

Molecular dynamics simulation of the transport of H₂, O₂, Ar, CH₄ and n-C₄H₁₀ in composite poly (4-methyl-2-pentyne) and nanoparticle of cristobalite silica and faujasite

Q. Yang and L. E. Achenie

Department of Chemical Engineering, Virginia Tech, Blacksburg, VA, 24060, quany@vt.edu

ABSTRACT

In industrial processes membranes made of composite polymer material are widely employed to separate gas mixtures. These membranes have better performance than membranes consisting of polymer alone. To understand the mechanism and therefore aid membrane design it is essential to explore the penetrant transport in the complex composites from the molecular level, but few researchers have done such research to our knowledge. Silica has different crystalline form. The transport properties of penetrants in the composite of PMP and nanoparticles of these two types of silica are obviously different. Molecular dynamics method was done successfully in the research to explore the transport of different penetrants in the composites of PMP and nanoparticles of two forms of silica, the cristobalite form (PMPC) and the faujasite form (PMPF).

Keywords: composite, silica nanoparticle, molecular dynamics, cristobalite, faujasite

1 INTRODUCTION

In industry, the separation of methane from higher hydrocarbons, organic monomers from nitrogen, and others are important processes. In the production of natural gas, raw gas is treated to separate butane and higher hydrocarbons from methane in order to bring the heating value and the dew point to pipeline specification, and to recover the valuable higher hydrocarbons as chemical feedstock.

In these processes, membranes made of composite material [1,2] are used due to their better performance than membranes consisting of polymer solely. For example, the composite PMP and silica nanoparticle is used to separate C₄H₁₀ (n-butane) from mixtures of C₄H₁₀ and CH₄, H₂, etc.

Silica has different crystalline forms. In cristobalite, the Si and O atoms are so densely packed that there are probably no pores through which penetrants can pass, while in faujasite crystalline form, there exists pores that are probably large enough to allow penetrants to pass through. Amorphous silica may contain a mixture of small and large pores. The transport properties of penetrants in the composites PMPC and PMPF are different. It is essential to explore the reasons that lead to the difference; this knowledge would aid the design of membrane made of

composite PMP and silica nanoparticles. In the research the transport of different penetrants in PMPC and PMPF was simulated and compared.

2 COMPUTATIONAL THEORY

Like Tamai et. al.[3], the PMP sample is modeled as H(CCH₃CC₃H₇)₃₁H. The methyl (including the methyl in propyl) groups are taken as united groups, while H and C are treated as individual units. The density of PMP at 300K was used to determine the cell size.

The diameter of the nanoparticle is 2.5 nm. Most researchers[4-6] use nanoparticles of similar size in their MD simulation of composites. To facilitate comparison, simulation cells corresponding to composite PMPC and PMPF are composed of same number of PMP chains and same size of nanoparticle. The structures of both the cristobalite silica and the faujasite silica are presented in Figure 1.

In the composite, the nanoparticle is placed in the center of the simulation cell, among the PMP chains. The simulated systems were composed of 5 chains and 1 nanoparticle.

The DLPOLY [7] software package was employed here. The Verlet algorithm was used to solve equations of motion with time step of 2.5fs under constant pressure and temperature condition. Time step of 1.5fs was also tried. The simulation results are in agreement with that corresponding to time step of 2.5fs, except that much more computer simulation time is required. 5000 steps of energy minimization were performed using the steepest descent algorithm to obtain a reasonable starting configuration. Subsequently the structure was equilibrated with 500ps MD simulation in the NPT ensemble. The weak coupling technique[7] was used to modulate the T and P with relaxation time of 0.1ps and 0.5ps, respectively. The equilibration procedure was followed by 3 ns MD production run in NVT ensemble. The temperature was set to 300K. The pressure was 1 bar. The VDW interaction potentials were cut off at 1.2 nm. The electrostatic interaction potential cut off distance was also 1.2 nm.

When the penetrants enter the Fickian diffusive regime, the mean square displacement of penetrants averaged over different time origin can be employed to calculate diffusivity with the following equation :

$$D = \lim_{\Delta t \rightarrow \infty} \frac{\langle [R(t_0 + \Delta t) - R(t_0)]^2 \rangle}{6 \times \Delta t} \quad (1)$$

where $R(t)$ is vector position of penetrants at time t and $\langle \rangle$ means an ensemble average.

