Computational Study on Purification of CO₂ from Natural Gas by C₆₀ Intercalated Graphite

Xuan Peng,*† Dapeng Cao,‡ and Wenchuan Wang‡

College of Information Science and Technology, Beijing University of Chemical Technology, Beijing 100029, Guangzhou Center for Gas Hydrate Research, Chinese Academy of Sciences, Guangzhou 510640, P. R. China, and Division of Molecular and Materials Simulation, Key Lab of Nanomaterials, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, P. R. China

By combining grand canonical Monte Carlo (GCMC) simulations with adsorption theory, we perform a computational study on adsorption of CH₄ and CO₂ gases and purification of CO₂ from the CH₄–CO₂ and N₂–CO₂ binary mixtures by the C₆₀ intercalated graphite. The adsorption isotherms, isosteric heats and snapshots of pure gases have been examined extensively. It is found that the maximum excess uptakes at 298 K are relatively low, only giving 4.04 and 4.96 mmol/g for CH₄ and CO₂, respectively, due to a low porosity of 0.45 and a large crystal density of 1.57 g/cm³ of this material. It indicates that the pristine material is not suitable for gas storage. However, this material provides excellent selectivity for CO₂, and the selectivity at ambient condition can reach 8 and 50 for the CH₄–CO₂ and N₂–CO₂ mixture, respectively. Furthermore, the selectivity of CO₂ is almost independent of the bulk gas composition for P > 0.1 MPa. The dual-site Langmuir–Freundlich (DSLF) equation is used to fit the adsorption isotherms of pure gases from GCMC simulations, and the corresponding parameters are obtained. Moreover, we further predicted the adsorption behavior of binary mixtures by the DSLF-based ideal adsorption solution theory (IAST). Although the IAST theory slightly overestimates the selectivity, compared to GCMC results, the uptakes and selectivity from both methods are basically consistent. To improve the adsorption capacities, we further tailor the structural parameter “g” of the C₆₀ intercalated graphite by GCMC simulations. For equimolar gas composition, at the condition of g = 1.4 nm and 6 MPa, the CO₂ uptakes could be raised by 200%, approaching 12 mmol/g for both mixtures, without loss of the selectivity for CO₂. In summary, this work demonstrates that the C₆₀ intercalated graphite is an excellent material for CO₂ purification, especially for N₂–CO₂ system at room temperature.

Introduction

Porous carbon materials are extensively applied in gas storage¹,² and separation³,⁴ for their hydrothermal and chemical stabilities. Graphite nanofibers (GNFs) that consist of parallel graphitic platelets stacked in layers forming fibers many micrometers in length, is a typical representative of porous carbons.⁵ Rodríguez and co-workers have proposed that the GNFs is a promising adsorbent for H₂ storage because the experiment shows that the material can adsorb a great deal of H₂ at room temperature.⁶,⁷ However, this viewpoint has been subsequently questioned by the grand canonical Monte Carlo (GCMC) simulation studies from Wang and Johnson.⁵,⁸ They concluded that the experimental results could not be interpreted by any reasonable physisorption model. Recent studies have shown that the interlayer distance of the GNFs is the key to determine the H₂ uptake.⁹–¹¹ In a slit pore model, the optimum pore size for the maximum storage capacity was around 0.6 nm.⁹–¹¹ At the interlayer distance of 0.335 nm, the H₂–graphene interaction is repulsive and thus no H₂ can penetrate between the graphene layers. But if the graphene sheets are intercalated by spacer molecules, the interlayer distance could be increased to meet the requirement of the optimum pore size.

C₆₀ fullerenes¹²,¹³ are suitable spacer molecules intercalated to graphite. Actually, using C₆₀ as intercalation reagent initially originated from the development of a new class of superconduc-

tors.¹⁴ In 1994, Saito et al. first designed the model of C₆₀ intercalated graphite and theoretically predicted the stability of such structures.¹⁴ Until 2004, Gupta and co-workers synthesized for the first time this carbon material by directly combining two carbon allotropes of C₆₀ and graphite.¹⁵ During the intercalation process, the van der Waals (vdW) contact between two adjacent parallel layers is broken and a two-dimensional hexagonal symmetry of C₆₀ fullerenes is formed. The transmission electron microscopy (TEM) image indicates that no covalent bonds exist between fullerenes, and between the fullerenes and the layers. Recently, using density functional theory (DFT) calculation, Kuc et al. confirmed the experimentally observed geometrical properties of the C₆₀ intercalated graphite and evaluated its capability for H₂ storage.¹⁶ Their study indicates that this material may be promising to store H₂.

