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The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Examining the Reason of the Observed Influence of the Lattice Flexibility on the Diffusion of Ethane in Zn(tbip)

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1. Introduction

Zn(tbip) (H_2tbip=5-tert-butyl isophthalic acid) is a new metal-organic framework (MOF) material that is of particular interest for storage and separation applications because of its high thermal stability and gas storage capability [1]. To improve its efficiency in industrial purposes, it is essential to understand the diffusion behaviour of the guest molecules in detail. Molecular Dynamics (MD) simulation is a powerful technique widely used to obtain detailed information on structure and dynamics of the guest molecules in MOFs. However, most of the simulations were assumably done with the rigid framework which normally works well with the relatively stiff solid zeolites. This assumption has recently been questioned when the importance of framework flexibility has been initiatively found for the diffusion of benzene in MOF-5 [2]. Also, surprising results have been announced in our previous MD simulations for the diffusion of ethane in Zn(tbip) as shown in Fig. 1 [3]. A monotonic decrease of the self-diffusion coefficient, D_s, with increasing loading is found in the rigid framework while a non-monotonic concentration dependence of D_s is observed when taking account of the framework flexibility. The underlying reasons for the observed influence of the framework flexibility on the diffusion of ethane in Zn(tbip) will be examined in our present study.

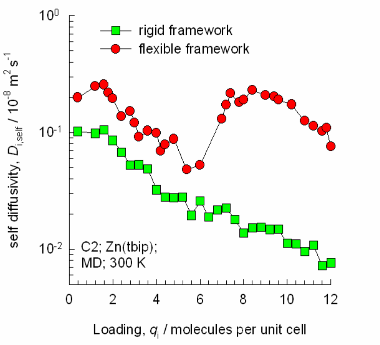

Fig. 1. The self-diffusion coefficients at different loadings of ethane in the rigid and flexible framework.

2. Model and simulations

The MD simulations are carried out with a periodic simulation box comprising six one-dimensional channels. Each channel has five double three-leafed clover topology segments linearly linked together through the windows having the effective diameter of

4.5 Å. In each loading, every channel of Zn(tbip) is firstly loaded with an equal number of ethane molecules before being randomly added with the remainders. The simulation details have been described in our previous work [3].

3. Results and discussion

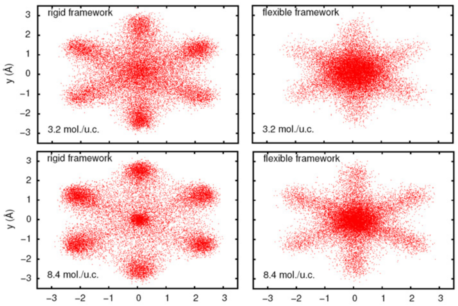

Fig.2: Location of an ethane molecule projected into the *xy* plane tracked every 0.5 ps during a simulation period of 10 ns.

An analysis of the molecular position in the rigid framework shows that molecules preferably adsorb near the center of the channel and the middle of the segments at low loadings (Fig. 2). At loadings higher than 6 molecules/unit cell, they prefer to adsorb locally at the leaf positions in the outer regions of the segment center due to the intermolecular repulsion between molecules in the same segment, leading to lower probability to occupy the sites close to the windows (Fig. 2). The influence of the framework flexibility causes the adsorption at the leaf sites to be much less favored as compared to that in the rigid framework. Molecules prefer to be located in the center region of the channel and to be adsorbed closer to the windows. Thus, the hops between segments become more readily as found in the narrow-window-structure LTA zeolite [4]. The examination of the cross section area of the window connecting adjacent segments reveals that the adsorption of molecules near the window and at the emerging sites within the window at loadings higher than 7 molecules/unit cell lead to the larger window diameter. This significantly reduces the free energy barrier for hopping between segments.

3. Conclusion

The framework flexibility has a significant influence on the adsorption and diffusion behavior of ethane in Zn(tbip). It allows the intermolecular repulsion between ethane molecules to extend the space at the window regions available for hopping. This results in the decrease of the free energy barrier for the intersegment hops and, hence, the self-diffusivity increases with increasing loading.

References

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