Rietveld Structural Analysis of Tl^+-Exchanged K-L Zeolite from Powder Diffraction Data

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The high toxicity and mobility of thallium (Tl^+) in aqueous environments pose a significant risk to ecosystems and human health, making its efficient removal a critical challenge. In this context, the incorporation of Tl^+ in zeolitic frameworks is investigated through a detailed structural study based on X-ray powder diffraction (XRPD) and Rietveld refinement. *Potassium-form L zeolite* (K-L) was selected as a model system to explore cation exchange mechanisms and the resulting structural response of the framework over a wide range of Tl^+ concentrations. LTL zeolite is characterized by a one-dimensional channel system defined by 12-membered rings, providing large pore openings and well-defined extraframework cation sites [1, 2], making it particularly suitable for ion-exchange studies.

Rietveld refinements of XRPD data reveal a clear concentration-dependent evolution of the structure. At low Tl^+ loading, the zeolite framework remains largely preserved, with only minor variations in lattice parameters (a = b = 18.381 Å, c = 7.529 Å) and limited perturbation of T–O bond distances and angles. Extraframework K^+ cations retain their original positions, while water molecules undergo slight displacements within the channels, maintaining an overall hydration level of approximately 28 H_2O per unit cell.

At higher Tl^+ concentrations, significant structural modifications are observed. The framework exhibits anisotropic expansion, predominantly in the a/b plane (a = b = 18.443 Å, c = 7.549 Å), reflecting the larger ionic radius and higher polarizability of Tl^+. Rietveld analysis indicates substantial substitution of K^+ by Tl^+, accompanied by redistribution of extraframework cations and a reduction in water content to approximately 21 H_2O per unit cell. Concomitantly, the hydration network is reorganized, with partial displacement of water molecules and the formation of new coordination environments associated with Tl^+.

Thermal analysis supports the structural findings, showing distinct dehydration behavior as a function of Tl^+ content. Samples with higher Tl^+ loading display reduced weight loss and broader thermal events, consistent with stronger interactions between residual water molecules and redistributed cations.

These results demonstrate how Tl^+ exchange drives a progressive structural adaptation of the L zeolite framework, combining anisotropic lattice expansion, cation redistribution, and hydration network reorganization. The study further highlights the effectiveness of XRPD coupled with Rietveld refinement in resolving subtle structural variations associated with ion exchange processes in zeolitic materials.

[1] G. Beltrami, T. Chenet, L. Pasti, L. Gigli, S. Pollastri, and A. Martucci. Catal. Today (2020), vol. 345, pp. 147–156.

[2] N. Precisvalle et al., Journal of Physical Chemistry C (2023), vol. 127, no. 27, pp. 13276.