Modeling New Adsorbents for Ethylene/Ethane Separations by Adsorption via π-Complexation

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The adsorption of olefins and paraffins in new porous is studied by means of molecular simulations. The new adsorbents are synthesized be effective dispersion of CuCl on substrates with hydrocarbon-phobic surfaces, such as γ-Al_2O_3. The Cu(I) cations are able to form π-complexation with olefin molecules. The ethane and ethylene molecules are modeled as two Lennard-Jones sites. Ethylene molecules have two additional associating square-well sites placed in the line perpendicular to the symmetry axis of the molecules in order to reproduce the π-complexation. The γ-Al_2O_3 surface is modeled as a single cylindrical pore showing the (100)-face of a cubic close-packing stacking of oxygen layers. Only the interactions with oxygen ions are explicitly taken into account, modeled as Lennard-Jones sites. Specific associating square-well sites are placed protruding from the γ-Al_2O_3 surface, having identical size and energy parameters to those used on the ethylene molecules, in order to mimic Cu(I) cations. We present Grand Canonical Monte Carlo simulation results for single-component adsorption isotherms for ethane and ethylene on bare γ-Al_2O_3 and CuCl/γ-Al_2O_3. Adsorption on bare γ-Al_2O_3 is very similar for both molecules, with no selectivity for ethylene. Preferential adsorption of ethylene is seen on CuCl/γ-Al_2O_3, whereas ethane adsorption is decreased, probably due to the presence of CuCl molecules. The olefin capacity, using CuCl/γ-Al_2O_3 as sorbent, is much higher that for other materials. The agreement between simulation results and experiments is excellent.

Introduction

Olefin/paraffin separations are one of the most important and costly class of separations in the chemical and petrochemical industry [1,2]. Their separation is of great economic consequence, since some of the separated olefins, such as ethylene and propylene, have many uses, one of the most important being as monomer feedstock for polyethylene and polypropylene elastomer production. The conventional method for separating olefin/paraffin mixtures is fractional distillation, which is very energy intensive

due to the small difference in their relative volatilities, specially if a high-purity product is desired.

One of the most alternative promising processes is the use of the selective adsorption on a molecular sieve in the gas phase. Adsorption is a very selective separation process and is generally used to remove a small quantity of an adsorbate from a fluid stream. A number of adsorbents have been investigated; the most promising one appears to be the π-complexation [2-5]. Separation by π-complexation is a sub-group of chemical complexation where the mixture is put in contact with a second phase containing a complexing agent. The advantage of chemical complexation is that the bonds formed are stronger than those formed by van der Waals forces alone, but weak enough to be broken using simple engineering operations. Thus, it is possible to get a high selectivity and capacity for component separation [2-5].

Recently, Yang and Kikkinides [3] and Yang and Foldes [4] have performed spontaneous monolayer dispersion [6] of $NiCl_2.6H_2O$, CuCl, etc. on a high-surface-area γ-Al_2O_3. It is experimentally observed that a high selectivity of olefins is obtained when the surface is activated.

The aim of this work is to provide a simple molecular model of adsorption of ethane and ethylene on γ-Al_2O_3 and CuCl/γ-Al_2O_3. We compare the predictions of the proposed model with the experimental results from reference [3]. The systems are studied by using Grand Canonical Monte Carlo simulations, obtaining the single component adsorption isotherms of ethane and ethylene in cylindrical γ-Al_2O_3 and CuCl/γ-Al_2O_3.

Intermolecular Potentials

Fluid molecules are modeled as united atoms, i.e., CH_3 and CH_2 are considered as single interaction units. The repulsive-dispersion interactions are described by the Lennard-Jones (LJ) potential with the parameters given in [7]:

$$\varphi_{ij}^{LJ}(r) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right]$$

which is a function of the center-to-center distance between different sites in different molecules. The molecular parameters, ε_{ij} and σ_{ij}, are related to the size of the united atoms and the energy of interaction, respectively. Another parameter is the bond length l_i, the center-to-center distance between the two sites of the molecule. The bond length of the ethane molecule is 0.153 nm, and the LJ parameters are ε/k_B=104.15 K and σ=0.3775 nm. In the ethylene model, the bond length is 0.134 nm, ε/k_B=70.44 K and σ=0.385 nm.