Besides H₂ storage, carbon dioxide capture and storage (CCS) has become one of the most urgent topics worldwide.¹⁷ The exhausted exploitation of fossil fuels in industrial processes increases the concentration of CO₂ in the atmosphere and leads to the serious problem of global warming.¹⁸ For example, the methane steam reforming reaction, which uses CH₄ and water vapor as raw materials to produce H₂, is a major industrial source of CO₂ as a byproduct. Additionally, CH₄ and CO₂ are the primary components in natural gas, except for N₂ and heavier hydrocarbons.³ The existence of CO₂ will reduce the energy content of natural gas and corrupt the transportation and storage system.³ As a consequence, CH₄ storage and CO₂ removal are equally important to effectively utilize the energy and sequester the greenhouse gases.
To the best of our knowledge, no experimental and theoretical studies have been conducted on the adsorption storage of CH$_4$ and purification of CO$_2$ by using the C$_{60}$ intercalated graphite. In 2009, Terzyk et al. investigated the storage of these gases on intercalated graphene nanocontainers (NanoBuds) by using GCMC simulations. They found that intercalation can improve the storage, in which the fullerenes of C$_{180}$ other than C$_{60}$ were used as intercalation reagent to construct the model of material. The adsorption behavior of gases on pristine C$_{60}$ intercalated graphite is still unknown. Furthermore, the selectivity of this material for CO$_2$ is not reported yet. Accordingly, here we intend to explore the adsorption and selectivity of this material for CO$_2$ by using a computational method. This paper is organized as below. First, we describe the structural and potential models, and the detail of molecular simulation and adsorption theory. Then, we perform the studies of adsorption storage and separation of the C$_{60}$ intercalated graphite for CO$_2$. Finally, we also further tailor the structural parameters to improve the adsorption and separation properties of this material.

### Molecular Simulation

#### Structure of C$_{60}$ Intercalated Graphite

As shown in Figure 1, the hexagonal area surrounded by dotted lines constitutes a lattice. The variables $c$ and $d$ denote the lattice constant and the distance between the centers of C$_{60}$ on two adjacent planes, and their values are 1.25 and 1.27 nm, taken from experimental measurement, respectively. The variable $g$ is defined as the distance between the centers of outmost carbon layer on two adjacent C$_{60}$ fullerenes and equals to $c$ minus the diameter of C$_{60}$. In molecular simulations, the structure of the material is assumed to be rigid without geometrical variation. To create the structure of the C$_{60}$ intercalated graphite, we used one C$_{60}$ molecule and one graphite plane with a chirality of (13,0) and a length of 3.2 nm as the elements. Then, we reproduced the C$_{60}$ molecule 15 times and the graphite plane 2 times and translated them to the suitable positions in terms of the structural schematic given by Kuc et al. Finally, we cut the structure to generate a rectangular simulation unit cell. Thus, for the default structure without refinement, there are 1080 carbon atoms in the unit cell and the cell size is 2.5, 2.165, and 2.54 nm in the $x$, $y$, and $z$ dimensions, respectively.

#### Potential Models

As usual, N$_2$ and CH$_4$ molecules are regarded as a single sphere, and the classical Lennard-Jones (LJ) potential is used to calculate their interactions. As for the CO$_2$ molecule with a linear geometry and noticeable quadrupole moment, the 3-site elementary physical model (EPM2) was used, where a three-center LJ potential plus a set of partial point charges is distributed at three electrostatic sites. Thus, the fluid−fluid interaction of CO$_2$ is composed of the LJ potential and electrostatic interactions. The fluid−solid interaction is described by the site-to-site method and the cross interaction parameters are obtained by the Lorentz−Berthelot combining rules. All the size and energy parameters of fluid molecules and adsorbent were given in Table 1.

#### Simulation Details

We used the GCMC method to study the adsorption and separation of gases in the C$_{60}$ intercalated graphite. In this method, the chemical potential, box volume and temperature are fixed in the simulation. For N$_2$ and CH$_4$ molecules, the GCMC procedure includes particle translation with the usual Metropolis scheme, particle destruction, and creation to ensure the chemical potential equilibrium between bulk and pore phases, while for the CO$_2$ molecule, an additional move of particle rotation is needed. For the adsorbent structure model used here, the inner void space of C$_{60}$ intercalated graphite is not blocked and thus GCMC simulations can insert molecules directly into these voids. Although it is theoretically possible, the probability of inserting such molecules is extremely low. To avoid the conversion of chemical potential into pressure, the normal move acceptance probability can be transformed to relate the component fugacity of the bulk phase, which is calculated by the Peng−Robinson equation of state (PR EOS). The binary interaction parameters in the PR EOS are $+0.092$ and $-0.017$ for the CH$_4$−CO$_2$ and N$_2$−CO$_2$ mixture, respectively. For all the simulations, the periodic boundary conditions were imposed in three directions. The cutoff radius is set to half the box size for the LJ and electrostatic potentials. On the basis of the simulation cell dimensions of the pristine structure, the cutoff distance for LJ and electrostatic potentials is 1.0825 nm. For the LJ potential, the cutoff is usually adequate. However, for the electrostatic potential, since we did not use the Ewald sum to save computational time, justification for the cutoff needs to compare the results with that from a larger simulation cell. In our test run, we used the C$_{60}$ intercalated graphite with the doubled cell dimensions for comparison. We found that both results are basically consistent and the average deviation is no more than 3%. To accelerate the simulation, the LJ potential between a fluid molecule and adsorbent was substituted by a pretabulated energy map with a grid of 0.2 × 0.2 × 0.2 Å cubic mesh. For each state, a total number of $2 \times 10^7$ configurations were generated, where the first 40% moves

