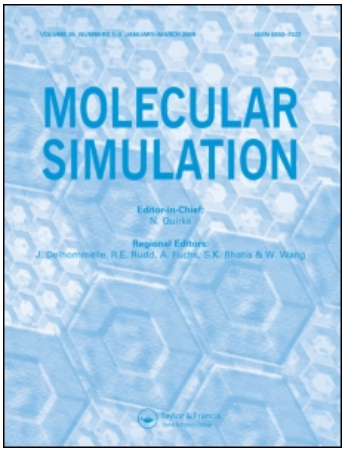

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Computational designing of gradient type catalytic membrane: application to the conversion of methanol to ethylene

Abhijit Chatterjee; Maya Chatterjee[a]
[a] Research Center for Compact Chemical Process, Sendai, Japan

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Computational designing of gradient type catalytic membrane: application to the conversion of methanol to ethylene

Abhijit Chatterjee[a]* and Maya Chatterjee[b]

[a]*Accelrys K. K., Nishishinbashi TS Bldg. 11F, 3-3-1 Nishishinbashi, Minato-ku, Tokyo 105-0003, Japan;* [b]*Research Center for Compact Chemical Process, AIST, Tohoku, 4-2-1 Nigatake, Miyagino-ku, Sendai 983-8551, Japan*

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We have developed a unique zeolite membrane with a combination of hydrophilic entrance and hydrophobic exit using computer simulation methodology. Based on the Si/Al ratio, a gradient type membrane reactor was designed in terms of stability and its capability to adsorption, diffusion process. A combination of Si/Al 300 (hydrophobic) and Si/Al 30 (hydrophilic) was found to be the best match in terms of percentage mismatch as well as binding energy. The adsorption and diffusion regarding the conversion of methanol to ethylene was examined on the resultant gradient type membrane. Depending on the Si/Al ratio a significant difference in the adsorption isotherm and diffusion behaviour of methanol and ethylene molecule was observed. Methanol was adsorbed selectively at high Al content part of the membrane reactor whereas ethylene passed easily without getting adsorbed independent to the Si/Al ratio. A plausible mechanism was proposed to justify the product formation and separation on the newly designed membrane material.

Keywords: zeolite; membrane; gradient type; density functional theory; Monte Carlo

1. Introduction

Zeolites are a nanometre sized crystalline porous material. Their small pore size and the possibility of their having different chemical compositions can give rise to a very selective interaction with adsorbed molecules depending on size, shape and chemical compositions. Zeolite surface can be changed from hydrophobic to hydrophillic, non-acidic to acidic simply by substitution of Si by Al, which significantly affects phenomena related to the structural properties like diffusion. During the last 10 years, interest in developing thin zeolite films or zeolite membranes has grown enormously [1,2]. Zeolite membranes are generally used as catalytic membrane reactors as they can combine separation [3–7] and catalytic activity [8] efficiently due to the significantly different diffusivities in the uniform, molecular-sized pores and the presence of catalytic sites. The selective sorption properties with their catalytic activity and thermal stability make zeolite an ideal candidate for the inorganic catalytic membrane. Most of the zeolite membranes reported in the literature are of the MFI type because of their pore architecture, which consists of straight channels interconnected by zigzag channels. This amazing pore structure leads to highly anisotropic diffusivity and MFI membranes have been widely used in gas separation [9] and catalytic reactors [10,11]. Silicalite is a MFI type zeolite comprise of only Si and O, is hydrophobic and inert, used in the hydroisomerisation [12], pervaporation [13], etc.

Despite the enormous success of the zeolite membrane, its practical application in the larger scale is still limited. Several factors, like cost of membrane development, reproducibility, long-term stability and the method for the preparation of the defect free membrane, restrict its implementation in the industry. Molecular simulations have become a powerful tool to predict the catalytic behaviour of zeolite [14]. Compared to the experimental process, they are rapid and convenient, cost effective, can handle more complex systems within a reasonable period of time and result in a better understanding on the system. Many computer simulation methodologies have been employed to understand the physicochemical properties of zeolite such as adsorption characteristics [15], diffusion and permeation [16], catalytic reaction [17] and also the nature of the acidic site [18,19]. The main concern of this work is to design a membrane using computer simulation methodology.

