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Adsorption of carbon dioxide using polyethyleneimine modified silica gel

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Abstract−To find an ideal adsorbent for carbon dioxide capture, a new polyethyleneimine modified silica gel material was synthesized with a simple procedure. Three silica gel materials with various particle sizes (15, 25 and 40-63 μm) were prepared and functionalized with polyethyleneimine. The carbon dioxide adsorption amounts of modified silica gel and non-modified silica gel were calculated using a mass balance equation at three different temperatures (298.15, 308.15 and 318.15 K), respectively, and the influence of gas pressure and particle size on adsorption was discussed. Experimental data showed that the carbon dioxide adsorption capacity of modified silica gel was better than non-modified silica gel, and the adsorption capacity gradually decreased with increasing particle size. The smaller particle size (15 μm) PEI modified silica gel had the largest adsorption capacity, at 298.15 K, and the adsorption amounts of various particle sizes of PEI-silica better fit the Langmuir isotherm model.

Key words: Adsorption, Adsorbent, Silica Gel, Carbon Dioxide, PEI

INTRODUCTION

Carbon dioxide (CO_2) is the human-produced greenhouse gas that contributes the most radiative trapping [1]. It is produced by fossil fuel burning and other human activities such as tropical deforestation, and can transmit visible light but absorb strongly in the infrared and near-infrared. CO_2 is the largest contributor in regard of its amount present in the atmosphere contributing to 60% of global warming effects, with 39% of total emissions released from electricity generation, 23% from transport and 22% from industry [2-5]. Therefore, there has been growing interest in developing technologies for efficient capturing and sequestration of large quantities of CO_2. An efficient and economical method is needed to capture and separate the CO_2 produced during various industrial processes. The major obstacle in CO_2 capture is the dynamic efficiency of the separation material.

Because CO_2 is an acidic gas, a basic group such as amino group can lead to preferential sorption of CO_2. Liquid amine is a common chemical material, but it has several drawbacks such as high energy consumption, volatility, viscosity, and large dilutions with water required to prevent equipment corrosion. Recently, some silica-based materials containing amino groups have been synthesized that demonstrated high capacities for CO_2 [6-9]. Polyethyleneimine (PEI) is a polymer with a large quantity of nitrogen atoms of amino groups on the line-type macromolecular chains [10-14], and it is also well known as a polymer for its affinity towards gas molecules, especially CO_2. PEI has received widespread attention around the world, and its applications in adsorption separation fields of gases and metal ions are developing [15]. Silica gel is a granular, vitreous, highly porous form of silica made synthetically from sodium silicate. The properties of silica can be easily tailored by surface modification to prepare materials with desired properties and applications [16-18]. As for a practical approach, PEI is used in production of modified silica material [19-22], but some PEI modified materials have the complex production process [23].

In the present study, a new PEI-silica gel material was synthesized for capture and separation of CO_2, and the adsorption capacity of CO_2 on this material was evaluated. This new amine modified silica adsorbent will have the advantage of high selectivity for CO_2 capture.

EXPERIMENTAL

1. Reagents and Materials

PEI was purchased from Supelco (Bellefonte, PA, USA). Meth-

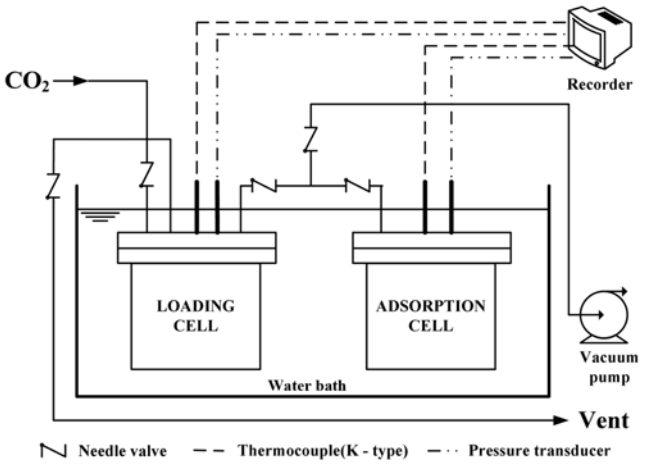

Fig. 1. Apparatus of static volumetric method.

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anol was obtained from Pure Chemical Co., Ltd. (Ansan, Korea). Three types silica gel (15 μm, 25 μm, 40-63 μm) were bought from YMC Co., Ltd. (Kyoto, Japan). Distilled water was filtered with a vacuum pump and filter (HA-0.45; Millipore, Waters, USA) before use. All the other solvents used in the experiment were analytical grade.

