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Synthesis of Organic-Functionalized Zr-MOF Membranes for Desalination

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Summary

Metal organic frameworks (MOFs) have attracted attention as a new class of crystalline porous materials because of their high specific surface area and exceptionally broad chemical and structural diversity. In a decade, MOFs have been attractive attention as materials for membrane separation. UiO-66 is one of the most chemically stable MOFs consisting $Zr_6O_4(OH)_4$ cluster and 1,4-benzene dicarboxylate, exhibiting high chemical stability in organic solvents and acidic aqueous solutions. Therefore, UiO-66 can be applied to liquid separation such as organic/water separation and desalination. Additionally, the physicochemical property of this material can be easily modified by using organic linkers with functional groups such as -OH, -COOH and $-NH_2$. In this study, we prepared amino-functionalized UiO-66 (UiO-66-NH_2) membrane for desalination and investigated the effect of the post-synthetic defect healing to improve the membrane performance.

UiO-66-NH_2 membrane was prepared on porous α-Al_2O_3 tube by secondary growth method. The gas permeation property of the membrane was improved by an adequate concentration of seed solution and repetition of solvothermal synthesis. This membrane exhibited high rejection of divalent cations such as Ca^{2+} and Mg^{2+} although the rejection of monovalent cations (K^+ and Na^+) were not high. Considering the size of divalent hydration ions (8.6Å for Mg^{2+}) and pores of UiO-66-NH_2 (5.2 Å), the membrane would include defects in the rage of 8-9Å. To improve its desalination performance, the membrane was post-treated solvothermally in organic linker solution. After the post-synthetic defect healing, the rejection to Mg^{2+} were improved from 88.9% to 94.2%. However, the enhancement on the rejection to monovalent cations were rather limited. This implies the defects in the membrane would not be owing to missing linkers in the framework but grain boundaries.