



**Note:**

## Molecular simulation of the adsorption of linear alkane mixtures in pillared layered materials\*

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**Abstract:** The adsorption isotherms of mixtures of linear alkanes, involving *n*-pentane, *n*-hexane, and *n*-heptane in pillared layered materials (PLMs) with three different porosities  $\Psi=0.98, 0.94$  and  $0.87$ , and three pore widths  $H=1.02, 1.70$  and  $2.38$  nm at temperature  $T=300$  K were simulated by using configurational-bias Monte Carlo (CBMC) techniques in grand canonical ensemble. A grid model was employed to calculate the interaction between a fluid molecule and two layered boards here. For alkane mixtures, the *n*-heptane, the longest chain component in alkane mixtures, is preferentially adsorbed at low pressures, with its adsorption increasing and then decreasing as the pressure increases continuously while the *n*-pentane, the shortest chain component in alkane mixtures, is still adsorbed at high pressures; the adsorption of the longest chain component of alkane mixtures increases as the pore width and the porosity of PLMs increase.

**Key words:** Molecular simulation, Alkane mixtures, Pillared layered materials (PLMs)

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### INTRODUCTION

In petrochemical industry, studies on adsorption behaviors of *n*-paraffins such as *n*-pentane, *n*-hexane, and *n*-heptane etc. in porous materials are very important because many petrochemicals containing *n*-paraffins need to be treated by porous materials. For example, the content of *n*-paraffins in light naphtha can be decreased by adsorption and separation effect of porous materials from the view of increasing octane number (Jeanneret, 1997). Recently, pillared layered materials (PLMs), a new class of porous materials, have attracted continuously growing attention of researchers because they have a special 2D pore structure as well as excellent molecular sieve properties and a higher thermal stability. PLMs are generally obtained by intercalating rigid oxide pillars between layers of clay. The pore structure of PLMs can be controlled regularly through variations of layer dis-

tance and the distribution of metal oxide pillars in interlayer space; as a result, their separation and adsorption properties can also be modulated (Li *et al.*, 2004).

To find and design PLMs with the proper pore length and porosity applied in adsorption and separation of alkane mixtures requires a great deal of experimental data. However, experimental data obtained are still scarce until now because experimental measurements of adsorption isotherms of pure alkanes and their mixtures are very complicated and expensive (Vlugt *et al.*, 1999). Comparatively, the molecular simulation techniques as cheap methods on cost, including molecular dynamics (MD) and Monte Carlo (MC), have been used in adsorption and separation of fluids in PLMs. At present, MC simulations on PLMs reported in literature is only for nitrogen, carbon tetrachloride, carbon dioxide, methane, ethane and propane, etc. (Yang *et al.*, 2005) while there are few articles on molecular simulation of the adsorption behavior of *n*-pentane, *n*-hexane and *n*-heptane, or their mixtures in PLMs. In this work, the adsorption

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equilibria of ternary mixtures of *n*-pentane, *n*-hexane and *n*-heptane in PLMs are simulated by using CBMC techniques in grand canonical ensemble.

## METHODS

### Grid model

The grid model employed to calculate the alkane-PLMs interactions here is similar to that described in (Lu *et al.*, 2003). Although the grid model has been extensively used in molecular simulations on zeolite and been proven to be very effective, few papers about using the grid model to calculate the alkane-PLMs interactions can be seen in molecular simulations on PLMs, a kind of important pore materials. Whether the potential models and the programs used in the molecular simulation is effective or not can be proved by the adsorption isotherm of nitrogen at 77 K (Cao *et al.*, 2002). In our simulation, an  $N_2$  molecule is described as a single center L-J molecule, and its parameters of energy and size are,  $\epsilon_{N_2} / k_B = 95.2$  K and  $\sigma_{N_2} = 0.375$  nm from (Cao *et al.*, 2002). Our simulation isotherm accords very well with the experimental data obtained by Bash *et al.* (1992). In particle, it is found that pore filling pressures denoted by A for the experiment and B for the simulation are in satisfactory agreement (Fig.1). Therefore, it is thought that to employ the grid model in this work can yield reasonable simulation results for the adsorption of alkane mixtures in PLMs according to the proof mentioned before.