The Widom test particle insertion method [8] is employed to calculate the solubility coefficients. It is assumed that the particle is inserted into the system randomly and the potential change due to the penetrant insertion is ΔE_k . If N times of insertions are done and N is large enough, then the solubility coefficient can be determined with Eq. (2).

$$K = \frac{\sum_{k=1}^N e^{-\Delta E_k / RT}}{N} \quad (2)$$

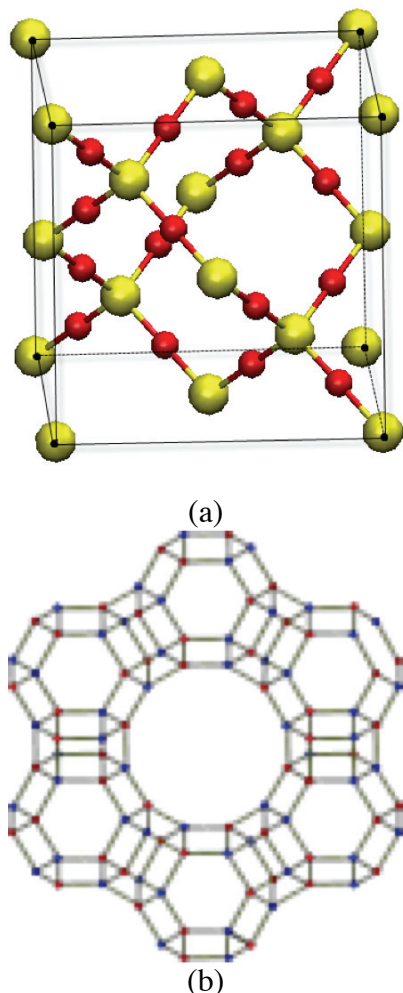


Figure 1. The structures of the cristobalite (a) silica and the faujasite (b) silica

3 RESULTS AND DISCUSSION

The number of cavities with radius in a certain narrow ranges $(r, r + \Delta r)$ was counted first. The counted cavities number $N(r)$ divided by the total number of cavities over the whole range, N_t , and radius range width, Δr , will give the probability density, $p(r)$, in Figure 2. That is:

$$p(r) = \frac{N(r)}{N_t \cdot \Delta r} \quad (3)$$

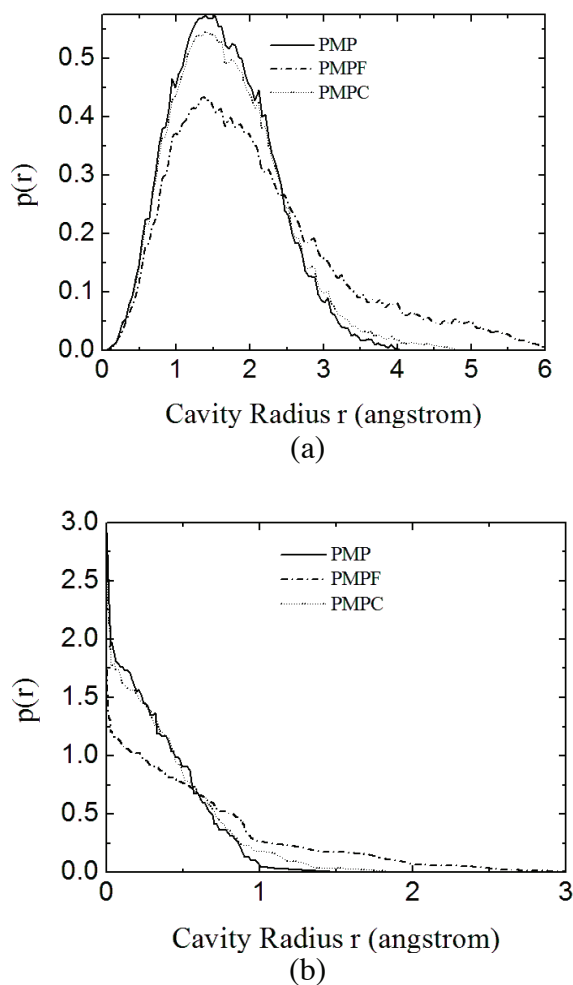


Figure 2. The cavity size distribution in PMP, PMPC and PMPF; $p(r)$ is the probability density of the cavity radius being r . (a) shows the cavity radius distribution when the size of the matrix units is ignored (regarded as zero). (b) shows the cavity radius distribution when the radius of the matrix units is considered as one half of the Lennard-Jones size parameters of the corresponding units.

From Figure 2, it is observed that in the composite PMP and silica nanoparticle, the fraction of large cavities is higher than in pure PMP. Therefore, due to the existence of the silica nanoparticle, the cavity size distribution varies, which lead to higher diffusivity in the composite. Furthermore, the fraction of large cavities in the composite PMPF is higher than that in the composite PMPC. The pores in the faujasite silica nanoparticle contribute to the difference.

The logarithmic plot of mean square displacement averaged over different time origin versus time was used to determine if the transport is in the Fickian diffusive regime. Subsequently the values of the diffusivity were determined via the slope of the line obtained from a least squares fit.

