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**A Molecular Dynamics Study of SO₂ Sorbed in Nonporous Silica Y
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A Molecular Dynamics Study of SO₂ Sorbed in Nonporous Silica Y Zeolite: Temperature and Loading Dependence

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Abstract: The dynamical and structural properties of sulfur dioxide (SO₂) guest gas inside nonporous silica Y zeolite were studied by molecular dynamics (MD) simulation for different loadings (8, 12, 16, 20 and 24) of SO₂ per unit cell at temperatures of 300, 400, 500 and 600 K. The order of calculated self-diffusion coefficient of SO₂ guest molecules at different temperatures, is in the range of 10⁻⁹ up to 10⁻⁸ m²s⁻¹. Overall rate for cage-to-cage diffusion shows an Arrhenius temperature dependence with $E_{act} \sim 3.5$ to 5.5 kJ. mol⁻¹. Generally, the SO₂ self-diffusion coefficients increase with temperature.

Keywords: Molecular dynamic simulation; Y zeolite; Diffusion coefficient

Introduction

The emissions of SO₂ are known to cause clear impacts on human health and the environment. Therefore, the removal of SO₂ mainly from the burning of fossil fuels in power plants is a goal of many air pollution researchers [1]. Acidic gases such as SO₂ are one of the main causes for the greenhouse effect, photochemical smog, acid rain, ground layer ozone formation and great hazards to human health [2]. But besides these risks, SO₂ is fundamental for chemical industry, for instance, in producing sulfuric acid [3].

Zeolites are crystalline inorganic microporous materials with well-defined pore structure and cages of varying dimensions. The basic building blocks of zeolites are mainly composed of corner-sharing SiO₄ tetrahedra, and by repeating their periodic tetrahedral network [4]. Because of their regular structure, high internal surface, and high hydrothermal stability, faujasite (FAU) zeolites have been broadly employed in practical applications such as adsorption, separation, and catalysis, especially as desulfurization adsorbents in the process of producing clean fuels [5]. Y zeolite has a network of almost spherical supercages which are interconnected with each other in a tetrahedral manner by 12 membered oxygen rings forming windows. The diameter of these windows is about 7.8 Å while the supercages have a diameter of 11.8 Å [6].

In this work, molecular dynamic (MD) simulation technique, has been employed to investigate static or dynamic behavior at the molecular level.

Computational method

All simulations have been done using DL_POLY_2.17 [7] program on a Linux workstation. One unit cell of FAU was used as the simulation box. Moreover, periodic boundary conditions were applied. The behavior of SO₂ was investigated for loadings of 8, 12, 16, 20 and 24 mol/u.c.(molecule per unit cell). Simulations are carried out in 300 ,

400, 500 and 600 K. The initial structure was equilibrated for 2000 ps. The length of MD runs for data production is 1000 ps. Time step in all simulations was 1 fs and cut-off radius was considered 12 Å.

The self-diffusion coefficient can be obtained from the long time limit of mean square displacement (MSD) using well-known Einstein relation,

$$D_i = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle [r_i^c(t) - r_i^c(0)]^2 \rangle \quad (1)$$

where $r_i^c(t)$ is the location of the center of mass of particle if at time t .

To calculate the diffusion activation energy, Arrhenius equation is used,

$$D = D_0 e^{-\frac{E_{act}}{RT}} \quad (2)$$

where E_{act} , R , and T are the diffusion activation energy, gas constant and temperature, respectively [4].

Results and Discussion

MD simulations at different temperatures and loadings are carried out for SO₂ guest molecules in the fixed silica Y zeolite framework.

The center of mass MSD, self-diffusion, activation energy for SO₂ diffusion process, and main radial distribution functions (RDFs) are computed and discussed.

For instance, Fig. 1 shows the time variation of center of mass MSD of SO₂ diffusion within the pores of silica Y zeolite for loading 8 SO₂ molecules per unit cell at different temperatures.

