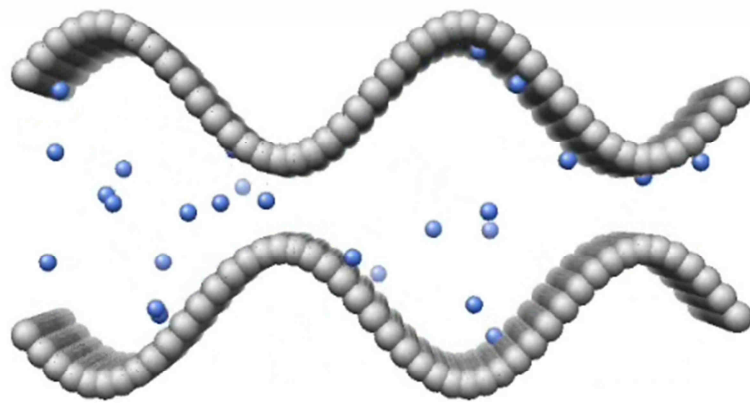


ChE 210D Final report

Prof. M. Schott Shell

Effect of pore geometry on oxygen diffusion kinetics in mesoporous carbon



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Summary

Mass transport in porous medium is highly dependent on the pore size, shape, and tortuosity, which have been interesting factors on porous materials. The effect of pore geometry (pore shapes and tortuosity) on oxygen diffusivity was studied by using NVT molecular dynamic simulations with 6-12 Lennard-Jones potential. In the implicitly built slit-like pore walls, oxygen diffusion was appeared to be strongly affected by pore geometry.

Movie

Mass transport in porous medium is highly dependent on the pore size, shape, and tortuosity, which have been interesting factors on porous materials. This movie shows diffusion of oxygen molecules in mesopores with different pore shapes, which were studied by using molecular dynamic simulation. Three dimensional pore shapes were simplified into slit-like pores with different surface curvatures to simulate 2D hexagonal, gyroid, and cubic pore structures, respectively. Implicit pore walls were built for the simulation but were displayed explicitly in the movie. Interactions between oxygen molecules - oxygen molecules and oxygen molecules – pore walls were modeled with 12-6 and 9-3 Lennard-Jones soft sphere potentials, respectively. This model quantitatively shows diminish of diffusivity by the pore shape and tortuosity.

Background

Mesoporous materials have been highly interested materials, which are widely used as catalysts, catalyst supports, and absorbents, due to their high surface areas, relatively large pore sizes, and high degrees of mesostructural orderings. While conventional porous materials provide exceptionally high surface areas to enhance the reactions occurring on the surfaces, their relatively small pore sizes ($< 2\text{nm}$) and high tortuosities diminish mass transport in the pore and limit the use of entire internal pore surface areas. By comparison, mesoporous materials prepared by self-assembly of surfactants with controlled molecular weights can easily change the pore sizes, shapes and periodicities and provide more accessible internal pore surfaces.

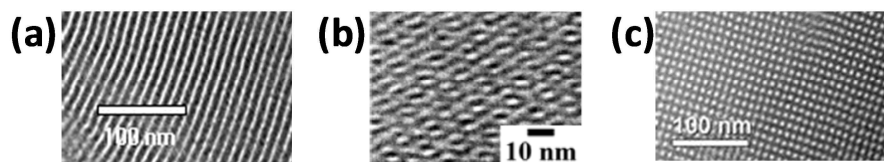


Figure 1. TEM images of mesoporous silica materials with (a) hexagonal, (b) gyroid, and (c) cubic pore structures.¹

Pore structures of mesoporous materials have been adjusted to improve the mass transport in the pores. One example is cathodes of hydrogen fuel cells. In the cathodes of hydrogen fuel cells, oxygen molecules are reduced into water by reacting with proton ions and electrons. Use on non-precious metal catalysts (e.g., Fe/N/C catalysts) increases catalysts loadings without significant increases on the cost, but the loadings of catalysts are limited by mass transport of reactants. Slow oxygen diffusion in the cathode electrodes with increased thickness prevents high loadings of catalysts. Mesoporous carbon materials with large pore sizes and high degree of pore orderings are expected to improve the mass transport of oxygen and allow increasing the catalyst loadings. In addition, pore shape and tortuosity are also important factors for oxygen diffusion. In this work, self-diffusivities of oxygen in the mesoporous channels with different pore shapes and tortuosities were studied with molecular dynamics.