Figure 3 shows the relationship between the mean square displacement averaged over different time origin and the time when CH₄ diffuses in PMP, PMPC and PMPF.

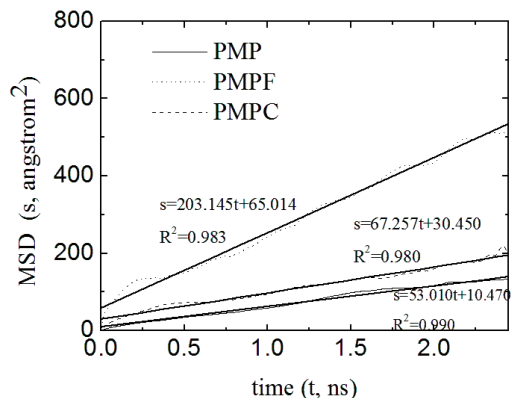


Figure 3. The relationship between the mean square displacement averaged over different time origin and time when CH₄ diffuses in PMP, PMPC and PMPF. R^2 is the square of correlation coefficient.

Table 1 shows the diffusivity of different penetrants in PMP, PMPC and PMPF.

Table 1. Diffusivity of penetrants in PMP, PMPC and PMPF ($D \times 10^9 m^2/s$). The data in the parenthesis is the standard deviation.

Penetrants \ Diffusivity	D_{PMP}	D_{PMPC}	D_{PMPF}
H ₂	47.5(16.1)	31.7(8.9)	136.1(39.2)
O ₂	0.610(0.17)	4.31(1.23)	7.52(3.21)
Ar	0.166(0.07)	0.732(0.327)	1.053(0.345)
CH ₄	0.092(0.05)	0.112(0.051)	0.338(0.171)
n-C ₄ H ₁₀	0.030(0.02)	0.108(0.054)	0.115(0.063)

At different production time, the values of the calculated solubility coefficients would fluctuate, because during the production run, the PMP structures and the composite structures have minor variation due to minor oscillation of atoms around their equilibrium positions. As a result, to get suitable results of the solubility coefficients, the values of the solubility coefficients corresponding to structures at different time with certain interval were calculated first. Then the average value of all the coefficients obtained would be regarded as the solubility coefficients of the corresponding penetrants in that material. The solubility coefficients of CH₄ in PMP, PMPC and PMPF at different time are presented in Figure 4.

Then after the values of diffusivity and solubility coefficients were obtained, the permeability values of different penetrants in PMP and composite PMP and silica nanoparticle were calculated and listed in Table 2.

Table 2. The calculated permeability of different penetrants in PMP and composites; the date in parenthesis are the corresponding experimental results.

matrix \ pene	PMP	PMPC	PMPF
	$P(10^3 \text{ barrer})$	$P(10^3 \text{ barrer})$	$P(10^3 \text{ barrer})$
H ₂	15.623	13.349	129.85
O ₂	0.216(0.185)	2.161	13.311
Ar	0.183	3.116	17.415
CH ₄	0.203(0.191)	1.113(0.873)	29.015
n-C ₄ H ₁₀	4.236(2.735)	43.403(22.311)	908.39

From Table 2, it is observed that these two types of composites both have higher permeability than PMP for the same penetrants. Especially for n-C₄H₁₀ the insertion of silica nanoparticle in PMP significantly increases permeability. The selectivity of CH₄ over O₂ does not differ much from one in both PMP and composites, as the molecule sizes and VDW interaction of CH₄ with matrix atoms are close to O₂. The selectivity of n-C₄H₁₀ over CH₄ increases from 20 to 31 due to the insertion of nanoparticle of faujasite silica, and to 38 because of the insertion of nanoparticle of cristobalite silica. The ratio of the computed value of selectivity of n-C₄H₁₀ over CH₄ in PMPC to that in PMPF is therefore 38/31.