2. Apparatus

Adsorption equilibria data were obtained by using a static volumetric method. Fig. 1 shows a schematic representation of the apparatus. In this method, the amount of gas in the system is determined by using appropriate pressure, volume, and temperature measurements. The pressure and temperature were recorded with a mobile recorder (MV 100, Yokogawa Co.). Moreover, the temperature in each cell was measured by K-type thermocouple operated within an accuracy of ±0.01 K; the pressure was measured with a pressure transducer (Sensys, Sensor system tech.) with an accuracy of 0.133%. The adsorption cell, loading cell, and all connection tubes consisted of stainless steel. The volumes of the adsorption and loading cells were 154.7±1 mL and 156.4±1 mL, respectively, and determined from the expansion of hydrogen gas. 1/4 in. tubes and 1/4 in. valves were used. During the experiments, the adsorption and the loading cells were immersed in a water bath (BS-21, Jeio Tech.) maintained at a given temperature using a refrigeration circulator (MC-31, Jeio Tech.). A vacuum pump was used to eliminate gaseous impurities from the adsorption and loading cells. Microstructures of the dried adsorbents were observed by field emission-scan-

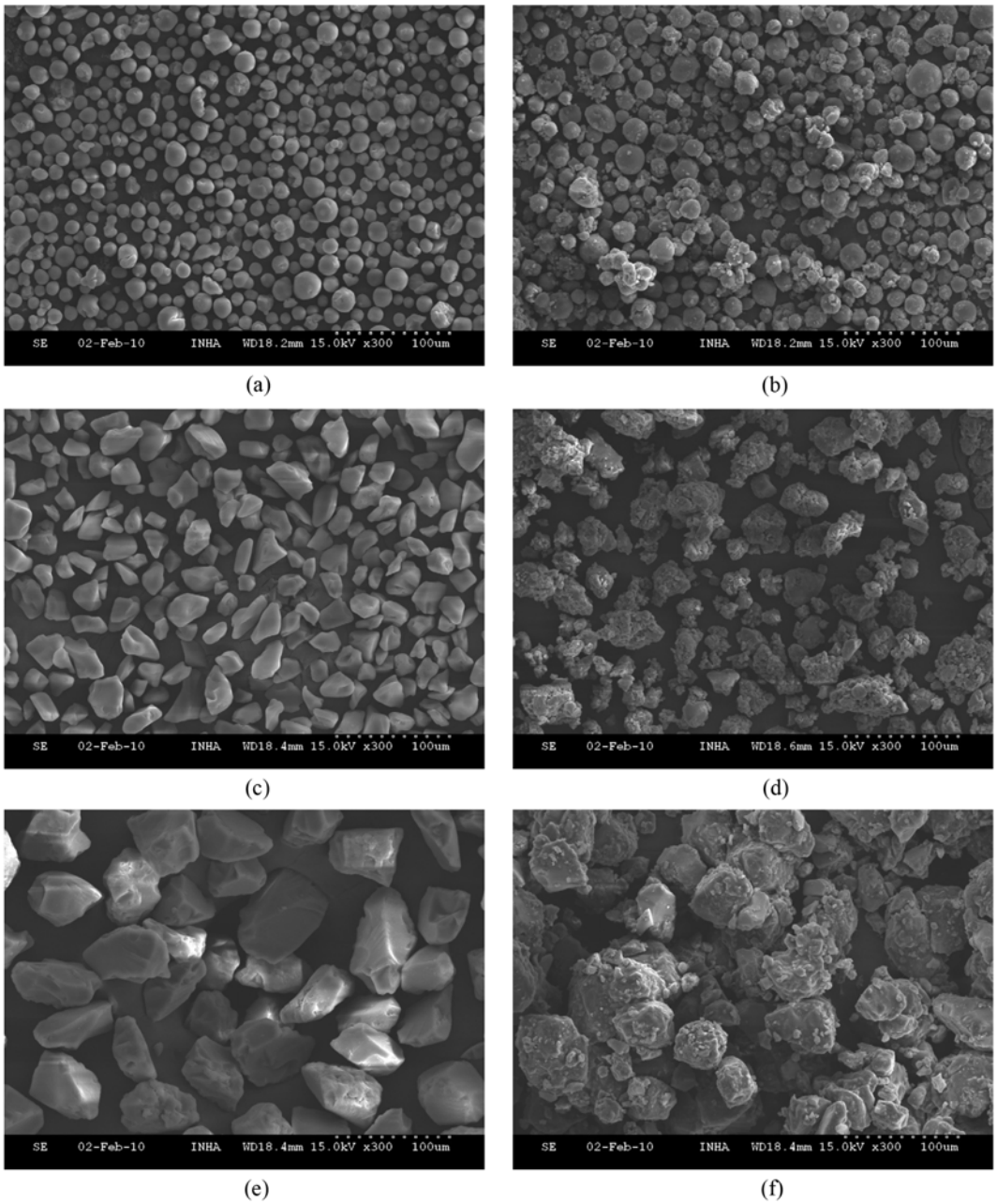

Fig. 2. FE-SEM images of adsorbents ((a) 15 μm silica; (b) 15 μm PEI-silica; (c) 25 μm silica; (d) 25 μm PEI-silica; (e) 40-63 μm silica; (f) 40-63 μm PEI-silica).

ning electron microscopy (FE-SEM) (S-4300 model, Hitachi, Japan) and it was operated at the voltage of 15 kV.

3. Synthesis of PEI Modified Silica Gel

PEI was added into the various particle sizes silica gel prepared by wet impregnation. 2 g PEI was mixed with 20 mL methanol in a flask under stirring for 30 min, and then 4 g silica was added to the PEI/methanol solution. The mixture was continuously stirred for 30 min, and the flask was placed in a water bath for polymerization at 333.15 K under reduced pressure (500 mmHg). After the polymerization was allowed to proceed for 24 h, the PEI/silica material with various particle sizes (15, 25 and 40-63 μm) was obtained and was dried in an oven at 323.15 K.

4. CO_2 Adsorption Measurement

The adsorbent was put into the adsorption cell. The adsorbent was regenerated to eliminate trace impurities under vacuum (<−1 kgf/cm^2) for at least 12 h by using a vacuum pump. The CO_2 was introduced into the loading cell, and its pressure and temperature were measured when the cell was stabilized. Then the valve between the loading and adsorption cells was opened, allowing the gas to contact the adsorbent. The pressure and temperature were measured after equilibrium was achieved, and the number of moles remaining in the two cells was calculated. The adsorption equilibrium state was considered to occur when the respective temperature and pressure of the cells were constant.