In addition, the ethylene molecule is modeled with two SW associating sites placed in the line perpendicular to the symmetry axis of the molecule, in order to reproduce the π-complexation between the olefins and the metals on the surface:

$$\varphi_{\pi} = \begin{cases} -\varepsilon_{\pi} & \text{if } r_{AB} \le \sigma_{\pi} \\ 0 & \text{otherwise} \end{cases}$$

The SW interactions are characterized by a diameter σ_{π} and an energy well ε_{π}; r_{AB} is the site-site distance. The site diameter is σ_{π}=0.2σ_{ff}, where ff refers to fluid-fluid parameters. The strength site is calculated from the isosteric heat of adsorption at low coverage [3]. The chosen value to mimic the association is approximately 1400 K. In order to allow the association between the ethylene molecules and the surface, the placement of the site is set at 0.5σ_{ff} from the center of the mass of the ethylene molecule. This way of mimicking the activated sites over the surfaces has been successfully used in other studies involving associating chains and water in activated carbons [8-11].

Alumina surface is certainly an extremely complicated surface. Lippens [12] did extensive studies in crystallographic structures of aluminas. The oxygen ions are built up by a cubic close-packed staking of oxygen layers, showing the (100)-face in the case of γ-

Al_2O_3 [12-17]. The adsorption of ethane and ethylene on γ-Al_2O_3 is determined by the presence of oxygen ions, so we have explicitly considered only the interactions of these sites. Since alumina is a good sorbent, the planar single slit-like pore geometry is not able to take it properly into account. Instead of that, a cylindrical geometry is adopted to model the alumina, with the (100)-face exposed to the inner side of the cylinder.

Cascarini et al. [18] have carried out some experiments of adsorption on alumina, obtaining the molecular parameters of oxygen ions modeled as LJ sites. The presence of Al^{3+} ions are considered in the obtained parameters. The interaction between molecules and γ-Al_2O_3 is:

$$\varphi_{sf}^{LJ}(r) = 4\varepsilon_{sf}\left[\left(\frac{\sigma_{sf}}{r}\right)^{12} - \left(\frac{\sigma_{sf}}{r}\right)^{6}\right]$$

where we have taken $\sigma_{sf}=(\sigma_{ss}+\sigma_{ff})/2$ as the solid-fluid size, with σ_{ss}=0.303 nm. Values for ε_{sf} will be given and discussed later. The density of the oxygen ions in γ-Al_2O_3, 52 O^{2-} ions/nm^3 approximately, is taken from Cascarini et al. [18]. The layers are alternative square lattices of side 0.3 nm. The pore is modeled as a cylinder of 20 oxygen ions along the symmetry direction, consisting of 16 rolled-up oxygen ions layers separated by 0.2125 nm from each other, with a pore diameter fixed. The potential due to the wall is performed prior to the simulation to determine it at a large number of grid points in the pore. The grid is stored, and the potentials during the simulations are calculated by trilinear interpolation.

The structured pore surface of CuCl/γ-Al_2O_3 ,with a monolayer of Cu^+ ions over the surface, is modeled placing associating sites on the oxygen ions of the innermost layer of the cylinder. Associating sites are placed at a distance $0.5\sigma_{ss}$=0.1515 nm from the wall, i. e., protruding from the surface, and have identical size and energy parameters to those used for the ethylene molecules. Site density is found from the experimental spreading of CuCl over γ-Al_2O_3 [6]. The site distribution, mimicking the Cu^+ distribution, is chosen placing the association site a random way.

Molecular simulations

We are using the Grand Canonical Monte Carlo simulations (GCMC) to obtain the properties of the inhomogeneous system. In GCMC, the temperature, T, the volume of the pore, V, and the chemical potential, μ, are kept fixed [19]. The number of molecules is thus allowed to vary. The main variable of interest is μ, which has the same value for both phases, i.e., bulk phase and pore phase. The system evolves through Monte Carlo steps, each step consisting of attempts of displacement, rotation, addition or removal of a molecule. The relative probability of these Monte Carlo moves is such that 90% of moves are attempts to displace and to rotate a molecule and 10% of the moves are attempts to add or remove a molecule. At higher loading, the number of attempts to add or to remove a molecule is increased.

In the simulations, the total chemical potential is sometimes replaced by the more convenient activity, z, defined as:

$$z = \frac{\exp\left(\mu / k_B T\right)}{\Lambda^3}$$

where Λ is the De Broglie wavelength, which includes contributions from translational and rotational degrees of freedom.