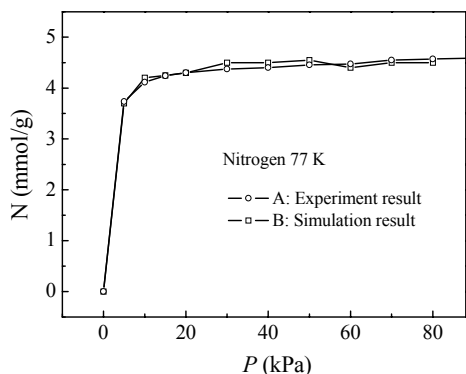


Fig.1 A comparison of experimental data and simulation results for adsorption of nitrogen in PLMs at 77 K

## RESULTS AND DISCUSSION

We investigate the mixture isotherms of *n*-pentane, *n*-hexane, and *n*-heptane in PLMs with variations of pore width and porosity at 300 K here. Considering the adsorption to be a function of pressures and changes in the composition of the gas phase, the composition of gas mixtures is fixed as 0.33-0.33-0.33 for the ternary system. From simulation results as shown in Figs.2~4, it is obvious that adsorption behaviors of every component in the mixture system are different from each other with pressures varying. At low pressures, the adsorption of alkane molecules preferentially in PLMs from large to small is *n*-heptane>*n*-hexane>*n*-pentane, indicating that PLMs have more selectivity for *n*-heptane than for *n*-pentane because the longer chain component has a larger heat of adsorption than the shorter chain component. As the pressure increases, the adsorption of *n*-heptane, the longest chain component in mixture, increases and then decreases while the adsorption amount of *n*-pentane increases continuously. At high pressures, the adsorption of *n*-pentane, the shortest chain component in mixture, is more than that of other components. The main reasons are that at low pressures, the adsorbed amount of a component is mainly dependent on the adsorption affinity between adsorbent and adsorptive, so the longest chain molecules

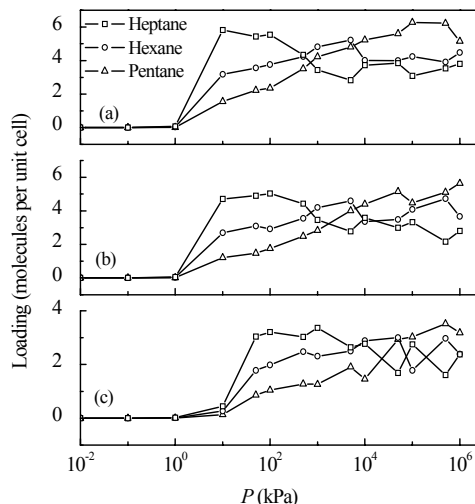
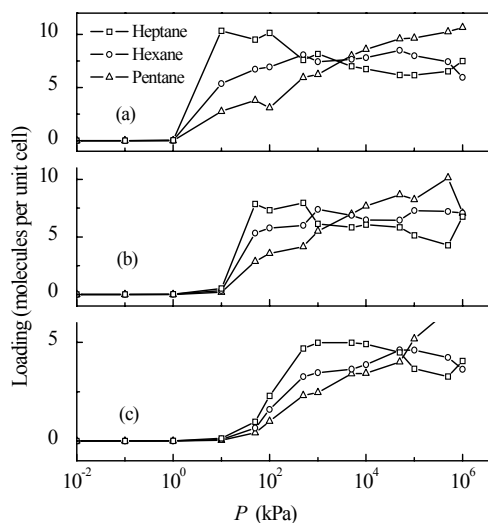
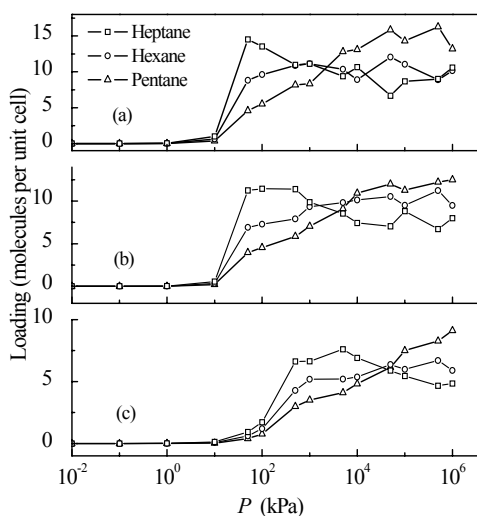


