활성탄 흡착제에 대한 순수 CH_4,C_2H_6, C_2H_4, N_2, H_2 단일성분의 흡착평형에 관한 연구

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A Study of Adsorption Equilibria for pure CH_4, C_2H_6, C_2H_4, N_2 and H_2 component onto activated carbon

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Introduction

Recently hydrogen is highly required in the areas such as fuel cell preparation and semiconductor process, and a demand for hydrogen in petrochemical industry has still been increasing. Also, hydrogen is regarded as a renewable and clean energy source. Mostly, hydrogen used in several industries has been produced from steam reforming of light hydrocarbon, partial oxidation of heavy hydrocarbon, recovery from coke oven gas and water electrolysis etc.

There are several methods for hydrogen recovery and purification. Especially, adsorption process has been generally recognized as a less energy consumption process and it is possible to separate some component precisely (99.999%, H2) using adsorbent's pore size and surface characteristics.

Of adsorption processes, pressure swing adsorption process has attracted increasing of its low energy requirements as well as low capital investment costs. Many more sophisticated pressure swing adsorption processes have been developed and commercialized since the introduction of the Skarstrom cycle. In fact, many researchers have studied on separation of hydrogen using pressure swing adsorption process.

To separate some component using pressure swing adsorption process, single and multi-component adsorption equilibrium data at ranges of high pressure are necessary. So, we studied adsorption equilibria of single components that were methane and hydrogen which were main products of natural gas pyrolysis and ethane, ethylene, nitrogen which were minor products onto activated carbon adsorbent. And we measured adsorption equilibrium data of those components at 293.15K, 303.15K and 313.15K temperature and at pressures up to 20atm. Also, the experimental data were correlated by Langmuir, Freundlich, Langmuir-Freundlich, Toth, Unilan equations and we chose the best..

Theory

For each equilibrium datum, rigorous assessments were performed and correlated by several pure species equilibrium models. The isotherm equations used in this study were Langmuir, Freundlich, Langmuir-Fruendlich(L-F), Toth and Unilan. The mathematical forms of these models are as follows:

Langmuir

$$q = \frac{q_m BP}{1 + BP} \tag{1}$$

Freundlich

$$q = kP^{1/t} \tag{2}$$

Langmuir-Freundlich

$$q = \frac{q_m BP^{1/t}}{1 + BP^{1/t}} \tag{3}$$

Toth

$$q = \frac{q_m P}{\left(B + P^t\right)^{1/t}} \tag{4}$$

Unilan

$$q = \frac{q_m}{2s} \ln\left[\frac{c + P\exp(+s)}{c + P\exp(-s)}\right] \tag{5}$$

where q is the amount adsorbed, P is the equilibrium pressure, and q_m, B, k, t, c, s are isotherm parameters.

Isosteric heat of adsorption can be calculated by the Clausius-Clapeyron equations[17] for adsorption,

$$\frac{q_{st}}{RT^2} = \left[\frac{\partial \ln P}{\partial T}\right]_N \tag{6}$$

where P is the pressure, T is the temperature, R is the gas constant, and q_{st} is the isosteric heat.

Experiment

Activated carbon (Calgon Co.) was chosen as an adsorbent. Prior to measurement, the adsorbent was kept at 423.15K in a drying vacuum oven more than 12hr to remove impurities. Adsorbates were Methane, ethane, ethylene, hydrogen and nitrogen.

The adsorption apparatus in Figure 1 is based on the static volumetric method. There are a reaction cell and a loading cell. The volume of the reaction cell is 521.615ml and the loading cell is 522.735ml. The temperature was measured by K-type thermocouple and the pressure was measured by pressure-transducer in each cell. The temperatures and the pressures were recorded at constant time interval by the mobile recorder (MV100, Yokogawa Co.). Prior to the introduction in the reaction cell, the

mass of the adsorbent was weighed with an accuracy of ±10mg after eliminating the traces of impurity at 423.15K and at high vacuum for more than 12hr. Also, after the adsorbent was put in the reaction cell, the traces of impurity in the reaction cell were eliminated by vacuum pump for more than 3hr, so did the loading cell. the experiment was conducted up to pressures at 20atm by elevating the pressure step by step and at 293.15K, 303.15K and 313.15K temperature..