The amount adsorbed was calculated by using a mass balance equation (Eq. (1)). This balance was derived from generalized equation of state before and after adsorption equilibrium.

$$\left.\frac{PV}{ZRT}\right|_{L1} + \left.\frac{PV}{ZRT}\right|_{A1} = \left.\frac{PV}{ZRT}\right|_{L2} + \left.\frac{PV}{ZRT}\right|_{A2} + qM \quad (1)$$

P is pressure, T is temperature, V is volume, R is the gas constant, M is the molecular weight, Z is the compressibility factor, and q is the amount adsorbed. Subscripts 1 and 2 represent the state before and after adsorption equilibrium, respectively.

Adsorption equilibriums of CO_2 on variable adsorbents were obtained by taking the experimental data of CO_2 adsorption measurement with different pressures and temperatures into OriginPro 7.5 software (OriginLab Corporation, MA, USA). The experimental adsorption isotherms were fitted to the linear, Langmuir, and Freundlich models. This was accomplished with the solver function in OriginPro 7.5 software by varying the fitting parameters to reach a value of 1 for the squared correlation coefficient (r^2).

RESULTS AND DISCUSSION

1. Performance Evaluation of Adsorbents

The PEI layer is very resistant to chemical and physical stress, and its molecules have branch chains [16], containing primary, secondary and ternary amino groups in a ratio of approximately 1 : 2 : 1. To obtain 33 wt% PEI modified samples, the ratio of silica gel and PEI was kept at 2 : 1. Silica gel is a granular, vitreous, highly porous form of silica made synthetically from sodium silicate, and it has high surface area. The different sized adsorbents were fractured into small pieces, and studied by FE-SEM (Fig. 2). The FE-SEM images revealed that PEI was bound to the silica gel surface producing a material of porous structure and specific functional group with an irreversibly bound amino group on the surface. High surface area and 3-D channel arrangement can enhance the adsorption capacity of the material by accommodating a larger amount of PEI to capture CO_2 [23].

2. CO_2 Adsorption Capacity

2-1. Compressibility Factors of CO_2

The compressibility factor (Z) is a useful thermodynamic property for modifying the ideal gas law to account for the real gas behavior. Compressibility factors of CO_2 with three different temperatures in this adsorption measurement experiment are shown in Fig. 3. From this figure, the compressibility factor of adsorbent became bigger with the temperature increasing and pressure decreasing.