A gradient type membrane is defined as a membrane when there is a regular or graded ascent or descent in terms of any measurable parameter like adsorption and diffusion. The most important aspect of a gradient membrane is its compatibility with its constituents, which can be measured by the diffusivity and as well by the mismatch of the components. Experimentally, the synthesis of zeolitic gradient type membrane is very critical and challenging due to the surface matching. Moreover, complete interpretation of adsorption and diffusion processes of guest molecules in zeolites only by experiment is quite difficult or impossible.

*Corresponding author. Email: achatterjee@accelrys.com

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So computer simulation is highly desirable to get the fundamental insight into the nature of the adsorption and diffusion behaviour of the zeolite and adsorbate system.

Here, we will describe the designing of functionally gradient material for a catalytic membrane reactor depending on adsorption and diffusion with varying Si/Al ratio to find the mismatch. To test the efficiency of the designed material, transition state calculation and diffusivity calculation were performed to track the feasibility of the reaction and to monitor the diffusion path of the reactant and product to validate the design of the gradient type membrane, respectively.

The current scheme consists of four parts. (1) The membrane was designed by a combination of different Si/Al ratio and then the lattice was optimised using quantum mechanical calculations. (2) Then the adsorption capability of the reactant and product molecules for the conversion reaction of methanol to ethylene was tested at varying composition of the zeolite using grand canonical Monte Carlo simulation. Cvff_aug forcefield with Ewald summation for the electrostatic interaction and an atom based Van der Wall scheme was used for the Monte Carlo simulation. (3) Once the adsorption capability had been monitored then the following reaction scheme with transition state was tested using density functional calculation.

Step 1:. $2CH_3OH{=}CH_3{-}O{-}CH_3 + H_2O$

Step 2:. $CH_3{-}O{-}CH_3{=}CH_2{=}CH_2 + H_2O$

The reaction was tested in the presence and the absence of the gradient membrane. (4) Finally, to monitor the isolation of the product, a diffusion test calculation was performed with density functional based energy calculation, where the molecules are moved in a specific direction for a specified step. Energy at each point was calculated and plotted to prescribe a diffusion path.

2. Computational methodology

Ab initio total energy pseudopotential geometry optimisation calculations of zeolite unit cell were performed using Cambridge Serial Total Energy Package (CASTEP) and associated programmes of Accelrys, with imposed periodic boundary conditions [20,21]. For the calculation, a unit cell of varying Si/Al ratio followed by a combination of high Al and low Al content was taken. Non-local ultra soft pseudopotentials [22] and Becke–Perdew parameterisation [23,24] of the exchange correlation functional including gradient correction (GGA) were employed. The k-point set used in a calculation defines the accuracy of the Brillouin zone sampling. The Monkhorst–Pack [25] k-points used in CASTEP are characterised by divisions along three reciprocal space axes and by an optional origin shift. Thus, the k-points setup procedure simply involves selecting three integer divisions. The quality of the k-point set can be quantified in a number of ways; CASTEP uses the distance between the points in reciprocal space as a numerical measure. Sampling of reciprocal space has been performed using $2 \times 2 \times 2$ k-point in the Brillouin zone with kinetic energy cutoff of 350 eV using the Monkhorst–Pack scheme [25].

All the calculations related to the transition state (TS) were performed with density functional theory (DFT) [26] using DMol^3 [27–29] code of Accelrys Inc., DNP basil set [30] and BLYP exchange correlation functional [31,32]. The transition state calculations were performed using the synchronous transit methods as included in the DMol^3 module of Accelrys Inc., Complete Linear Synchronus Transit (LST)/Quadratic Synchronus Transit (QST) begins by performing an LST/Optimisation calculation. The TS approximation obtained in that way is used to perform the QST maximisation. From that point, another conjugate gradient minimisation is performed. The cycle is repeated until a stationary point is located or the number of allowed QST steps is exhausted. DMol^3 uses the nudged elastic band (NEB) method for minimum energy path calculations. The NEB method introduces a fictitious spring force that connects neighbouring points on the path to ensure continuity of the path and projection of the force so that the system converges to the minimum energy path (MEP), which is as well called intrinsic reaction co-ordinate if the co-ordinate system is mass weighted. We also calculated the vibration mode to identify the negative frequency to confirm the transition state. We have further used DMol^3 to calculate the diffusion energy for the interacting molecules to propose a diffusion path.