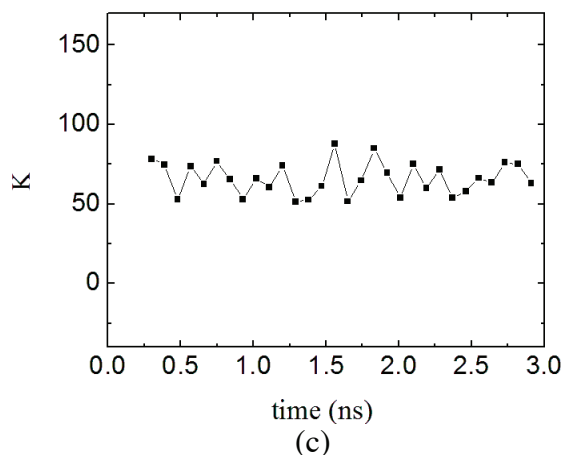
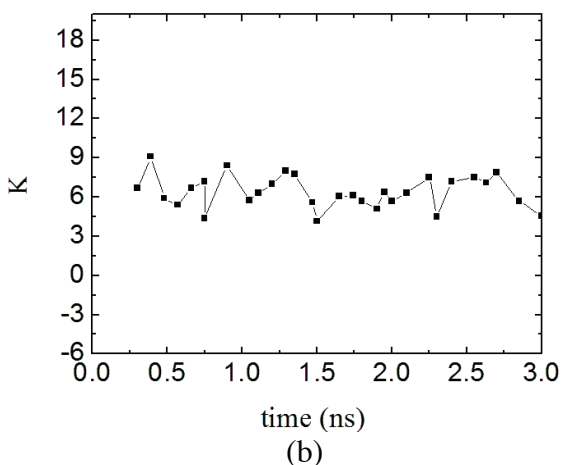
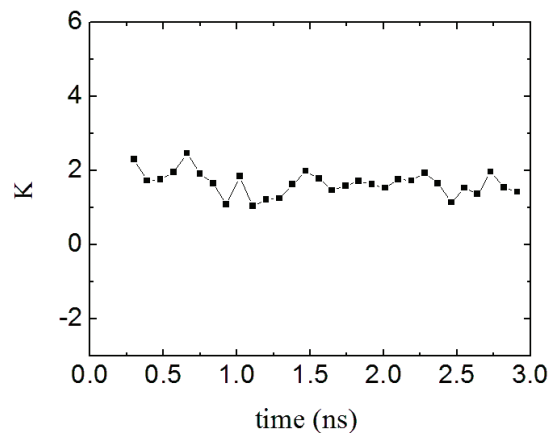


Figure 4. The solubility coefficients of CH₄ in PMP (a), PMPC (b) and PMPF (c) at different time

4 CONCLUSION

In industry, the processes to separate gas mixtures are rather significant. Silica has different crystalline forms.

The transport properties of penetrants in the composite PMP and nanoparticles of these two forms of silica are different. It is essential to explore the real reasons that lead to the difference from molecular level in order to aid the design of membrane made of composite PMP and silica nanoparticles. Molecular dynamics method was employed in the work to explore the transport of different penetrants in PMP and the composites of PMP and two forms of silica nanoparticles, the cristobalite form and the faujasite form. The complicated structures of PMPC and PMPF were established and relaxed. With the structure, the cavity size distribution was analyzed and it is observed that composite PMP and silica nanoparticle has more large cavities than pure PMP, while PMPF has more large cavities than PMPC. The diffusivity, solubility coefficients and the permeability of different penetrants in PMP and the composite were calculated. The calculated results show that these two types of composites both have high permeability compared with PMP for the same penetrants and PMPF has higher permeability than PMPC for the same penetrants. The selectivity of n-C₄H₁₀ over CH₄ increases from 20 to 31 due to the insertion of nanoparticle of faujasite silica, and to 38 because of the insertion of nanoparticle of cristobalite silica. PMPC has better performance than PMPF and is widely employed to separate the mixture of n-C₄H₁₀ with other gas molecules, like CH₄, in industry.

REFERENCES

- [1] Yampolskii, Y.; Pinnau, I.; Freeman, B. D. "Materials science of membranes for gas and vapor separation". John Wiley & Sons Ltd, West Sussex, England, 2006
- [2] Strathmann, H. Wiley-VCH Verlag & Co. KGaA, Weinheim, Germany, 2011
- [3] Tamai, Y.; Tanaka, H.; Nakanishi, K. "Molecular Simulation of Permeation of Small Penetrants through Membranes. 1. Diffusion Coefficients. Macromolecules", 27, 4498, 1994
- [4] Selvan, M. E.; He, Q.; Calvo-Munoz, E. M.; Keffer, D. J., "Molecular dynamic simulations of the effect on the hydration of nafion in the presence of a platinum nanoparticle". J. Phys. Chem. C 116 (23), 12890, 2012
- [5] Kasemagi, H.; Aabloo, A.; Klintenberg, M. K.; Thomas, J. O., "Molecular dynamics simulation of the effect of nanoparticle fillers on ion motion in a polymer host. Solid State Ionics". 168 (3-4), 249, 2004
- [6] Spearot, D. E.; Sudibjo, A.; Ullal, V.; Huang, A., "Molecular Dynamics Simulations of Diffusion of O₂ and N₂ Penetrants in Polydimethylsiloxane - Based Nanocomposites". J. Eng. Mater. Technol. 134 (2), 21013, 2012
- [7] Smith, W.; Forester, T. R. Todorov, I. T. "The DLPOLY user manual". STFC Daresbury Laboratory, Cheshire, UK, 2010
- [8] Widom, B. "Some topics in the theory of fluids". J. Chem. Phys. 39, 2808, 1963