Simulation method

Modeled system is a mesoporous carbon electrode filled with oxygen at $80\text{ }^\circ\text{C}$ and 2 atm , which is close to a real hydrogen-fuel-cell operating conditions.² Velocity Verlet method with time step of 0.45 fs was used for oxygen molecules, which are simplified to soft spheres with 12-6 Lennard-Jones potentials with truncation,

$$u_{oo}(r) = \begin{cases} 4 \epsilon_{oo} \left[\left(\frac{r}{\sigma_{oo}} \right)^{-12} - \left(\frac{r}{\sigma_{oo}} \right)^{-6} \right], & r \leq r_c \\ 0, & r > r_c \end{cases},$$

where $\sigma_{oo}=3\text{ \AA}$, $\epsilon_{oo}=0.102937\text{ kcal/mol}$, and $r_c=9\text{ \AA}$.³ Initially, oxygen molecules were regularly distributed in the mesopores to result in a density corresponding to $\sim 2\text{ atm}$ of pressure.²

Three dimensional mesopores are simplified into slit-like pores to reduce computational complication. Implicit slit-like pore walls with different surface curvatures are built by sinusoidal

functions, as shown in Figure 2. The pore walls have two dimensional periodic boundaries on the directions parallel to the pore walls. Pore shape was controlled by phase difference between the top and bottom walls. Surface curvature was controlled by a parameter T, which is related tortuosity, while pore width values were fixed as 4.2 nm. This value was selected to make ~ 6 nm spherical pores for cubic pore structure.

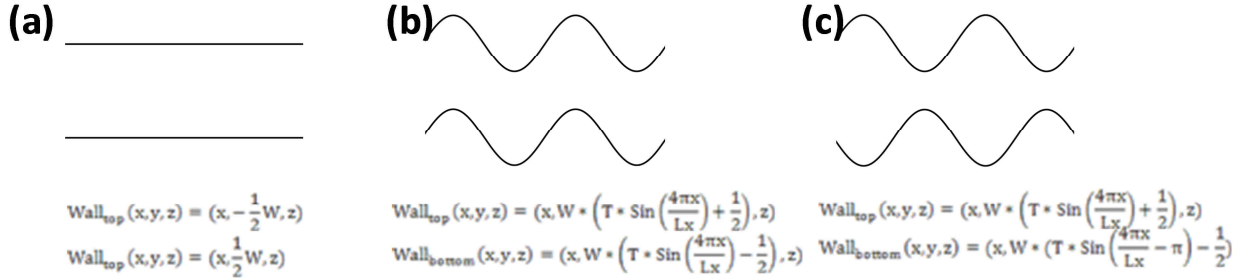


Figure 2. Side views of implicit pore walls for (a) hexagonal, (b) gyroid, and (c) cubic pore structures.

The interactions of oxygen molecules with the pore wall were calculated by assuming waved surface as a flat surface. The closest point of the wall from an oxygen molecule was established for each step to make an imaginary flat wall with 9-3 Lennard-Jones potentials

$$u_{oc}(r) = \frac{4\pi\epsilon_{oc}\rho_c\sigma_{oc}^3}{3} \left[\frac{1}{15} \left(\frac{r}{\sigma_{oc}} \right)^{-9} - \frac{1}{2} \left(\frac{r}{\sigma_{oc}} \right)^{-3} \right],$$

where $\epsilon_{oc}=0.0803$ kcal/mol, $\rho_c = 2g/cm^3$, and $\sigma_{oc}=3.28 \text{ \AA}$.³ Temperature was maintained as 80 °C² by using Berendsen thermostat with time constant 45 fs. After two equilibration periods for 4.5 ps, displacements of oxygen molecules were traced for 27 ps. Four experiments were conducted for each system with different pore shape and tortuosity.

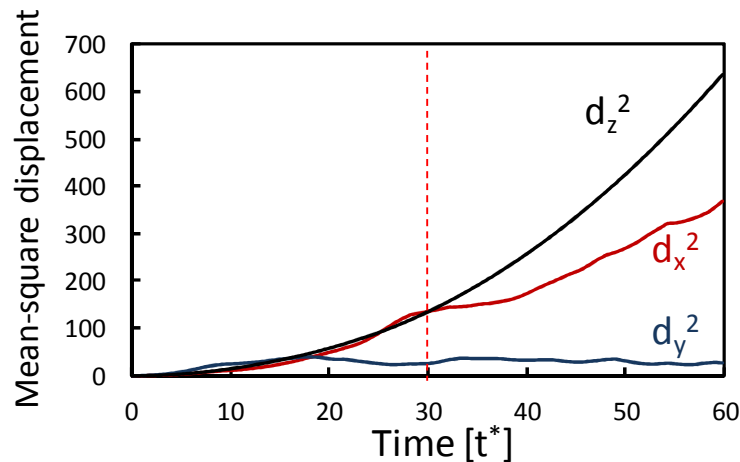


Figure 3. Mean square displacements of oxygen molecules on each direction (dx^2 , dy^2 , dz^2) vs time in normalized units.