#### Table 1. Potential Parameters of N$_2$, CH$_4$, CO$_2$, and C$_{60}$ Intercalated Graphite

| species | atom | $b_l$ (nm) | $q$ (e) | $\sigma$ (nm) | $\epsilon/k_B$ (K) | ref |
|---------|------|------------|---------|---------------|-------------------|-----|
| N$_2$   |      | 0.375      | 95.2    | 2, 20         |                   |     |
| CH$_4$  | C    | 0.381      | 148.2   | 1, 21         |                   |     |
| CO$_2$  | O    | 0.2757     | 28.129  | 22, 23        |                   |     |
|         | C    | 0.3033     | 80.507  |               |                   |     |
|         | C    | 0.34       | 28.0    | 1, 2          |                   |     |

* $b_l$ is the distance from the interaction site to molecular mass center.
were discarded to guarantee the equilibrium and the others were divided into 20 blocks for the ensemble average. All the simulations here were performed using the MUSIC code.28

Definitions of Adsorption Amount, Isosteric Heat, and Selectivity. The excess adsorption amount \( N_{\text{ex}} \), which can be measured experimentally, is commonly calculated by the absolute adsorption amount \( N_{\text{ab}} \) from GCMC simulation according to the following relation

\[
N_{\text{ex}} = N_{\text{ab}} - \rho_b V_{av}
\]

where \( \rho_b \) is the bulk density obtained by PR EOS and \( V_{av} \) is the available volume to fluid molecules. Different from the other method integrating the configurational energy of the adsorbed molecule, we performed a Monte Carlo integration with the reentrant surface definition29 to calculate the \( V_{av} \), where the argon molecule with a size of 0.34 nm was used as a probe.30 The porosity is expressed by the ratio of \( V_{av} \) to the adsorbent volume. The method had been tested for the porosity of the IRMOF-1 material, and it gives excellent agreement with the value reported.31

The isosteric heat \( q_{st} \), a thermodynamic property that reflects the strength of forces between adsorbent and fluid molecules, is approximated by

\[
q_{st} = RT - \left( \frac{\partial U}{\partial N} \right)_{T,V}
\]

where \( R \) and \( T \) are the universal gas constant and temperature and \( U \) and \( N \) are the total adsorbed energy and number of fluid particles, respectively.

The adsorption selectivity of CO\(_2\) in N\(_2\)–CO\(_2\) and CH\(_4\)–CO\(_2\) binary mixtures is defined as

\[
S_{ij} = \left( \frac{x_i}{y_i} \right) \left( \frac{y_j}{x_j} \right)
\]

where subscript \( i \) denotes CO\(_2\), subscript \( j \) denotes the species N\(_2\) or CH\(_4\), and \( x \) and \( y \) denote the molar fractions of species in adsorbed and bulk phases, respectively.

Adsorption Theory

Fitting of Pure Adsorption Isotherms from GCMC Simulations. As is well-known, no experimental data are available for adsorption of the pure and binary mixtures of the N\(_2\)–CH\(_4\)–CO\(_2\) system in the C\(_{60}\) intercalated graphite. To examine the results from molecular simulation, the dual-site Langmuir–Freundlich (DSLF) adsorption model is adopted.31 Therefore, the pure-component equilibrium data were used to correlate theoretical models, and to further predict the adsorption of mixtures, aiming at the comparison with those from molecular simulation. The DSLF model is given by

\[
N^o(f) = \frac{N_i k_i f^{n_i}}{1 + k_i f^{n_i}} + \frac{N_j k_j f^{n_j}}{1 + k_j f^{n_j}}
\]

where \( f \) is the fugacity of the bulk gas at equilibrium with the adsorbed phase and in the units of MPa here and \( N_i, k_i, \) and \( n_i \) are model parameters of maximum adsorption amount at site \( i \) \((i = 1 \) or \( 2))\), the affinity constant, and the deviation from the simple Langmuir equation, respectively.

Prediction of Binary Mixture Adsorption by IAST Theory. On the basis of the available model parameters of pure gas adsorption, we used the ideal adsorption solution theory (IAST),32 which proposed by Myer and Prausnitz in 1965, to predict the multicomponent adsorption. Analogous to Raoult’s law for vapor–liquid equilibrium, the IAST assumes that the adsorbed solutions are ideal and all activity coefficients in the adsorbed phase are unity. Thus, the adsorption equilibrium between adsorbed and gas phases will lead to the following equation

\[
P_y \phi_i = x_i f_i^o (\pi)
\]

where \( f_i^o \) is the fugacity of the equilibrium gas phase corresponding to the spreading pressure \( \pi \) for the adsorption of pure gas \( i, \phi_i \) is the gas fugacity coefficient of component \( i \) calculated by PR EOS, and \( x_i \) and \( y_i \) are the molar fraction of component \( i \) at adsorbed and bulk phases, respectively. The binary gas mixing process is carried out at constant spreading pressure \( \pi \) and indicated by

\[
\int_0^{f_1^o} N_i^o f_i d \ln f_i = \int_0^{f_2^o} N_j^o f_j d \ln f_j
\]

where the single-component adsorption amount and selectivity are further obtained from the above equation by numerical integration and root exploration.

