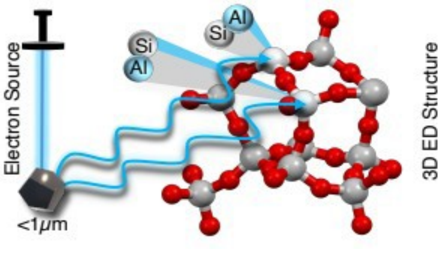

Figure 1. Determining Aluminum Content in Zeolite Structures through 3D Electron Diffraction

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