Result and discussion

During the simulation, mean square displacements of oxygen molecules were recorded to extract the effect of pore geometry on diffusion coefficients. 1D diffusivity was calculated from the slope of mean square displacement on each direction vs time by using $\langle d_x^2 \rangle = 2D_x t$. Figure 3 shows the change of mean square displacement on each direction with time for cubic pore structure with $T=0.3$. In early stage of simulation, mean square displacements are comparable on each direction until t is ~ 17 . Mean square displacement at this point is ~ 36 , which is slightly smaller than pore radius. After this point, d_y^2 is maintained at constant, due to pore confinement. d_x^2 varies without any effect of pore wall until t is ~ 30 (d^2 is ~ 124). After this point, d_x^2 shows the effect of surface curvatures and changes slower than d_z^2 . Both of d_x^2 and d_y^2 start to be affected by pore geometry before the time corresponding to the pore diameter (~ 20 or ~ 400 in d^2).

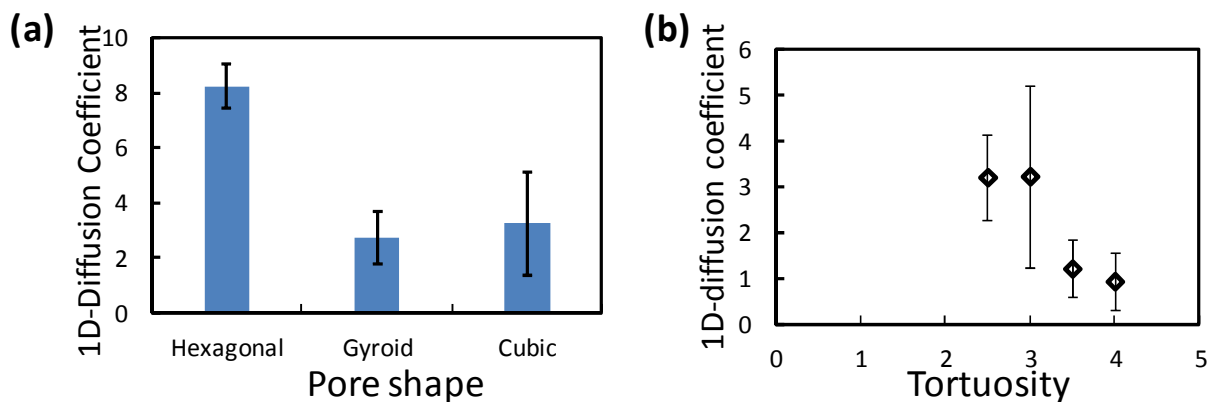


Figure 4. 1D diffusion coefficient (D_x) of oxygen molecules at 80 °C and 2 atm in (a) hexagonal, gyroid, and cubic mesopores with $T=0.3$ and (b) cubic mesopores with various T .

The effect of pore geometry on the diffusivity was investigated with various pore structures. 1D Diffusion coefficients of oxygen molecules were calculated in mesoporous carbon with different pore shapes (hexagonal, gyroid, and cubic structure as previously mentioned) and tortuosities ($W=2.5, 3, 3.5,$ and 4). Figure 3a show the 1D diffusivities (D_x) of oxygen in mesoporous carbon, which is strongly affected by pore structures. While hexagonal structure yield ~ 8.3 of D_x (dimensionless), gyroid and cubic pore structures result in D_x s less than a half of D_x for hexagonal structures.

Tortuosity of mesoporous carbon diminishes diffusivity of oxygen molecules significantly. Cubic pore structures with various tortuosities (T) were built, and diffusivities of oxygen molecules were established. As tortuosity of cubic pore increases, dramatic decreases of D_x were observed, as shown in Figure 4b. The tortuosity of cubic pore structure, also named pore neck, well confines oxygen molecules in single spherical pore.

Conclusion

The effect of pore geometry (pore shapes and tortuosity) on oxygen diffusivity was studied by using NVT molecular dynamic simulations. In the implicitly built slit-like pore walls, oxygen diffusion was appeared to be strongly affected by pore geometry. This clear reveal that pore shape and tortuosity should be tuned to provide high transport kinetics, in addition to the pore size. Although the pore structures were simplified to reduce the number of calculations, geometry effect can be well described with this model. While pore-wall surface interaction is not significant in this model (oxygen molecules and carbon surface), this interaction may become important in many other systems. For example, water vapor is generated in cathode of fuel cells, and easily condensed in the mesopore and block the oxygen diffusion, when pore surface is hydrophilic, and pore size is small. Such interactions would be very interesting, when they are combined with geometric effects and possibly studied.

References

- 1) Haward *et al.*, *Langmuir*, **2004** 20, 5998
- 2) Wu *et al.*, *Science*, **2011**, 332, 443
- 3) Bouanich, *J. Quant. Spectrosc. Radiat. Transfer*, **1992**, 47, 243