

Synthesis of a Zr-mellitate MOF and Its Ion-Exchange Property

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Metal-organic frameworks (MOFs) are microporous materials containing metal ions and organic linkers, and are applicable toward catalysis, gas storage/separation, molecular sensing, drug delivery, etc. MOFs are also attracting attention as ion-exchange materials, and the adsorption of heavy atoms ions such as mercury or cadmium ions has been vigorously studied^{1,2}. However, due to the low stability of MOFs against water, reversible ion-exchange by MOFs has not yet been realized. In this study, we report a novel MOF composed of zirconium and mellitic acid, which is resistant to acid or ammonium ion aqueous solution. The ion-exchange properties of this MOF were evaluated.

The hydrothermal reaction of zirconium oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) and mellitic acid in an aqueous solution containing acetic acid and ammonium chloride to give microcrystalline powder (hereafter Zr-mellitate). The powder X-ray diffraction (PXRD) pattern indicated that the structure is isostructural to a previous MOF consisting of sulfoterephthalate and zirconium³, and four carboxyl groups were present without coordination in the framework. According to the elemental analysis, pristine Zr-mellitate contains one ammonium cation per ligand. With the treatment of 12 mM hydrochloric acid, 77% of the ammonium ions were released into the solution. From the result, one carboxy group per ligand can act as the ion-exchange site (Figure 1). The protonated Zr-mellitate can adsorb ammonium and potassium cations by the further ion-exchange reaction. The PXRD pattern showed that the structure of Zr-mellitate was maintained during these ion-exchange processes (Figure 2).

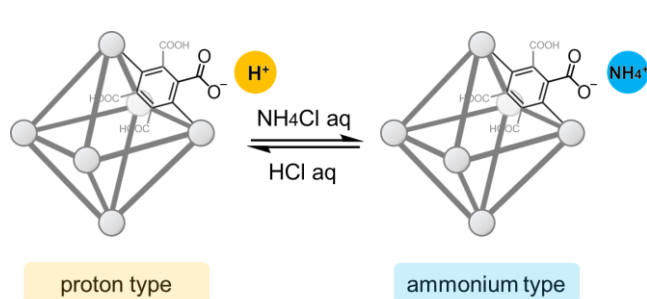


Figure 1. Reversible ion-exchange in Zr-mellitate

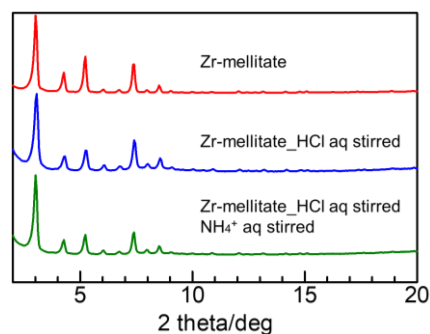


Figure 2. PXRD of Zr-mellitate

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