**Direct quantitative and localisation of Aluminum in individual zeolite crystals by 3D Electron Diffraction**

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Zeolites are crystalline microporous aluminosilicates extensively used as catalysts and adsorbents due to their shape-selective micropore network and tunable acidity, which arises from the isomorphous substitution of Si(IV) by Al(III) in the framework. This substitution introduces Brønsted acid sites when balanced by protons, making zeolites highly effective for catalytic transformations across petroleum refining, biomass valorisation, and CO₂ utilisation [1, 2]. The activity and selectivity of zeolites depend not only on the total Al content but also critically on the precise location of Al atoms within specific crystallographic T-sites [2, 3].

Despite this importance, determining the framework Al positions remain a persistent challenge. Techniques such as solid-state ²⁷Al NMR and UV-vis spectroscopy provide indirect information and are often limited in resolution. More direct structural insights have been achieved using synchrotron anomalous X-ray powder diffraction (AXRD), which has allowed quantification of Al occupancies in frameworks such as MFI and FER, although its effectiveness diminishes for high Si/Al zeolites and nanosized crystals due to the minimal scattering contrast between Si and Al [4].

In this study, we employ three-dimensional electron diffraction (3D ED), an emerging technique that enables structural analysis of sub-micrometre zeolite crystals with high sensitivity to differences in valence electron density. Unlike conventional X-ray methods, 3D ED can distinguish between framework Si and Al, even in materials with high Si/Al ratios [5]. Building on previous studies demonstrating Al/Si discrimination by 3D ED [6], we demonstrate its capability to directly identify Al occupancy at specific T-sites, offering a powerful tool for atomic-scale characterisation of zeolites and guiding the rational design of advanced catalytic materials (ss Fig. 1).

A structure of a molecule

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###### Figure 1. Direct localisation of aluminum (blue) and silicon (grey) atoms in a ZSM-5 zeolite framework from individual crystals using electron diffraction.

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