Absolute adsorption isotherms were computed using a grand canonical Monte Carlo (GCMC) calculation algorithm, which allows displacements (translations and rotations), creations and destructions. The GCMC method was convenient to simulate adsorption [33,34] and was carried out by the Sorption module in Materials Studio® software of Accelrys Inc., which can execute a series of fixed pressure simulations at a set temperature in a single step. At the start of the Sorption run, a fixed pressure simulation was performed for a specified number of steps between the start and end fugacity set. In the default setup, the start fugacity of each component is increased linearly to the end fugacity with an equidistant step. However, it is also possible to regulate those steps to space logarithmically; in that case, the logarithm of the start fugacity of each component is increased linearly to the logarithm of the end fugacity in equidistant steps (the fugacity thus increases exponentially). Sorption result reports the sum of component fugacities as the total fugacity. This is equal to the pressure if the reservoir is an ideal gas. The equilibration steps and the production steps were set to 1,000,000 and 1,000,000,000, respectively, Monte Carlo moves. We have saved the frames for every 1000 steps. Materials Studio database provides various types

of forcefields. A cvff_aug forcefield was applied in this study. The zeolite structure was assumed to be rigid during the sorption process. This assumption is not as drastic as the flexibility of the lattice more significantly influences the diffusion properties [35].

3. Model

ZSM-5 (silicalite) exists in three distinct forms: monoclinic, *Pnma* and $P2_12_12_1$ orthorhombic. We have used a unit cell with *Pnma* symmetry containing 288 atoms and the starting composition was $O_{192}Si_{96}$, where Si atoms were substituted by Al to change the Si/Al ratio. The charge after Al replacement is saturated by attaching the hydrogen atom at the bridging oxygen connecting the Si and Al. The reactant and product molecules are drawn using the Vizualizer of Accelrys Inc.

4. Results and discussions

To design a gradient type membrane, the model structure of ZSM-5 with different Si/Al ratios such as 1, 10, 30, 60, 90, 300 and only silica was generated. An all silica model is shown in Figure 1. We have optimised the individual bulk structure of one unit cell with CASTEP and Si/Al ratio of 300 was chosen to mimic a situation of very low Al content. It has to be mentioned that for a gradient type membrane the compatibility of its component is an integral part of achieving a stable membrane.

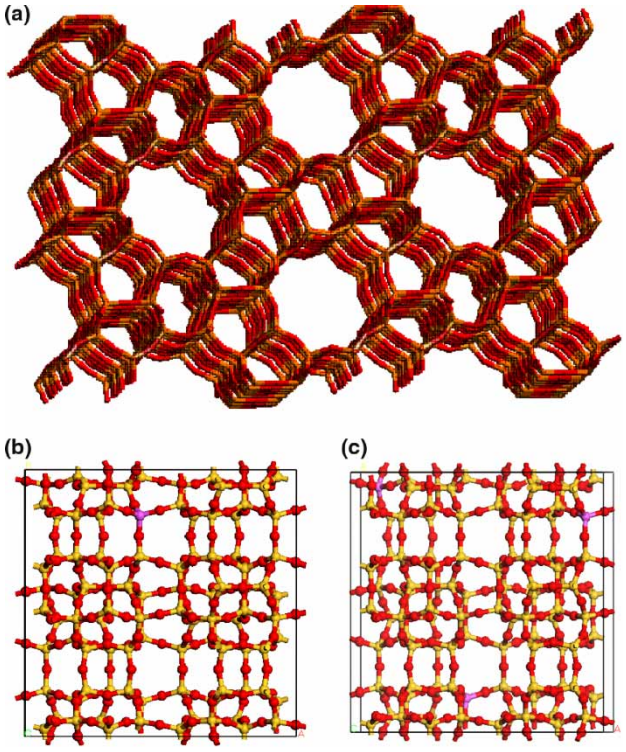

Figure 1. Structural model of MFI (a) all silica (b) Si/Al = 30 and (c) Si/Al = 300.

4.1. Ab initio *first principle calculation*

Ab initio first principle calculation was performed to find out the mismatch of component from the best combination of two-bulk structures with different Si/Al ratios, which will be energetically stable. We first optimised the individual zeolite structure with a specific Si/Al ratio and then designed a layer with the two possible matrices. A possible combination of low and high Si/Al ratios was tried and then we fixed the high Si/Al ratio to 300. After that the other entire low Si/Al ratios (1, 10, 30, 60 and 90) were combined with the high Si/Al ratio (300) and each of these combined structures with high Si/Al and low Si/Al ratio was optimised for the mismatch and stabilisation of the structure. The stabilisation energy was calculated using the following formula:

$$E_{\text{stabilisation}} = E_{\text{complex}} - [E_{\text{component 1}} + E_{\text{component 2}}],$$

where E_{complex} is the total energy of the complex resulted form the combination of two different set of Si/Al ratio. $E_{\text{complex 1}}$ and $E_{\text{complex 2}}$ are the energies of the optimised individual zeolite framework used to make the complex. According to the stabilisation energy it was possible to predict the energetically most stable combination depending on the Si/Al ratio. Table 1 shows the stabilisation energy and percentage mismatch of the different combination of Si/Al ratio. The highest and the lowest stabilisation energy of -6.19 and -53.34 kcal/mol were obtained for 90/300 and 30/300 combination, respectively. Hence, in terms of stabilisation energy, Si/Al 30 and Si/Al 300 were chosen as the best combination for gradient type membrane. A reasonable relative energy difference of ~ 30 kcal/mol was obtained between the most stable composition (Si/Al 300 and Si/Al 30) and others (Table 1). A little quench was observed in the structures with higher Al content as a result of the mismatch. However, Si/Al 300 and Si/Al 30 exhibit mismatch of less than 2%. Thus, considering the stability

Table 1. The stabilisation energy and the percentage mismatch for the different combination of zeolite matrix with varying Si/Al ratio.

Membrane matrix with different Si/Al ratio combination[a]	Stabilisation energy (kcal/mol)	Percentage mismatch
0/300	−6.19	19.23
1/300	−15.2	12.14
10/300	−22.56	6.56
30/300	−53.34	1.86
60/300	−23.23	12.47
90/300	−5.19	21.67

[a]We have tested here the lowest and highest Si/Al ratio.

and mismatch, an optimum combination of Si/Al 300 (hydrophobic) and Si/Al 30 (hydrophilic) was obtained for developing the gradient type of membrane. Figure 1(b) and (c) show the distribution of the Al centres within membrane matrix of Si/Al 300 and Si/Al 30 structure, respectively. Particular cell parameters and the cell volumes were compared to find the best match among the candidates.

4.2. Adsorption process

Adsorption and diffusion of the guest molecule in the zeolite host strongly influence the product distribution of catalytic reaction. For the above-mentioned gradient type membrane, the conversion of methanol to ethylene was chosen as the target reaction. Hence, the adsorption behaviour of methanol (reactant) and ethylene (product) on Si/Al 30 and Si/Al 300 was studied. Figure 2(a) and (b) (methanol) and (c) and (d) (ethylene) showed adsorption isotherms for each adsorbed species at 298 K using standard GCMC methods. From the results, it was encouraging to note that the loading of methanol (reactant) and ethylene (product) on the membrane varies greatly with the Si/Al ratio. Methanol showed maximum loading at higher Al content part of the membrane whereas ethylene barely had any effect. It is well known that the low Si/Al ratio (high Al content) of zeolite prefers polar molecule to adsorb, whereas at a high Si/Al ratio (low Al content), as the surface property of zeolite changes from hydrophilic to hydrophobic, the adsorption affinity towards the polar molecule decreases [36]. For instance, the hydrophilic part of the membrane, which is associated with high Al content was more polar, adsorbed methanol easily, and hindered the diffusion, whereas ethylene can be passed easily. Hence, the difference in loading of reactant and product depending on Si/Al ratio could be a perfect gradation to design a gradient type zeolite membrane. Regarding the conversion of methanol to ethylene, methanol needs to get adsorbed in the zeolite matrices followed by the formation of ethylene, which could be separated easily because of its smooth diffusion through the membrane. Thus, considering the adsorption results of methanol and ethylene, the best possible combination will be a hydrophilic (high Al content) entrance through which methanol could adsorb and ethylene formed as a result can pass easily through the hydrophobic (low Al content) environment. This proposed the easy separation of the product after the reaction. The energy distribution calculation shows that the adsorption energy of ethylene remains low compared to methanol throughout the process and it is even lower in the higher Si/Al ratio where methanol shows stronger adsorption behaviour.