Periodic boundary conditions and minimum image conventions are applied along the symmetry direction of the cylinder [19]. The Lennard-Jones potential between molecules is cut at $r_c=5\sigma_{ff}$. No long-range corrections are applied to the confined fluid due to the computational difficulties associated with it. However, care is taken so that the pore length is greater than $10\sigma_{ff}$

The relation between the absolute activity z and the bulk pressure of the fluid is found using the ideal relationship:

$$p= k_B T z$$

Adsorption isotherms of ethane and ethylene on γ-Al_2O_3

We present Grand Canonical Monte Carlo simulation results for ethane and ethylene on γ-Al_2O_3. The systems are studied under conditions of temperature T=333 K, pressure varying from 0.1 atm to 1.0 atm and diameter pore H=1.15 nm. We have chosen this size to mimic the experimental behavior at low coverages, since the actual alumina has an unknown pore size distribution. The dispersive energy parameters between molecules and oxygen ions (ε_{sf}) have been increased with respect to the values given by the Lorentz-Berthelot combining rules to describe the low pressure adsorption, using 111.79 K and 103 K for ethane and ethylene molecules, respectively.

Two single component adsorption isotherms are calculated for ethane and ethylene on bare γ-Al_2O_3, as shown in figure 2. Adsorption of ethane is stronger than that of ethylene, since the dispersive energy of the last one is larger. The agreement between simulation results and experiments is excellent in both cases. Small deviations observed for ethylene are probably due to the defects on the actual surface (presence of Al^{3+} ions on the surface, OH groups, etc.), and to the dipolar moment of the ethylene molecule. In any case, the error is lower than 5%.

Adsorption isotherms of ethane and ethylene on CuCl/γ-Al_2O_3

In this section we study the single component adsorption isotherm for ethane and ethylene on near monolayer CuCl/γ-Al_2O_3. The temperature and pressures studied are the same as in the previous section. The presence of the CuCl molecules has a double effect on the pore: it decreases the available space for the adsorbate molecules and the effective interaction between the molecules and the inner oxygen ions. This double effect is taken into account reducing the pore size (now 0.8 nm) and the dispersive energy parameters of ethane and ethylene (48.5 K and 87 K, respectively).

Two single component adsorption isotherms are calculated for ethane and ethylene on near monolayer CuCl/γ-Al_2O_3, as shown figure 3. Adsorption of ethane is decreased with respect to that on bare γ-Al_2O_3. This may be due to a screening effect of the oxygen

ions by the presence of the Cu^+ ions. On the other hand, the π-complexation bonds between ethylene molecules and Cu^+ ions increase immensely the adsorption of ethylene. The ethylene shows a great selectivity over the ethane on CuCl/γ-Al_2O_3. The agreement between simulation results and experiments is excellent in both cases, with an error less than 5%.

Conclusions

We have presented a model for the adsorption of ethane and ethylene molecules on γ-Al_2O_3 and near monolayer CuCl/γ-Al_2O_3. This model is expressed in terms of simplified intermolecular potentials and its properties are readily found by means of computer simulations. The intermolecular forces which are thought to be of main importance, repulsion, dispersion, and π-complexation bonds between ethylene molecules and Cu ions, are explicitly taken into account. The model is in quantitative agreement with experimental results, showing no selectivity of ethylene over ethane when bare γ-Al_2O_3 is used as adsorbent. If γ-Al_2O_3 is activated with near monolayer of CuCl, the adsorption of ethylene is increased immensely, due to the π-complexation bonds.

List of symbols

$\varphi_{ij}^{LJ}(r)$ = Lennard-Jones potential between segments i and j separated a distance r

$\varepsilon, \varepsilon_{ij}, \varepsilon_{ss}, \varepsilon_{sf}, \varepsilon_{ff}$ = dispersive energy (between i and j, solid-solid, solid-fluid, fluid-fluid)

$\sigma, \sigma_{ij}, \sigma_{ss}, \sigma_{sf}, \sigma_{ff}$ = segment size (between i and j, solid-solid, solid-fluid, fluid-fluid)

r = distance between molecules

k_B = Boltzmann's constant

φ_π = Square-well potential due to p-complexation

ε_π = bond energy due to p-complexation

σ_π = size of the SW sites (Cu+ ions)

r_{AB} = Distance between SW sites

$\varphi_{sf}^{LJ}(r)$ = Lennard-Jones potential between molecules and solid surface

