

The Constraint Ability of the Pore Enhances the Accessibility of Open Metal Sites and Enhances the Separation Ability of H₂/D₂

Fenglei Wang, Zining Wang, Chuanqin Xia, Lijian Ma*

College of Chemistry, Sichuan University, Chengdu, China

Email address:

jinshiwfl@126.com (Fenglei Wang), 1254147047@qq.com (Zining Wang), xiachqin@163.com (Chuanqin Xia), ljma@scu.edu.cn (Lijian Ma)

*Corresponding author

Abstract

One of the greatest challenges of modern separation technology is separating and purification of isotope mixtures. The separation of hydrogen isotopes, in particular, can generate significant economic value by yielding deuterium (D) and tritium (T), which are crucial for a variety of industrial and scientific applications. However, existing separation methods exhibit low efficiency due to the similar chemical properties of isotopes. In this study, we investigate two metal–organic frameworks (MOFs), Cu-ATC and Cu-bptc, composed of Cu²⁺ ions coordinated to 1,3,5,7-adamantanetetracarboxylate (ATC) and 3,3',5,5'-biphenyltetracarboxylate (bptc) linkers, respectively. Although the pore sizes of two MOFs are comparable, their pore structures differ substantially. Cu-bptc exhibits a cage-like structure, with window diameters of approximately 6 Å and cage diameters of around 10 Å. In contrast, Cu-ATC adopts a one-dimensional channel structure with a more compact distribution of open metal sites. Experimental data indicate that Cu-ATC demonstrates higher H₂/D₂ uptake at low pressures, with a significantly greater isosteric heat of adsorption (Q_{st}) at initial adsorption compared to Cu-bptc. Simulations confirmed that the exposed Cu²⁺ ions in the copper paddlewheel structures serve as the primary binding sites for H₂/D₂ in both MOFs. The shorter Cu²⁺–Cu²⁺ distance in Cu-ATC (5.98 Å) enables one H₂/D₂ molecule to interact with two neighboring Cu²⁺ ions simultaneously, resulting in synergistic interactions. In contrast, one H₂/D₂ molecule in Cu-bptc interacts with only one single Cu²⁺ ion, leading to a weaker interaction and a significantly lower Q_{st} at initial adsorption. Notably, Cu-ATC also exhibits superior efficiency in hydrogen isotope separation, as demonstrated by dynamic column breakthrough experiments conducted at atmospheric pressure and 77 K.

Keywords

Metal–Organic Framework (MOFs), Hydrogen Isotope, Separation, Breakthrough Experiments