4.3. Transition state calculations

The conversion of methanol to ethylene consists of the dehydration of methanol on acidic zeolite with the formation of an equilibrium mixture containing methanol and dimethyl ether (DME) followed by the formation of olefins through the carbon–carbon bond formation. In transition state calculation, first the intermediate is identified and then the normal mode is located to rationalise the intrinsic reaction co-ordinate. In this study, a transition state search calculation using DFT formalism was performed to check the applicability of the designed gradient type membrane reactor to the conversion of methanol to ethylene. Table 2 shows the barrier height of DME and the product formation in the presence and in the absence of the gradient type catalytic membrane. The result indicates that irrespective of the presence of the membrane, the barrier height of DME is higher compared to that of ethylene which is attributed to the formation of ethylene as primary product from DME. Moreover, in the presence of the membrane, the barrier height of DME and the product is decreased, suggesting the increase in conversion due to the easy removal of the product forcing the equilibrium of the reaction 'to the right' (according to Le Chatelier's Principle). This activation barrier tests the hydrophobic capability of the membrane. The reaction energy confirms the effect of water on the reaction process as well. We mentioned earlier that diffusion of guest molecule in the zeolite host determines the utility of the zeolite in the product distribution. More exhaustive study with the reaction mechanism is under progress; the goal for the transition state calculation here is to identify the barrier height and to figure out the dependence of the membrane composition over the reaction. The composition is detrimental for the gradient type membrane. Once the product formation is confirmed then it is necessary to confirm the easy separation of the product and also to check the reaction pathway at the boundary of the hydrophobic and hydrophilic domain.

4.4. Diffusion process

To validate the adsorption of methanol on the hydrophilic site (low Si/Al ratio), the diffusion behaviour of the methanol is tested. The methanol molecule is moved in the channel direction to monitor the contribution of the gradient membrane in the adsorption process. Generally, the diffusivity behaviour of a molecule in the zeolite channel is strongly influenced by the specific location of the molecule in the pore system and some energy is needed to move the molecule from one location to another. We moved the molecules at a rate of 1.5 Å and then calculated the energy at that point, which will allow to trace a diffusion path through the specified channel. This is an indirect way to measure the diffusion path. We have optimized the energy for each of the structures using the DMol^3 of Accelrys Inc., as described in Section 2. The increase and decrease in energy from the previous step

