Molecular Dynamics Simulation on Permeation of Acetone/Nitrogen Mixed Gas through Al_2O_3 Microporous Membranes

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Prepared for presentation at the 2004 Annual Meeting, Austin, TX, Nov. 7-12

Abstract:

In this work, molecular dynamics (MD) was performed to simulate the dynamic processes of 1:4 acetone/nitrogen permeating through different Al_2O_3 membranes by Materials Studio 2.2 software package. Three modeling systems were constructed applying different modeling box lengths as well as different hollow size and texture of Al_2O_3 membranes to compare different permeation behaviors. In each system, initial mixed gas contained 20 acetone molecules and 80 nitrogen molecules and its density was set to 0.1g/cm^3 of which could be seen as a high-pressure fluid. Analysis on the concentration profiles of three systems at different sampling time was implemented to discuss the permeation behaviors of smaller nitrogen molecules (N2) and larger acetone molecules (Ace). In each system, we had found that: (1) adsorption and diffusion occurred synchronously but adsorption was dominant in acetone case; (2) adsorption was easier to reach equilibrium than diffusion; (3) during the simulation time period 2ns, none of acetone was found to diffuse into the vacuum region; (4) when elevating the systematic temperature, adsorptive amount of nitrogen gas decreased whereas their diffusion rate increased, while both adsorptive amount and diffusion rate of acetone increased, which means that higher temperature is favor to the adsorption of acetone by the membrane; (5) larger microporous of the membrane is favor of diffusion against adsorption; (6) when applying COMPASS force field, adsorptive layer was found to be double-layer which up was acetone layer and down was nitrogen gas dominant layer, while monolayer mixed adsorption of nitrogen and acetone molecules was found when applying pcff force field.

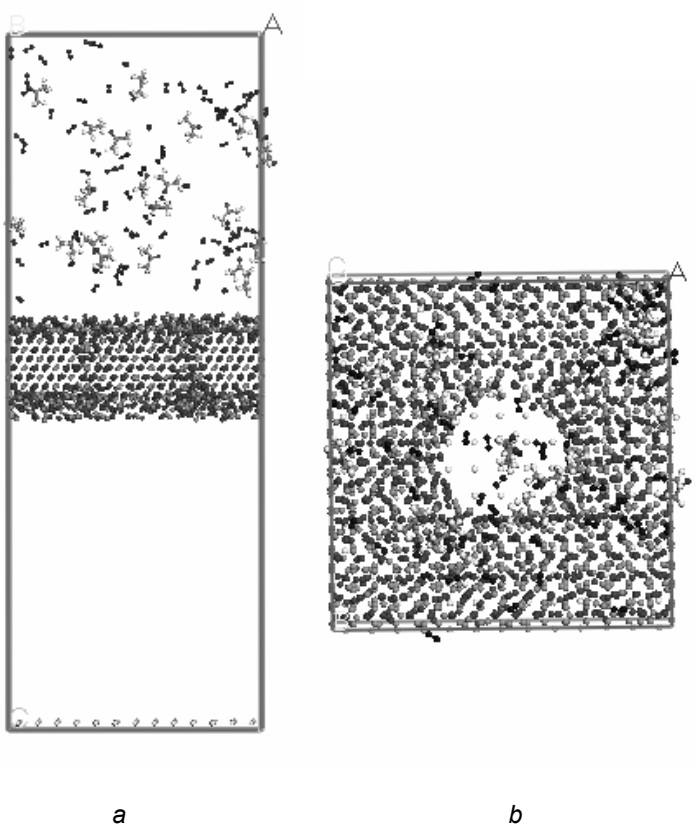
Keywords: Al_2O_3 membrane, Nitrogen molecule, Acetone, Molecular dynamics, Permeation

Modeling and simulation

1. Modeling methods

To build Al_2O_3 membrane, α- Al_2O_3 crystal whose space group is No. 167 and lattice length is 4.759×4.759×12.991Å was imported from the Materials Studio 2.2 package [Accelrys 2002]. The crystal was cleaved to form two surfaces: miller index (0 -1 0) and miller index (0 0 -1) which **u×v** was set to 38.072×38.973 Å and 29.477×33.313 Å respectively and each thickness of the layer was set to about 16 Å. These two different layers were then subjected to different strategies to form three different membranes.

Each permeation 3D model included three layers: upper is gas mixture layer which density is set to 0.1 g/cm^3 so it can be seen as a kind of high pressure fluid and contains twenty acetone molecules and eighty nitrogen molecules, middle is Al_2O_3 membrane with a hole, nether is vacuum with a height about 50 Å and a bottom plane composed of 160 to 200 helium atoms (fig. 1*a*).



a *b*

Fig. 1 Initial permeation model of system I: *a* lateral view, *b* top view.

2. Simulation conditions

Materials studio 2.2 software package was applied to execute MD simulation. For each system, *NVT* canonical ensemble was adopted and periodic boundary condition was used. Systematic temperature was set to 278K or 303K in MD runs and a constant temperature control method developed by Andersen which collision frequency was every 142 steps was used. The initial velocities of all unfixed atoms were designated randomly according to systematic temperature and Boltzmann distribution. Iteration step time was chosen as 1 fs, sampling time was set to 1ps, and total 2ns trajectories were collected for the analysis. For three systems, two different force fields COMPASS and pcff were applied to compare different adsorption behaviors. COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) is the first *ab initio*-based force field to have been parameterized using extensive data for molecules in the condensed phase while PCFF (Polymer Consistent Forcefield) is intended for application to polymers and organic materials. It is useful for polycarbonates, melamine resins, polysaccharides, other polymers, organic and inorganic materials, about 20 metals, as well as for carbohydrates, lipids, and nucleic acids. In our modeled membranes, partial charge of Al and O is designated as 1.200 and -0.800 respectively in COMPASS case while all being designated as zero in pcff case. In each system, all nitrogen, oxygen atoms in membrane and helium atoms in bottom were fixed in space during the simulation.