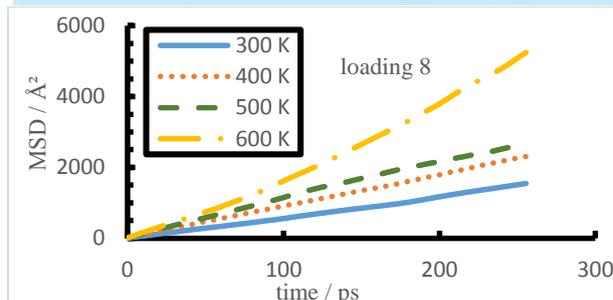


Fig. 1: The effect of temperature on the computed center of mass MSD of SO_2 within pores of silica Y zeolite from simulation at loadings 8.

These results show that within the range of simulation conditions, the motion is in the diffusion regime and there is a linear relationship for MSD over time. As expected generally, the slope of MSD curves increases with increasing temperature due to an increase in the kinetic energy of the guest molecules which allows them to move more easily within the pores of zeolite.

Fig. 2 indicates the time variation of center of mass MSD of SO_2 calculated from simulations at different loadings of guest molecules at 500 K, as a typical sample. It can be expected that at higher loadings collisions between guest molecules may prevent the diffusion of guest molecules which causes a reduction in MSD of guest molecules at high loading.

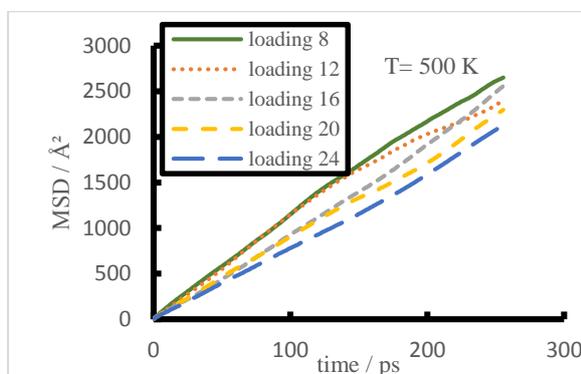


Fig. 2: The effect of loading (molecules per unit cell) change on the computed center of mass MSD of SO_2 within pores of silica Y zeolite from simulation at 500 K.

The calculated self-diffusion coefficients and activation energy values for SO_2 in the silica Y zeolite at different temperatures and loadings have been presented in Table 1.

T (K)	8 mol/u.c.	12 mol/u.c.	16 mol/u.c.	20 mol/u.c.	24 mol/u.c.
300	1	0.95	0.79	0.56	0.69
400	1.49	1.39	1.39	0.88	0.94
500	1.74	1.58	1.64	1.45	1.36
600	3.41	2.24	1.65	1.28	1.36
E_{act}	5.44	3.93	3.84	4.22	3.66

After our initial studies of the dynamics and self-diffusion coefficient of SO_2 molecules in the silica Y zeolite, we particularly focus on RDF between the center of mass of SO_2 and Si atom of zeolite framework. For instance, the RDF curves between center of mass of SO_2 and Si atom of the zeolite framework is given in Fig. 3 for loading 8 at different temperatures.

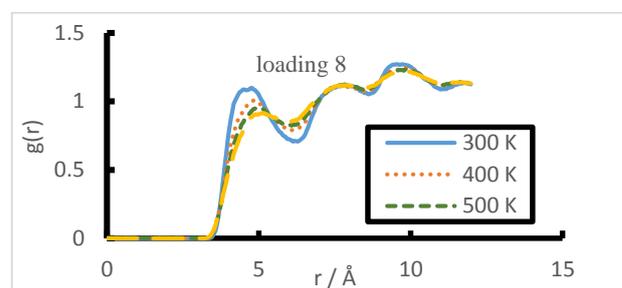


Fig. 3: The RDFs between the center of mass of SO_2 and Si atom of the zeolite from simulation at different temperatures and loadings 8.

As seen in Fig. 3, increasing the temperature decreases the intensity of the RDF peak. Furthermore, with decreasing the temperature the first RDF peak of SO_2 with Si atom appears in shorter distances.

Fig. 4 displays RDFs of COM SO_2 - Si (COM refers to the mass of the center of a sulfur dioxide molecule) in silica Y zeolite at 500 K, with the loading of SO_2 varying from 8 to 24 molecules/u.c. The position of the main peaks over the whole loading range remained at 4.975 Å, which represents that the locations of SO_2 molecules adsorbed before kept their original positions when new molecules came into the zeolite. That means the molecules that adsorbed later had no effect on the relative location of molecules that existed before. This can also be confirmed by RDFs between sulfur atoms (Fig. 5), where the main peak always remained at 4.675 Å.