μ = chemical potential

T = Temperature

z = Absolute activity

Λ = De Broglie wavelength

r_c = cutoff distance

Subscripts

i,j = molecules

π = π-complexation

AB = SW sites

s,f = solid, fluid

Superscripts

LJ = Lennard-Jones

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Figure captions

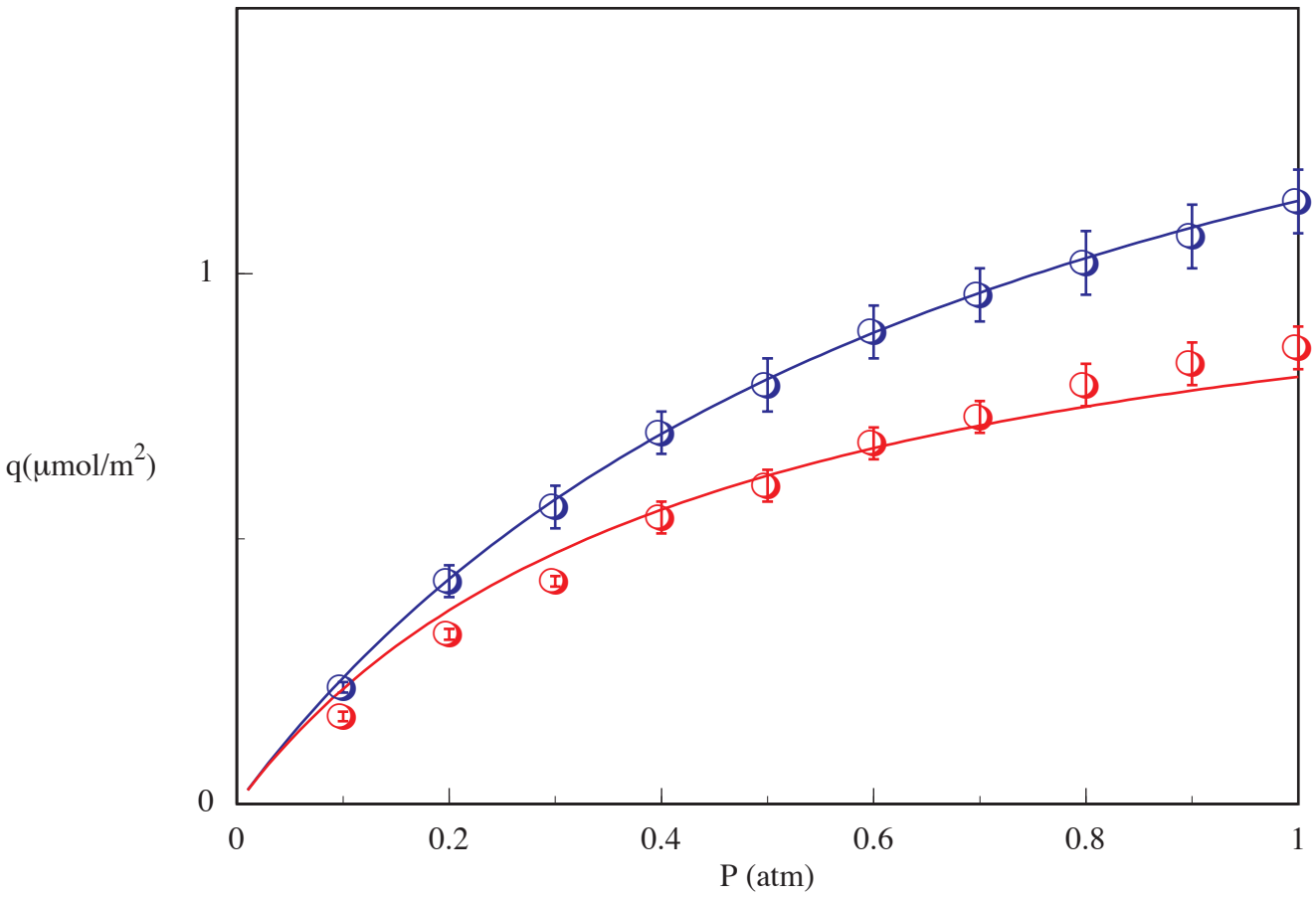
Figure 1. Two dimensional view of the ethane and ethylene molecules. Large circles represent the Lennard-Jones sites of σ_i diameter. In the case of ethylene molecule, small circles mimic the possibility of association with the ion metals on the surface (SW sites of σ_π diameter). L_i is the bond length.

Figure 2. Adsorption isotherms for ethane and ethylene on γ-Al_2O_3 surface at 333 K. Symbols represent simulation results for ethane (circles) and ethylene (squares). Lines are correlations from experimental results for ethane (solid line) and ethylene (dotted line).