Results and Discussion

Adsorption for Pure N\(_2\), CH\(_4\), and CO\(_2\) on C\(_{60}\) InterCalated Graphite. Figure 2 shows the absolute adsorption isotherms of pure gases in the C\(_{60}\) intercalated graphite at 298 K. The filled symbols are GCMC simulation results, and the lines are fits of the dual-site Langmuir–Freundlich equation to GCMC simulation results.
to accommodate any fluid molecule. As a result, the adsorption only occurs in the space between the two adjacent C60 fullerenes. At the distance \( g \) of 0.55 nm, the fluid molecules are adsorbed in a single layer by confinement and form a ringlike structure where two rings are interconnected side by side (top view). Even at this low porosity, the pore volume is not filled completely by adsorbed molecules (side view). On the other hand, the crystal density of the C60 intercalated graphite is estimated to be 1.57 g/cm\(^3\), about 2.65 times that of IRMOF-1 adsorbent.\(^{31}\) Since the gravimetric loading is inversely proportional with the bulk density of material, the large crystal density would lead to the decrease of the adsorption.

The excess adsorption isotherms of pure gases are plotted in Figure 4. Due to the far-away supercritical state at 298 K, we do not find the maximum on the N\(_2\) adsorption isotherm. Instead, a maximum of excess uptake is noticeably observed at 3.5 and 2 MPa for CH\(_4\) and CO\(_2\), respectively. In addition, both the gravimetric and volumetric uptakes are relatively low at the whole pressure range, less than 4.035 mmol/g and 141.6 v/v for CH\(_4\), and 4.959 mmol/g and 174.04 v/v for CO\(_2\). In particular, the volumetric adsorption of CH\(_4\) is lower than the DOE target of 180 v/v at 3.5 MPa and 298 K that proposed by the U.S. Department of Energy.\(^{34}\) It reveals that the C60 intercalated graphite with the pristine structure cannot meet the requirement of gas storage at ambient temperature.

The adsorption isotherm at low pressures usually reflects essential characteristic of material. Thus, we calculate the Henry constant of each species by using the adsorption data at 0.001 MPa. They are 0.019, 0.135, and 0.939 mmol/kPa for N\(_2\), CH\(_4\), and CO\(_2\), respectively, in which CO\(_2\) shows the greatest value of about 49 times of N\(_2\) and 7 times of CH\(_4\). It indicates that the CO\(_2\) molecule has a stronger fluid–pore interaction than other species. For a further explanation, we present in Figure 5 the isosteric heat \( q_u \) as a function of absolute adsorption amount. We can see that the \( q_u \) first gradually increases with the uptake to a faint maximum for N\(_2\) (22.58 kJ/mol) and CH\(_4\) (28.44 kJ/mol) at about 0.5 mmol/g, and finally falls down slightly. As to CO\(_2\), the \( q_u \) drops from 39.06 kJ/mol all along until 4.5 mmol/g, and then fluctuates with the uptake owing to the near-condensation state of bulk phase. Moreover, the varied range of \( q_u \) approaches that of the C\(_{168}\) material for CH\(_4\) and CO\(_2\) but is significantly greater than IRMOF-1 adsorbent.\(^{28}\) Similarly, the \( q_u \) presents an increase with the same species order as found in Figure 2 for the adsorption isotherms. This phenomenon also confirms the above conclusion from the Henry constant; i.e., the CO\(_2\) molecule is preferentially adsorbed.

**Purification of CO\(_2\) from N\(_2\)–CO\(_2\) and CH\(_4\)–CO\(_2\) Binary Mixture on C\(_{60}\) Intercalated Graphite.** As discussed above, the gas storage performance of the C\(_{60}\) intercalated graphite is not satisfactory. However, by comparison with Henry’s constant, it is found that this material might be
uptake of N2 is almost close to zero for both gas compositions.

than that at high pressures the IAST will produce a big deviation from experiment due to the fluid nonideality. To examine this point, we test the approach by using the experimental data reported on activated carbon. From Figure 6, we can see that even at a high pressure up to 13 MPa, both the fitting and the IAST prediction are in excellent agreement with experiment. It demonstrates that if a suitable adsorption model is adopted for pure gases, the IAST approach used here is still effective for the prediction of binary mixtures.

Figure 2 shows the fitting of the DSLF equation to GCMC simulation results for the C60 intercalated graphite. To further explore the fitting effect, the average relative deviation (ARD) from GCMC simulation is given in Table 2, in which CO2 gives the best fitting with the smallest ARD of 0.75%, CH4 with ARD of 2.5%, and N2 with ARD of 3.35%. On the whole, the fitting is quite good in view of the large number (31) of data points evaluated. Using the regressed model parameters in Table 2, we investigate the separation performance of CO2 in the C60 intercalated graphite by IAST prediction. In general, an equimolar composition is a good choice for a binary mixture. A mole fraction of yCO2 = 0.2 is also specified for the CH4–CO2 and N2–CO2 mixtures, because the former represents a rich CH4 natural gas, while the latter represents the postcombustion mixtures. Figure 7 shows the comparison of the single-component adsorption isotherms between the IAST prediction and GCMC simulation. It is found that all the GCMC simulation data are very consistent with the IAST prediction curves. For both mixtures, the uptake of CO2 at yCO2 = 0.5 is always higher than that at yCO2 = 0.2, indicating that C60 intercalated graphite prefers the CO2 in a rich CO2 gas mixtures. Interestingly, the uptake of N2 is almost close to zero for both gas compositions. Clearly, this material exhibits an excellent selectivity of CO2 for the N2–CO2 mixture.

