

# Molecular Simulation for the Adsorption and Separation of Alkanes in Metal-Organic Frameworks

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## ABSTRACT

Metal-organic frameworks (MOFs) are a new family of nanoporous materials consisting of metal-oxide clusters and organic linkers. Due to high porosities and fine-tunable pore structures, some of these materials are promising alternatives to zeolites and other nanoporous materials for the storage of gases, the separation of mixtures, and catalysis.

Many industrial processes involve alkanes and their mixtures, and how to separate and store these fluids is of great importance in applications. Adsorption is one of the technically feasible and cost-effective technologies. A proper adsorbent is significant to separate and store alkanes efficiently. Currently, most experimental and simulation studies of alkane adsorption were carried out in zeolites and carbon materials. There have been scarce studies of the adsorption of alkanes in MOFs.

In this paper, a systematic computational study was performed toward an understanding of the adsorption and separation characteristics of alkanes ( $C_1$ - $C_5$ ) in two representative MOFs, MOF-5 and Cu-BTC. First the single component adsorption isotherms of  $CH_4$  in MOF-5 and Cu-BTC were simulated using Monte Carlo method to validate the potential models and potential parameters by comparing with the corresponding experimental isotherms from the literatures. Then the single component isotherms of linear alkanes ( $C_1$ - $nC_5$ ) in MOF-5 and Cu-BTC were simulated at 298 K. The results indicated that the adsorbed amounts of alkanes in MOF-5 and Cu-BTC increased with increasing pressure. At low pressure, the adsorbed amounts increased with increasing alkane length. However, at high pressure, the adsorbed amounts increased with decreasing alkane length. The adsorption sites of alkanes in MOF-5 and Cu-BTC were analyzed and the sequences of pore filling in MOF-5 and Cu-BTC were obtained as follows: in MOF-5, alkanes first occupied near metal oxide  $Zn_4O$  clusters and then occupied the center of the cavities; in Cu-BTC, alkanes first occupied the tetrahedron-shaped side pockets and then occupied the main channels. Additionally, the adsorption isotherms of three binary alkane mixtures,  $CH_4/C_2H_6$ ,  $CH_4/C_3H_8$ ,  $n-C_5H_{12}/neo-C_5H_{12}$ , in MOF-5 and Cu-BTC were simulated. For linear alkane mixtures, the adsorbed amounts were greater with the longer alkanes. For  $C_5$  isomer mixture, the adsorbed amounts of *n*-pentane were larger than those of *neo*-pentane. For linear alkane mixtures, the selectivity for the long alkanes in MOF-5 increased with increasing pressure, while in Cu-BTC it decreased with increasing pressure. For  $C_5$  isomer mixture, the selectivity for *n*-pentane in MOF-5 first increased at low pressure and then decreased, while in Cu-BTC it decreased with increasing pressure.

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