Pinpointing Aluminum Substructure in Zeolites by X-ray Anomalous (Resonant) Diffraction

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Al substructure within the zeolite framework critically influences the presence and behavior of catalytically active centers. In Al rich zeolites (Si/Al < 10), Al-O-Si-O-Al sequences stabilize divalent cations or adjacent acid sites. In Si rich zeolites (Si/Al > 10), Al atoms occur as isolated species, Al pairs (Al(-O-Si-O-)$_{1-2}$Al), or nearby Al atoms (Al(-O-Si-O-)$_3$Al). Zeolites with a higher fraction of Al pairs show greater catalytic activity. The arrangement of Al atoms depends strongly on synthesis conditions, enabling tailoring zeolite structures and optimizing catalytic properties. However, no universal method currently exists to directly identify the specific T sites occupied by Al atoms, because substitution for Si is typically sparse and fractional, and Al has a scattering power very similar to that of Si (atomic form factors f_0 are 13 and 14, respectively).

We developed an anomalous X-ray powder diffraction (AXRD) methodology at the Al K edge (1.56 keV), where the scattering form factor of Al changes significantly while that of Si remains constant (Fig. 1). These variations highlight aluminum in the structure. AXRD therefore provides quantitative information on the structural order of aluminum distribution, enabling unambiguous identification of Al sites within the framework.

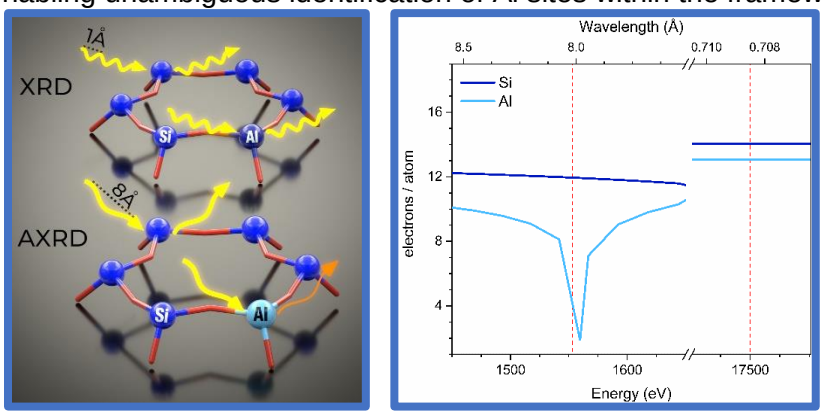


Figure 1. AXRD phenomenon: attenuation of the aluminum signal at the Al K edge (left). The real part (f_0+f_1) of the atomic scattering form factor ($f = f_0 + f_1 + i \cdot f_2$) for silicon and aluminum (right).

The industrially relevant H-ZSM-5 zeolite studied here has a framework containing 12 T atoms in the *Pnma* unit cell, forming a 3D network of intersecting straight and sinusoidal 10 ring channels [1]. Two samples with similar Si/Al ratios (18 and 15) but different Al pair concentrations (9% and 82%) were analyzed using Co(II) as a probe molecule. Previous spectroscopic studies identified divalent cobalt cations at elongated 6-rings formed by two folded 5 rings (α site) and at 5- or distorted 6-rings (β site), and assigned them to the straight and sinusoidal channel walls.

AXRD enabled precise quantification of Al concentration at specific T sites. Al pairs were localized at adjacent, T8 symmetry equivalent positions, near the intersection of straight and sinusoidal channels, and were identified as the β site. The β site can also form between T4 and T10 or T4 and T11 atoms within a 5-ring isolated from large voids. An Al pair at T8 and T11, with underlying Si at T3, corresponds to the α site. These assignments are corroborated by the refined positions of three Co atoms located at the α and β sites. This study shows that, although spectroscopic methods can identify the local structure of Al around cationic centers, their position within the periodic framework remains unresolved. Our results highlight the potential of AXRD at the Al K edge, supported by ^{27}Al MAS NMR and refined positions of divalent cations used as probes of A pairs, for revisiting other zeolites exhibiting variations in Al siting.

[1] P. Rzepka, T. Huthwelker, J. Dedecek, E. Tabor, M. Bernauer, S. Sklenak, K. Mlekodaj, J.A. van Bokhoven. Science (2025). 388,6745.

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