Table 1: The computed self-diffusion coefficients, D in $10^{-8} \text{ m}^2 \text{ s}^{-1}$ and activation barriers E_{act} ($\text{kJ} \cdot \text{mol}^{-1}$) of SO_2 in silica Y zeolite at different temperatures and loadings.

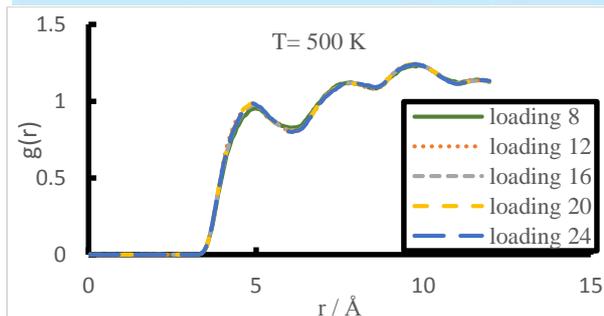


Fig. 4: The RDFs between the center of mass of SO₂ and Si atom of the zeolite from simulation at 500 K and different loadings.

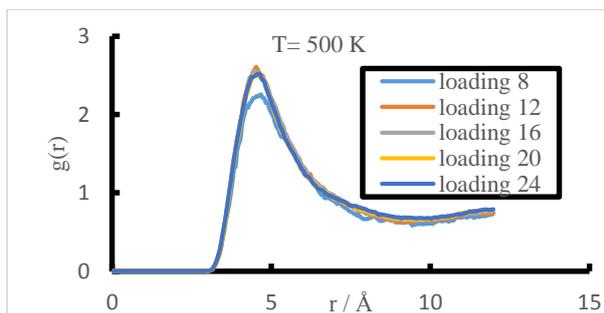


Fig. 5: The RDFs between the sulfur atoms guest molecules from simulation at 500 K and different loadings.

Conclusions

In this study, the dynamics, self-diffusion coefficient, and structural properties of SO₂ guest molecules within the pores of silica Y zeolite were investigated using MD simulations. It was observed that the computed center of mass MSD of SO₂ molecules in silica Y zeolite increases with increasing temperature. Moreover, at each temperature, the MSD of SO₂ decreases when the guest loading is increased in the range of 8-24 SO₂ molecules per unit cell of silica Y zeolite. Temperature dependence of the self-diffusion coefficient of SO₂ for this process is followed.

Structural study shows that height of first peak RDF of COM SO₂- Si decreases with increasing temperature. The simulation results can also help to better understand the roles of the temperature and loading parameters in the behavior of the guest gases through the crystalline compounds at molecular level.

References

- [1] J. Yang, G. Hu, H. Gao "Influence of operating parameters on performance of SO₂ absorption in fulvic acid solution", *Chem. Eng. J.*, 288 (2016) 724–738.
- [2] S. Yun, H. Lee, W. E. Lee, H. S. Park "Multiscale textured, ultralight graphene monoliths for enhanced CO₂

and SO₂ adsorption capacity", *Fuel*, 174 (2016) 36–42.

[3] M. C. C. Ribeiro "Molecular Dynamics Simulation of Liquid Sulfur Dioxide", *J. Phys. Chem. B*, 110 (2006) 8789-8797.

[4] M. H. Kowsari, S. Naderlou "Understanding the dynamics, self-diffusion, and microscopic structure of hydrogen inside the nonporous Li-LSX zeolite", *Microporous Mesoporous Mater.*, 240 (2017) 39-49.

[5] S. Dang, L. Zhao, J. Gao, C. Xu "Loading Dependence of the Adsorption Mechanism of Thiophene in FAU Zeolite", *Ind. Eng. Chem. Res.*, 55 (2016) 11801–11808.

[6] S. Mitra, V. K. Sharma, S. L. Chaplot, R. Mukhopadhyay "Diffusion of hydrocarbon in zeolite and effect due to pore topology: Neutron scattering and MD simulation studies", *Chem. Phys.*, 430 (2014) 69–77.

[7] W. Smith, T. R. Forester, I. T. Todorov, THE DL POLY 2 USER MANUAL", 2007, STFC Daresbury Laboratory, Version 2.17, Cheshire, UK.