Fig.2 Adsorption isotherms of *n*-pentane-*n*-heptane-*n*-hexane mixtures (0.33-0.33-0.33) in PLMs with the pore width  $H=1.02$  nm and different porosities at 300 K. (a)  $\Psi=0.98$ ; (b)  $\Psi=0.93$ ; (c)  $\Psi=0.85$



**Fig.3** Adsorption isotherms of *n*-pentane-*n*-heptane-*n*-hexane mixtures (0.33-0.33-0.33) in PLMs with the pore width  $H=1.7$  nm and different porosities at 300 K. (a)  $\Psi=0.98$ ; (b)  $\Psi=0.93$ ; (c)  $\Psi=0.85$

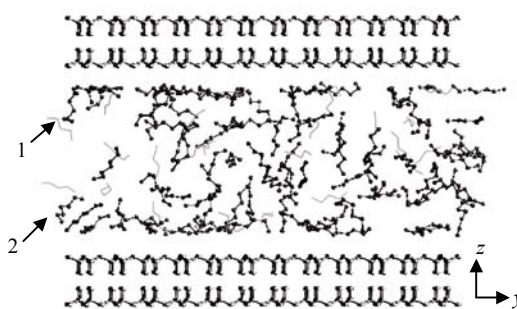


**Fig.4** Adsorption isotherms of *n*-pentane-*n*-heptane-*n*-hexane mixtures (0.33-0.33-0.33) in PLMs with the pore width  $H=2.38$  nm and different porosities at 300 K. (a)  $\Psi=0.98$ ; (b)  $\Psi=0.93$ ; (c)  $\Psi=0.85$

*n*-heptane has the highest adsorption affinity to the PLMs, resulting in selectivity for *n*-heptane over *n*-hexane and *n*-pentane while at high pressures, the layered pillared pore is almost completely filled and the entropy effect becomes more important, resulting in that the longer chain alkanes are squeezed out by the shorter chain alkanes (Talbot, 1997).

Moreover, the adsorption of alkane mixtures is also affected greatly by the pore widths and the po-

rosities of PLMs. From the simulation results, we can obtain two trends for the adsorption of alkane mixtures as follows: first, the adsorption amount of the longest chain component increases as the pore width increases, for example, the number ( $\theta$ ) of *n*-heptane molecules adsorbed in a unit cell of PLMs with the porosity of 0.98 at 100 kPa is in the order of pore widths: 2.38 nm ( $\theta=14.52$ )>1.70 nm ( $\theta=10.14$ )>1.02 nm ( $\theta=5.54$ ); second, the adsorption amount of the longest chain component increases as the porosity increases, for example, the number of *n*-heptane molecules adsorbed in a unit cell of PLMs with the pore width of 2.38 nm at 100 kPa is in the order of porosities: 0.98 ( $\theta=14.52$ )>0.93 ( $\theta=11.44$ )>0.85 ( $\theta=7.61$ ). One of the possible reasons is that there is much space to store more fluid molecules in pillared layered pores with large porosity and pore width. A snapshot of *n*-pentane and *n*-heptane of the *n*-pentane-*n*-hexane-*n*-heptane (0.33 mol fraction for each component in the gas component) in PLMs with the pore width of 2.38 nm and the porosity of 0.98 at 100 kPa and 300 K is presented in Fig.5. From the figure, it can be observed that the fluid molecules aggregate around two layered walls of PLMs, and that alkane molecules exhibit their different configurations and orientations between two layered walls of PLMs; the number of *n*-heptane is much more than that of *n*-pentane in PLMs, which coincides with the adsorption isotherms of alkane mixtures in PLMs as shown in Fig.4.



**Fig.5** A snapshot of *n*-pentane denoted by 1 and *n*-hexane denoted by 2 of *n*-pentane-*n*-heptane-*n*-hexane mixtures (0.33-0.33-0.33) in PLMs with the pore width  $H=2.38$  nm and the porosity  $\Psi=0.98$  at 100 kPa and 300 K from  $x$ -axis

In conclusion, the *n*-heptane in alkane mixtures is preferentially adsorbed at low pressures; however at high pressures, the adsorption of *n*-heptane of

mixtures in PLMs decreases while the adsorption of the *n*-pentane in alkane mixtures is more than that of *n*-heptane and *n*-hexane. The adsorption of the longest chain component of alkane mixtures increases as the pore width and the porosity of PLMs increase.

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