Results and discussion

1. Permeation mechanism

After collecting the trajectory of each system, analysis on the concentration profiles of three systems at different sampling time was implemented to discuss the permeation behaviors of smaller nitrogen molecules (N2) and larger acetone molecules (Ace). As an example, concentration distribution of N2 and Ace in system I at different sampling time (*t*) and different temperature *T* when applying pcff force field was listed in table 1.

Table 1 Distribution of molecules in different regions at different sampling time and temperature in system I

t (ns)	0.5		1.0		1.3		1.6		1.8		2.0	
T (K)	278	303	278	303	278	303	278	303	278	303	278	303
N2(surf)	31	34	36	34	37	35	39	36	39	35	40	36
N2(hole)	9	11	14	15	16	20	17	18	18	18	21	17
N2(vacu)	0	0	3	2	7	5	11	12	13	16	16	17
Ace(surf)	10	8	15	15	17	17	17	19	17	18	17	17
Ace(hole)	0	0	0	0	0	0	0	0	0	1	0	2
Ace(vacu)	0	0	0	0	0	0	0	0	0	0	0	0

From table 1 we can find that adsorption and diffusion occurred synchronously for both molecules but adsorption was dominant for acetone which can be attributed to its smaller diffusion velocity with larger molecule size. Under 278K, adsorption of nitrogen and acetone basically reached equilibrium at 1.6 ns and 1.3 ns respectively whereas diffusion equilibrium of both molecules wasn't observed till 2 ns, which means adsorption is easier to reach equilibrium than diffusion because of the large surface of the membrane. While elevating the temperature, similar behaviors of adsorption and diffusion were observed but showing some trends that (1) both diffusion rates increased because of both increased moving velocities, (2) in acetone case, time tended to adsorption equilibrium was almost unchanged (1.3 ns) which means temperature impacts its adsorption equilibrium in a slight degree while its equilibrated adsorption amount increased (from 17 to 18) which can been obviously observed in system II (from 15 to 19 in fig. 2) which means higher temperature is favor to the

adsorption of acetone by the membrane surface, (3) in nitrogen case, time tended to adsorption equilibrium was obviously shorter (from 0.5 to 1.6 ns) which means temperature impacts its adsorption equilibrium in a larger degree whereas its equilibrated adsorption amount decreased (from 39 to 36) which means lower temperature is favor to the adsorption of nitrogen.

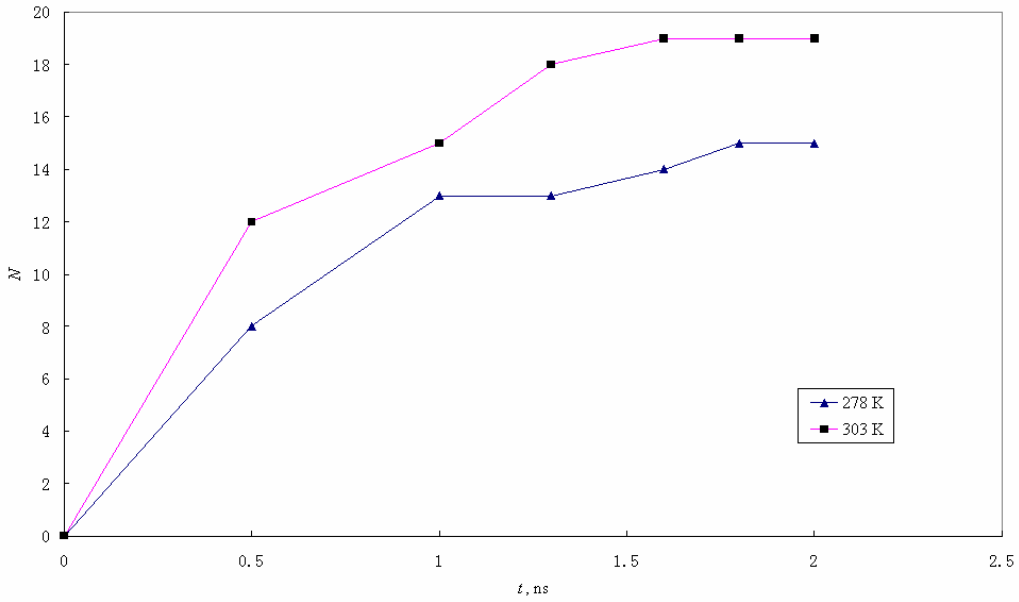


Fig. 2 Plot of adsorption amount of acetone by the membrane *N* vs. simulation time *t*.

Conclusions

Three systems and two force fields were used to investigate permeation behavior of small gas mixture CH_3COCH_3/N_2 through microporous Al_2O_3 membrane. In each system, adsorption and diffusion occurred synchronously but adsorption was dominant for acetone. In each system, adsorption was easier to reach equilibrium than diffusion. Elevating temperature is favor to the adsorption of acetone and can increase diffusion rate of both acetone and nitrogen molecules. Larger microporous of the membrane is favor of diffusion against adsorption. When applying COMPASS force field, adsorptive layer was found to be double-layer while monolayer mixed adsorption of nitrogen and acetone molecules was found when applying pcff force field. Comparing to COMPASS, pcff is preferred to be used for studying gas permeation.

Acknowledgement:

This work was supported by Jiangsu Nature Science Foundation (BK2003402).

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