Figure 8 shows the adsorption selectivity of CO2 in the C60 intercalated graphite at 298 K, in which the IAST predictions overestimate the selectivity slightly, compared to the GCMC simulation results. This phenomenon can be explained by the ARD of fractional uptakes between both methods (see Table 3). The ARD of CO2 is distinctly lower than other species, varying in the range 1.5–5%. In contrast, N2 and CH4 process much larger ARD of about 20% and 8%, respectively. In a competitive adsorption with CO2, these two gases, especially N2, are rarely adsorbed in the C60 intercalated graphite. As a consequence, a slight change of their uptake would result in a remarkable fluctuation of selectivity. This point has also been verified in Figure 8 by a visible deviation of selectivity between both methods. More interestingly, a maximum on the IAST prediction curve of yCO2 = 0.2 appears, whereas no maximum is found for the GCMC simulations. Although the reason for this difference is unknown, the variation trend of selectivity curves from both methods is totally coincident and the agreement is acceptable. For the CH4–CO2 mixture, the selectivity of CO2 goes down from about 14 to 8 and then begins leveling off at 100 kPa. The N2–CO2 mixture shows a similar trend but the selectivity drops from 120 to 50. In addition, the bulk composition has no pronounced effect on selectivity. At P < 0.1 MPa, the C60 intercalated graphite is favorable for separation of CO2 from a rich CO2 mixture (yCO2 = 0.5), but this favorite gradually becomes negligible when P > 0.2 MPa. Figure 9 presents the snapshots of a binary mixture at equimolar...
composition. For the N_2-CO_2 mixture, the material is fully filled with CO_2 molecules at three pressure points. Likewise, there are only several CH_4 molecules observed for the CH_4-CO_2 mixture at 0.1 and 6 MPa. For comparison, the theoretical studies on other model carbon materials, such as slit pores,^{35} carbon nanotubes,^{36} and C_{60} schwarzite^{37} are discussed here. For slit pores, at y_{CO_2} = 0.5, 318 K and 10 MPa, the selectivity of CO_2 over CH_4 is about 5.6 at the reduced pore width of H^*= 3 (1.13 nm),^{35} while it is 11.1 for nanotubes with a pore diameter of 1.356 nm at 303 K and 1 MPa and 5.4 for C_{60} schwarzite at 298 K and 0.1 MPa, respectively. It is clear that the C_{60} intercalated graphite shows a superior performance than C_{60} schwarzite and slit pores and nearly approaches nanotubes. As to the N_2-CO_2 mixture, Jiang and Sandler^{37} illustrated that in the C_{60} intercalated graphite, the ab initio potential-based GCMC simulation result of selectivity of CO_2 over N_2 at y_{CO_2} = 0.21 and 300 K is significantly larger than the Steele potential-based one.^{38,39} At 0.1 MPa, the Steele potential-based selectivity of CO_2 over N_2 is about 20, only being one-third of the C_{60} intercalated graphite at the similar condition. Although their result with the ab initio potential can be increased to 100 for the C_{60} schwarzite, the identical ascending behavior should be expected in the C_{60} intercalated graphite if an ab initio potential is used by accounting for the effects of the surface curvature on the C_{60} fullerenes. In summary, we propose that the C_{60} intercalated graphite is an excellent candidate for CO_2 purification at normal temperature and pressure, especially for the N_2-CO_2 system.

Structural Refinement of C_{60} Intercalated Graphite for Storage of Pure CH_4 and CO_2, as Well as Purification of CO_2. On the basis of the above information, we conclude that the primary obstacle to the applications of the C_{60} intercalated graphite into gas storage and purification is the low adsorption capacity with the pristine structure. Therefore, in this section, we discuss the structural refinement of this material for improving uptakes and selectivity of gases. In the structure of the C_{60} intercalated graphite, two geometrical parameters are concerned, i.e., the interlayer distance d and the term of vDW gap g. The interlayer distance d is unchanged, because the C_{60} and the two graphite layers should remain the stable contact. As pointed out by Kuc et al., a further tuning by reducing the amount of intercalated fullerene cages is necessary to enhance H_2 loadings, which are interesting for technical applications.^{16} It seems that a rational increase of g can achieve this aim. Recently, with the first-principles method, Wu and Zeng have designed a novel type material of periodic graphene nanobuds

Table 3. Average Relative Deviation of Single-Component Adsorption Amounts between IAST Prediction and GCMC Simulations

| y_{CO_2} | CH_4 | CO_2 | N_2 | CO_2 |
|----------|------|------|-----|------|
| 0.5      | 8.358| 1.957| 19.76| 1.756|
| 0.2      | 7.485| 3.632| 20.53| 4.880|

ARDS is the average relative deviation of IAST predictions from GCMC simulations, and 27 data points were evaluated for each isotherm.

Figure 7. Absolute adsorption isotherms of binary mixtures in C_{60} intercalated graphite at 298 K: (a) CH_4-CO_2 mixture; (b) N_2-CO_2 mixture. The filled symbols are GCMC simulation results, and the lines are IAST predictions.