Figure 3. Adsorption isotherms for ethane and ethylene on near monolayer CuCl/γ-Al_2O_3 surface at 333 K. Symbols represent simulation results for ethane (circles) and

ethylene (squares). Lines are correlations from experimental results for ethane (solid line) and ethylene (dotted line).


σ1
L1
σπ
L2
σ2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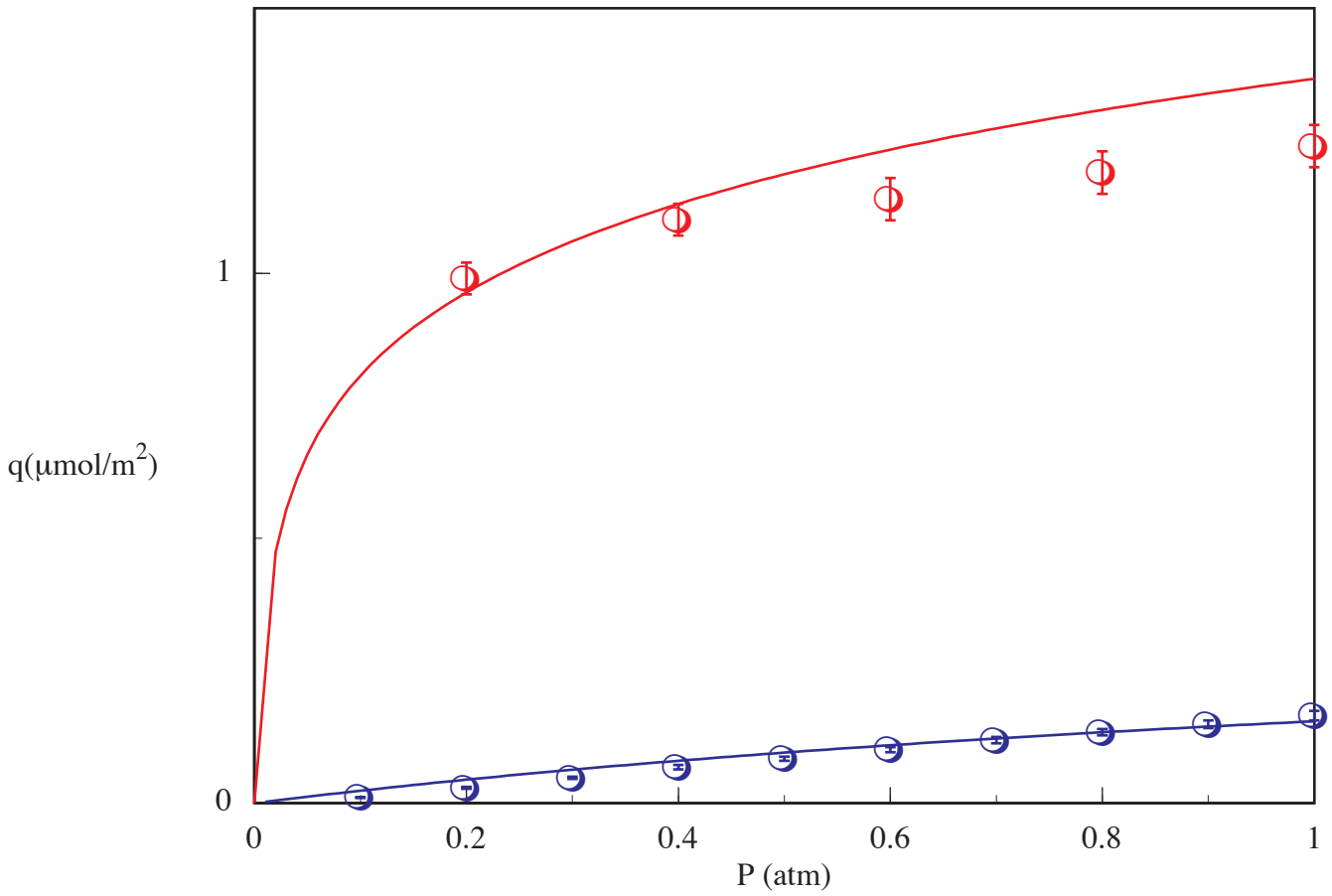
0
0
0.2
0.4
0.6
0.8
1
P (atm)


q(μmol/m2)
1
0
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0.2
0.4
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0.8
1
P (atm)