Results and Discussions

The adsorption data of methane, ethane, ethylene, hydrogen and nitrogen onto activate carbon adsorbent were obtained at 293.15K, 303.15K and 313.15K temperature and pressures up to 20atm. The experimental data were graphically represented in Figures 2 at 293.15K. The amount adsorbed of methane, ethane and ethylene increased highly at low pressure under 3atm, and the bigger is the molecule number the more is the amount adsorbed. Especially, at the same pressure and temperature the adsorbed amount of ethane and ethylene are always higher than the one of methane. For nitrogen, the behavior is similar to those.

For each equilibrium datum, rigorous assessments were performed and correlated by several pure species equilibrium models. The isotherm equations used in this study were Langmuir, Freundlich, Langmuir-Fruendlich(L-F), Toth and Unilan. The Langmuir-Freundlich equation was employed for all the systems because the Langmuir-Freundlich equation showed the minimum value of the average deviation parameter.

As shown in Figure 3, the isosteric heats of adsorption varied with the surface loading on activated carbon adsorbent. For methane, ethane and ethylene, the isosteric heat of adsorption decreased and then increased. This result indicates that the activated carbon adsorbents used have an energetically heterogeneous surface.

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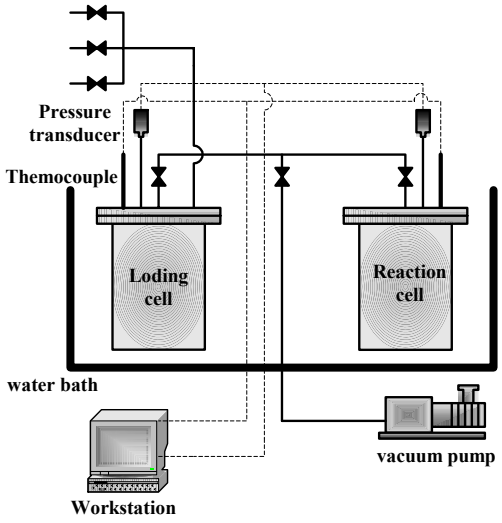

Figure 1. Schematic diagram of adsorption apparatus.

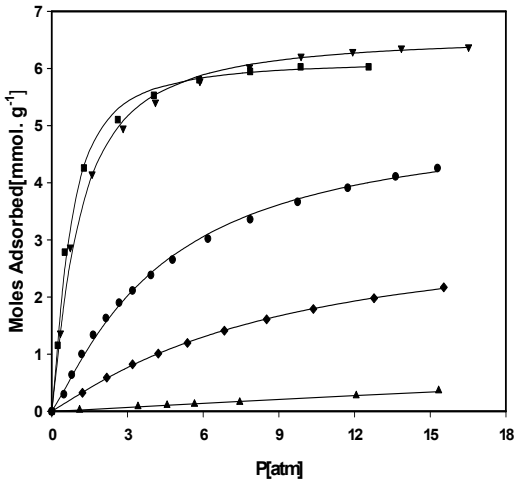

Figure 2. Measured and fitted isotherms of :●,CH_4 ;■,C_2H_6 ;▼,C_2H_4 ;◆,N_2 and ▲,H2 onto activated carbon at 293.15K

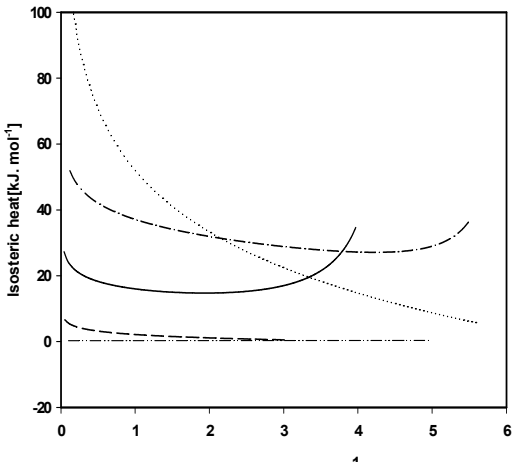

Figure 3. Isosteric heat of adsorption with respect to surface loading onto activated carbon: —, CH_4; ····, C_2H_6; -·-, C_2H_4; ---, N_2 and -··-, H_2