Figure 8. Adsorption selectivity of CO_2 in C_{60} intercalated graphite at 298 K: (a) CH_4-CO_2 mixture; (b) N_2-CO_2 mixture. The filled symbols are GCMC simulation results, and the lines are IAST predictions.
(PGNB) and found that the C60 fullerenes are covalently bonded to a graphene monolayer. Their study provides a possibility that the distance between the C60 fullerenes may be controllable in synthesis or modification of the material. Consequently, we only explore the effect of parameter $g$ on gas storage and purification.

Figures 10 and 11 show the excess adsorption isotherms of pure CH$_4$ and CO$_2$ at different $g$. All the isotherms reach their saturation states at the pressure range studied. Furthermore, if the parameter $g$ is increased from 0.55 to 1.4 nm, the maximum uptake of CH$_4$ could be enhanced to 8.02 mmol/g and 209.27 v/v at 4.5 MPa, showing a rise of 98.8% for gravimetric and 47.79% for volumetric adsorption, respectively. In contrast, $g$ has a more apparent influence on CO$_2$ storage. It corresponds to 11.50 mmol/g and 299.93 v/v at 3 MPa, raised by 122.85% and 72.33%, respectively. Actually, the improvement is mainly caused by the adjustment of material structure. As shown in Figure 12, the porosity increases monotonously with $g$, while...
the crystal density alters oppositely. A large porosity is beneficial to both gravimetric and volumetric uptakes, because more fluid molecules can be adsorbed. Similarly, the decrease of crystal density would directly induce an ascending of the gravimetric adsorption.

Figure 13 shows the dependence of adsorption selectivity of CO$_2$ on $g$ at equimolar composition and different pressures. With the increase of $g$, the CO$_2$ selectivity in the N$_2$–CO$_2$ mixture decreases slowly and the downtrend becomes quick at 0.001 MPa, while it is hardly affected by the $g$ in the CH$_4$–CO$_2$ mixture. Furthermore, the selectivity curves at $P \geq 0.1$ MPa get close each other at the whole range of $g$, indicating that pressure has no pronounced effect on selectivity under atmospheric conditions. The CO$_2$ selectivity can be at least 8 and 30 for the CH$_4$–CO$_2$ and N$_2$–CO$_2$ mixtures, respectively. In this situation, the adjacent parallel graphite layers play a more important role than C$_{60}$ fullerenes to separate the gas mixture, because the selectivity shows a poor correlation with $g$. However, it is worth enlarging the $g$ and elevating the pressure due to the fact that the CO$_2$ storage capacity is enhanced accordingly. From Figure 14, we see that for both mixtures, only the CO$_2$ uptakes at 0.001 MPa decline slightly with the increase of $g$. At $P \geq 0.1$ MPa, all the curves increase monotonously, where the higher the pressure, the greater the uptakes and the faster the rising trend. In particular, at 6 MPa, the uptakes of CO$_2$ can increase to 12 mmol/g at $g = 1.4$ nm, giving a 200% increment for both mixtures. In conclusion, the condition of $g = 1.4$ nm and 6 MPa is recommended for CO$_2$ purification.

Conclusions

Gas storage and purification in the N$_2$–CH$_4$–CO$_2$ system by the C$_{60}$ intercalated graphite were studied for the first time by using GCMC simulations and adsorption theory. In the GCMC simulation, the C$_{60}$ intercalated graphite was constructed by tailoring 3 parallel carbon graphite layers and 16 hexagonally arranged C$_{60}$ fullerenes into a rectangular box. The classical LJ potential was used to calculate the interactions among N$_2$, CH$_4$, and adsorbent, and the 3-site EPM2 model was adopted for CO$_2$ molecule.

By analyzing the adsorption isotherms, isosteric heats, and snapshots of pure gases, we found that the pristine material is not suitable for gas storage. This is because the material has a
low porosity of 0.45 and a large crystal density of 1.57 g/cm³. Accordingly, the maximum excess uptake only give 4.04 mmol/g for CH₄ and 4.96 mmol/g for CO₂ at room temperature. However, the Henry constant of CO₂ (0.939 mmol/kPa) shows a great advantage over other species, implying the possibility of separating CO₂ from the gas mixture with the material.

The adsorption separation was further explored for the CH₄–CO₂ and N₂–CO₂ binary systems. The DSLF equation was fitted to the GCMM simulation of pure adsorption isotherms, and they are in good agreement. With the available model parameters, the fractional uptake and selectivity were predicted by IAST and compared with the GCMM simulation. Although the IAST predicts the selectivity slightly higher than the GCMM method, their trend of the selectivity curves is basically consistent. In addition, at P > 0.2 MPa, the selectivity is not influenced by the bulk composition, while at P < 0.1 MPa, separating CO₂ via the C₆₀ intercalated graphite is effective for a rich CO₂ mixture. With the increase of pressure, the selectivity of CO₂ declines gradually and stabilizes at 8 for CH₄–CO₂ and 50 for the N₂–CO₂ mixture, respectively. It suggests that the C₆₀ intercalated graphite is a promising adsorbent for CO₂ purification.

