

The Formation of Al_{28}V_4 Polycation in Porous Ionic Crystal for Acetalization Reaction

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A rapid growth of interest in investigating the hydrolysis of aluminum salts in water produces an array of polyoxoaluminum clusters with various sizes, shapes, and compositions, which are widely used in catalysis, water treatment, and as pillaring agents.^[1, 2] Among those 1–2-nm-sized polyoxoaluminum clusters, Keggin-type $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ (Al_{13}) is the most classic one. Particularly, $\delta\text{-Al}_{13}$ isomer is utilized as the building block linked through octahedral AlO_6 sites to construct larger polyoxoaluminum clusters, such as Al_{26} , Al_{30} and Al_{32} .^[3] The heteroatom substitutions of those larger polyoxoaluminum clusters can fulfill the diversity of structural topologies of polyaluminum species. Herein, we demonstrate the first case of heteroatom substitutions of V^{5+} in aluminum Polyoxocation (Al_{28}V_4) isolated in the solid state from aqueous solution with polyoxometalate (POM) anions, $[\alpha\text{-}1,2,3\text{-PW}_9\text{V}_3\text{O}_{40}]^{6-}$. The present study describes the synthesis and structural characterization of this all-inorganic porous ionic crystal (PIC) of $[\text{V}_4\text{Al}_{28}\text{O}_{22}(\text{OH})_{48}(\text{H}_2\text{O})_{24}][\alpha\text{-}1,2,3\text{-PW}_9\text{V}_3\text{O}_{40}]_2 \cdot 45\text{H}_2\text{O}$ [**I**].

In a typical synthesis, $\delta\text{-Al}_{13}$ solution was mixed with an aqueous solution of $[\alpha\text{-}1,2,3\text{-PW}_9\text{V}_3\text{O}_{40}]^{6-}$ by using a hydrothermal method to obtain **I**. Single crystal X-ray diffraction analysis reveals that **I** crystallized in the orthorhombic *Cmce* space group (#64), in which the Al_{28}V_4 cations (Figure 1a) are arranged in a herringbone manner to form an extended 2D network structure in the *bc*-plane and the 2D network are alternately arranged along the *a*-axis to construct a 3D assembled structure. $[\alpha\text{-}1,2,3\text{-PW}_9\text{V}_3\text{O}_{40}]^{6-}$ anions (Figure 1b) are located between the 2D networks of Al_{28}V_4 cations and stabilized by electrostatic interactions and hydrogen bonds (Figure 1c). Further, **I** is applicable in acid-catalyzed acetalization of benzaldehyde and shows higher catalysis activity than Al_{13} based PICs.

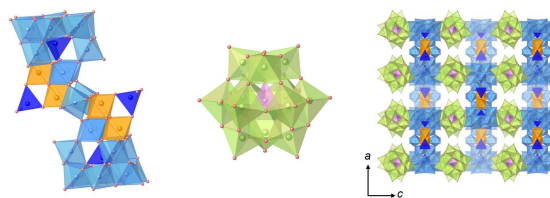


Figure 1. The crystal structure of (a) Al_{28}V_4 (b) $\alpha\text{-}1,2,3\text{-PW}_9\text{V}_3\text{O}_{40}^{6-}$ and (c) **I** along *b*-axis

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