Enhancing the basicity of polyoxometalates-based porous ionic crystals by substitution of Nb/Ta

(*Department of Basic Science, School of Arts and Sciences, The University of Tokyo*)
○Zhewei Weng, Naoki Ogiwara, Sayaka Uchida
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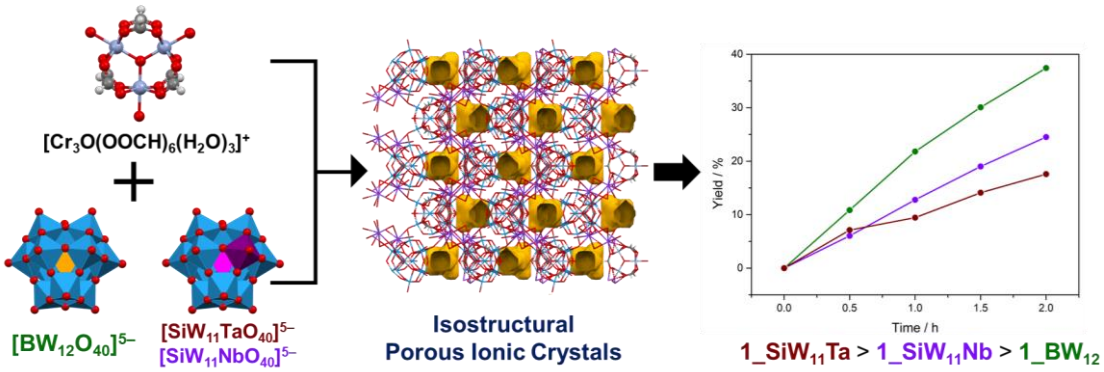
Base-catalyzed reactions are important for the manufacture of both bulk and fine chemicals.[1] Polyoxometalates (POMs), which are a large family of anionic metal oxide clusters containing early transition metals, are considered as promising base catalysts because of abundant surface metal-oxo moieties as well as tailorable structures and compositions.[2] We reported that a series of porous ionic crystals (PICs) composed of Nb/Ta-substituted Dawson-type POMs with a molecular cation (macrocation) serve as efficient solid base catalysts.[3] However, we failed to build a firm composition–structure–function relationship of PICs due to their different crystal structures. Therefore, we realized that isostructural PICs with different compositions would serve as a tunable platform for solid base catalysts to clarify the effects of composition towards catalytic activity.

Based on these considerations, we synthesized three isostructural PICs composed of macrocations $[Cr_3O(OOCH)_6(H_2O)_3]^+$ and a series of Keggin-type POMs ($[BW_{12}O_{40}]^{5-}$ for PIC **1_BW$_{12}$**, $[SiW_{11}NbO_{40}]^{5-}$ for PIC **1_SiW$_{11}$Nb** and $[SiW_{11}TaO_{40}]^{5-}$ for PIC **1_SiW$_{11}$Ta**). The substitution of Nb/Ta for W in POMs enhances the basicity of PICs, and the order is **1_SiW$_{11}$Ta** > **1_SiW$_{11}$Nb** > **1_BW$_{12}$**. The substitution effect on basicity is further characterized by adsorption of methanol as basic probe. Theoretical calculations indicated that the substitution of Nb/Ta increase the electron density in the terminal oxygen atom of Nb/Ta, which makes it more basic and active in reactions. These findings show that PICs can serve as a tailorable platform for the rational design of heterogeneous base catalysts by fine-tuning compositions of POMs.



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