To improve gas adsorption and separation, we finally tailor the structural parameter g of the C₆₀ intercalated graphite. At g = 1.4 nm, the gravimetric uptake exhibits a rise of 98.8% and 122.85% for pure CH₄ and CO₂ adsorption, respectively. While for volumetric adsorption, it corresponds to an improvement of 47.79% and 72.33%, respectively. The improvement is mainly attributed to the decreased crystal density and the increased porosity produced by an enlargement of g. Interestingly, at P ≥ 0.1 MPa, the adsorption selectivity of CO₂ is basically not influenced by the increase of g for the CH₄–CO₂ mixture, while it only slightly declines for the N₂–CO₂ mixture. It indicates that the parallel graphite layers play a more important role than C₆₀ fullerenes in gas separation. However, it is necessary to enlarge the g, because the fractional CO₂ uptake is enhanced accordingly. At the condition of g = 1.4 nm and P = 6 MPa, the CO₂ adsorption can reach 12 mmol/g, giving a 200% increment for both mixtures.

In conclusion, this work suggests that the C₆₀ intercalated graphite could be a suitable material for CO₂ purification, especially for the N₂–CO₂ system at room temperature. It is expected that our simulations will be verified experimentally in the future.

Acknowledgment

This work is supported by the NSF of China (Nos. 2086003, 20736002), the Young Scholars Fund of BUCT, the Guangzhou Center for Gas Hydrate Research, Chinese Academy of Sciences (No. CASHYD09073s), National Science and Research Foundation (ZD0901), Huo Yingdong Fundamental Research Foundation (No. 121070), and Chemical Grid Project of BUCT.

Literature Cited

(1) Peng, X.; Cao, D. P.; Wang, W. C. Heterogeneity characterization of ordered mesoporous carbon adsorbent CMK-1 for methane and hydrogen storage: GCMM simulation and comparison with experiment. J. Phys. Chem. C 2008, 112 (33), 13024–13036.
(2) Peng, X.; Cao, D. P.; Wang, W. C. Computational characterization of hexagonally ordered carbon nanoropes CMK-5 and structural optimization for H₂ storage. Langmuir 2009, 25 (18), 10863–10872.
(3) Peng, X.; Wang, W. C.; Xue, R. S.; Shen, Z. M. Adsorption separation of CH₄/CO₂ on mesocarbon microbeads: experiment and modeling. AIChE J. 2006, 52 (3), 994–1003.
(4) Peng, X.; Cao, D. P.; Zhao, J. S. Grand canonical Monte Carlo simulation of methane-carbon dioxide mixtures on ordered mesoporous carbon CMK-1. Sep. Purif. Technol. 2009, 68 (1), 50–60.
(5) Wang, Q. Y.; Johnson, J. K. Computer simulations of hydrogen adsorption on graphite nanotubers. J. Phys. Chem. B 1999, 103 (2), 277–281.
(6) Chambers, A.; Park, C.; Baker, R.; Rodriguez, N. Hydrogen storage in graphite nanotubers. J. Phys. Chem. B 1998, 102 (22), 4253–4256.
(7) Park, C.; Anderson, P.; Chambers, A.; Tan, C.; Hidalgo, R.; Rodriguez, N. Further studies of hydrogen with graphite nanotubes. J. Phys. Chem. B 1999, 103 (48), 10572–10581.
(8) Wang, Q. Y.; Johnson, J. K. Molecular simulation of hydrogen adsorption in single-walled carbon nanotubes and idealized carbon slit pores. J. Chem. Phys. 1999, 110 (1), 577–586.
(9) Patchkovskii, S.; Tse, J. S.; Yurchenko, S. N.; Zhechkov, L.; Heine, T.; Seifert, G. Graphene nanostructures as tunable storage media for molecular hydrogen. Proc. Natl. Acad. Sci. USA 2005, 102 (30), 10439–10444.
(10) Aga, R. S.; Fu, C. L.; Krčmár, M.; Morris, J. R. Theoretical investigation of the effect of graphite layer spacing on hydrogen adsorption. Phys. Rev. B 2007, 76 (16), 165040–165041.
(11) Kowalczyk, P.; Tanaka, H.; Holyst, R.; Kaneko, K.; Ohmori, T.; Miyamoto, J. Storage of hydrogen at 303 K in graphite slitlike pores from grand canonical Monte Carlo simulation. J. Phys. Chem. B 2005, 109 (36), 17174–17183.
(12) Kroto, H. W.; Heath, J. R.; O’Brian, S. C.; Curl, R. F.; Smalley, R. E. C₆₀: buckminsterfullerene. Nature 1985, 318, 162–163.
(13) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. Solid C₆₀: a new form of carbon. Nature 1990, 347, 354–358.
(14) Saito, S.; Oshiyama, A. Design of C₆₀-graphite cointercalation compounds. Phys. Rev. B 1994, 49 (24), 17413–17419.
(15) Gupta, V.; Scharaffa, P.; Rischa, K.; Romanus, H.; Müller, R. Synthesis of C₆₀ intercalated graphite. Solid State Commun. 2004, 131 (3–4), 153–155.
(16) Kuc, A.; Zhechkov, L.; Patchkovskii, S.; Seifert, G.; Heine, T. Hydrogen sieving and storage in fullerene intercalated graphite. Nano Lett. 2007, 7 (1), 1–5.
(17) Benson, S. M.; Orr, J. Carbon dioxide capture and storage. MRS Bull. 2008, 33, 303–305.
(18) Olajire, A. A. CO₂ capture and separation technologies for end-of-pipe applications - A review. Energy 2010, 35 (6), 2610–2620.
(19) Terzyk, A. P.; Furmaniak, S.; Gauden, P. A.; Kowalczyk, P. Fullerenes-intercalated graphene nanocontainers – mechanism of argon adsorption and high-pressure CH₄ and CO₂ storage capacities. Adv. Sci. Tech. 2009, 27 (3), 281–296.
(20) Pikunic, J.; Cinnar, C.; Cohaut, N.; Gubbins, K. E.; Guet, J.; Pellenn, R.; Rannou, I.; Rouzaud, J. Structural modeling of porous carbons: constrained reverse Monte Carlo method. Langmuir 2003, 19 (20), 8565–8582.
(21) Ohkubo, T.; Miyawaki, J.; Kaneko, K.; Ryuoo, R.; Seaton, N. A. Adsorption properties of templated mesoporous carbon (CMK-1) for nitrogen and supercritical methanes--experiment and GCMM simulation. J. Phys. Chem. B 2002, 106 (25), 6523–6528.
(22) Harris, J. G.; Yang, K. H. Carbon dioxide liquid-vapor coexistence curve and critical properties as predicted by a simple molecular model. J. Phys. Chem. 1995, 99 (31), 12021–12024.
(23) Peng, X.; Zhao, J. S.; Cao, D. P. Adsorption of carbon dioxide and CO₂ on pure-carbon 1-site and 3-site models in pillared clays: a Gibbs ensemble Monte Carlo simulation. J. Colloid Interface Sci. 2007, 310 (2), 391–401.
(24) Frenkel, D.; Smit, B. Understanding molecular simulations: Academic Press: New York, 2002.
(25) Allen, M. P.; Tildesley, D. J. Computer simulation of liquids; Clarendon Press: Oxford, 1987.
(26) Peng, D. Y.; Robinson, D. B. A new two-constant equation of state. Ind. Eng. Chem. Fundam. 1976, 15 (1), 59–64.
(27) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. The properties of gases and liquids; McGraw-Hill Press: New York, 1987.
(28) Gupta, A.; Chempath, S.; Sanborn, M. J.; Clark, L. A.; Surr, R. Q. Object-Oriented Programming Paradigms for Molecular Modeling. Mol. Simul. 2003, 29 (1), 29–46.
(29) Thomson, K. G.; Gubbins, K. E. Modeling structural morphology of microporous carbons by reverse Monte Carlo. Langmuir 2000, 16 (13), 5761–73.
(30) Garberoglio, G. Computer simulation of the adsorption of light gases in covalent organic frameworks. Langmuir 2007, 23 (24), 12154–12158.
(31) Babarao, R.; Hu, Z. Q.; Jiang, J. W.; Chempath, S.; Sandler, S. I. Storage and separation of CO₂ and CH₄ in silicate, C₆₀ intercalates, and...
IRMOF-1: A comparative study from Monte Carlo simulation. *Langmuir* 2007, 23 (2), 659–666.