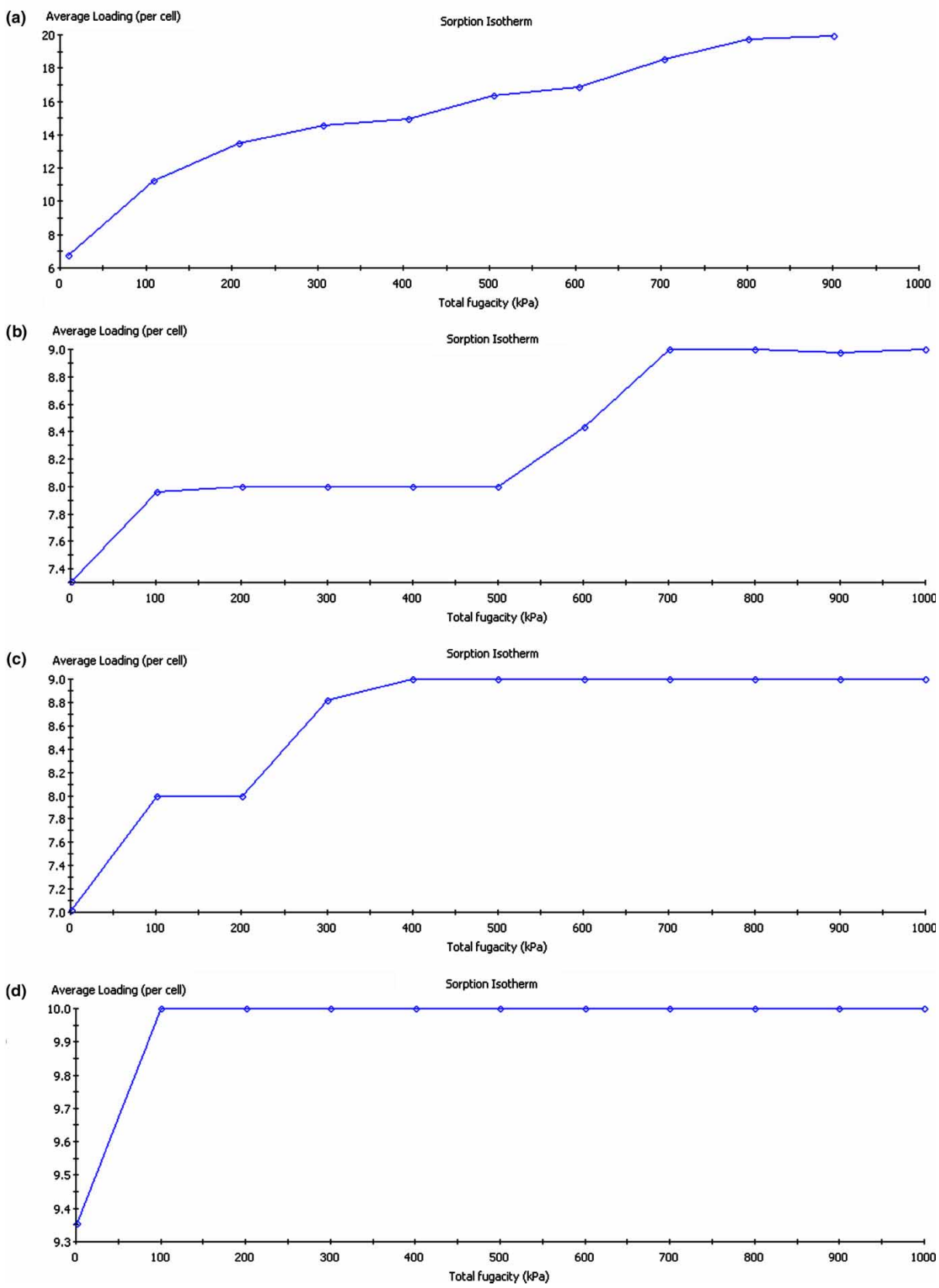

Figure 2. Adsorption isotherm of the reactant methanol (a) Si/Al = 30 (b) Si/Al = 300 and the product ethylene (c) Si/Al = 30 (d) Si/Al = 300.

Table 2. Barrier height of dimethyl ether (DME) and ethylene as obtained by DFT calculation.

System	Barrier height (kJ/mol)	
	No membrane	Gradient type membrane
DME formation	45.3	30.2
Ethylene formation	35.2	25.1

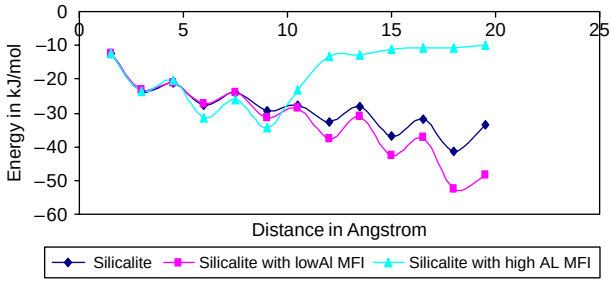

Figure 3. Diffusion path of methanol through silicalite and the gradient type membrane.

would correspond to the instability and the smooth diffusion of the molecule in that specific direction, respectively. Figure 3 shows the diffusion behaviour of methanol through the low and high Al content ZSM-5. The results clearly indicate that the zeolite matrix with low Al content part allows the diffusion of methanol quite smoothly, similar to silicalite, while a steep rise in energy was observed when methanol diffuses through the high Al content part of the membrane matrix, suggesting that the diffusion of methanol was prohibited. At the high Al content part methanol gets adsorbed close to the Al site and favours the DME formation because of the increase in acidity of the membrane [37]. On the other hand, independent to the Si/Al ratio, ethylene molecules continue to pass through the membrane and separate easily after the formation. From the above observation, it can be predicted that for the reactant (methanol), Si/Al ratio significantly influences the binding, but for the product, Si/Al ratio does not have any considerable effect on the diffusion process. Therefore, zeolite membrane with hydrophilic entrance modelled by increasing Al content and a hydrophobic exit with lower Al content significantly controls the conversion of methanol to ethylene along with the product separation.

5. Conclusions

In summary, this work successfully describes the designing of a gradient type zeolite membrane based on Si/Al ratio by computer simulation. This study is very relevant to the understanding of structure-function relationships that govern the applications of these materials as highly efficient catalytic membrane reactors from the reaction to the product separation. We have also shown that it is possible to propose the best composition for a zeolite membrane and have looked into the feasibility of the gas adsorption within the zeolite domain using first principle structural optimisation. Moreover, the transition state calculation suggested that the conversion of methanol to ethylene through the membrane reactor, followed by the product separation, was effectively done depending on the Si/Al ratio (hydrophobicity and hydrophilicity). We intend to apply this methodology to predict the various chemical composition to design catalytic membrane reactor depending on the nature of the reaction and also by varying the zeolite type.

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