(32) Myers, A. L.; Prausnitz, J. M. Thermodynamics of mixed-gas adsorption. *AIChE J.* 1965, 11 (1), 121–127.

(33) Sudibandriyo, M.; Pan, Z. J.; Fitzgerald, J. E.; Robinson, R. L., Jr.; Gasem, K. A. M. Adsorption of methane, nitrogen, carbon dioxide, and their binary mixtures on dry activated carbon at 318.2 K and pressures up to 13.6 MPa. *Langmuir* 2003, 19 (13), 5323–5331.

(34) Ma, S.; Sun, D.; Simmons, J. M.; Collier, C. D.; Yuan, D.; Zhou, H. C. Metal-organic framework from an anthracene derivative containing nanoscopic cages exhibiting high methane uptake. *J. Am. Chem. Soc.* 2008, 130 (3), 1012–1016.

(35) Kurniawan, Y.; Bhatia, S. K.; Rudolph, V. Simulation of binary mixture adsorption of methane and CO$_2$ at supercritical conditions in carbons. *AIChE J.* 2006, 52 (3), 957–967.

(36) Huang, L. L.; Zhang, L. Z.; Shao, Q.; Lu, L. H.; Lu, X. H.; Jiang, S. Y.; Shen, W. F. Simulations of binary mixture adsorption of carbon dioxide and methane in carbon nanotubes: temperature, pressure, and pore size effects. *J. Phys. Chem. C* 2007, 111 (32), 11912–11920.

(37) Jiang, J. W.; Sandler, S. I. Separation of CO$_2$ and N$_2$ by adsorption in C$_{60}$ swarzite: a combination of quantum mechanics and molecular simulation study. *J. Am. Chem. Soc.* 2005, 127 (34), 11989–11997.

(38) Bojan, M. J.; Steele, W. A. Virial coefficients for N$_2$ and CO adsorbed on the graphite basal plane. *Langmuir* 1987, 3 (1), 116–120.

(39) Bojan, M. J.; Steele, W. A. Interactions of diatomic molecules with graphite. *Langmuir* 1987, 3 (6), 1123–1127.

(40) Wu, X. J.; Zeng, X. C. Periodic graphene nanobuds. *Nano Lett.* 2009, 9 (1), 250–256.

Received for review May 7, 2010
Revised manuscript received July 25, 2010
Accepted July 26, 2010

IE1010433