2-2. Effect of Particle Sizes and PEI

The adsorbent was put into the adsorption cell (seen in Fig. 1) and the adsorption amount was calculated using a mass balance equation. The adsorption isotherms of CO_2 on various particle sizes PEI-silica gel at 298.15 K are plotted in Fig. 4. When the gas pressures is below 1.536 atm, the adsorption amounts of CO_2 on the three particle sizes of PEI-silica gel (15, 25 and 40-63 μm) are very close to each other. However, the adsorption amount of CO_2 increased with the particle sizes of adsorbents decreased, when the gas pressures

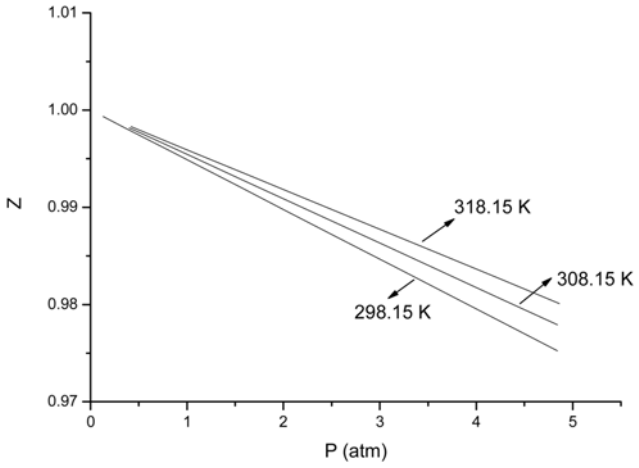

Fig. 3. Compressibility factors (Z) of CO_2 with three different temperatures in adsorption measurement experiment.

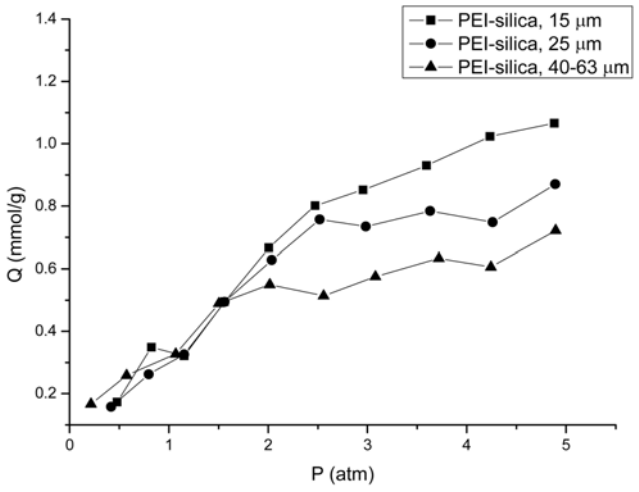

Fig. 4. Adsorption equilibriums of CO_2 at 298.15 K.

Table 1. Parameters in adsorption isotherm of PEI-silica at 298.15 K

Adsorbent	Equation no. of adsorption isotherm	Parameters			r^2
		a	b	c	
15 μm PEI-silica	(2)	0.2065	0.1689	-	0.9682
	(3)	0.4424	0.1969	-	0.9791
	(4)	0.3806	-	1.4508	0.9647
25 μm PEI-silica	(2)	0.1526	0.2060	-	0.9193
	(3)	0.4906	0.3560	-	0.9485
	(4)	0.3668	-	1.7437	0.9103
40-63 μm PEI-silica	(2)	0.1044	0.2350	-	0.9333
	(3)	0.6453	0.7624	-	0.9479
	(4)	0.3577	-	2.3417	0.9467

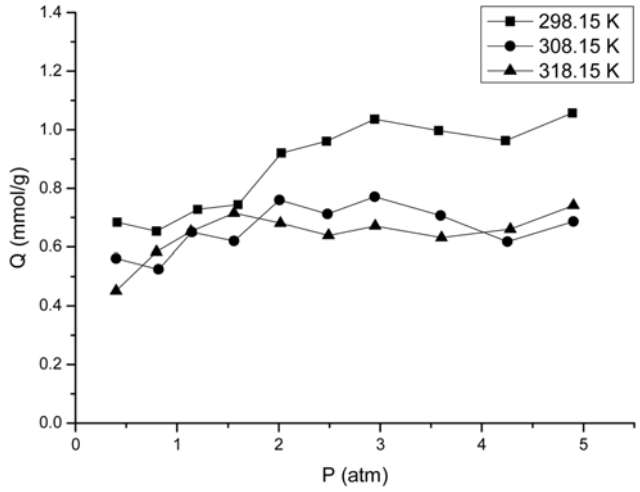

Fig. 5. Adsorption equilibriums of CO_2 on sample A (silica, 15 μm).

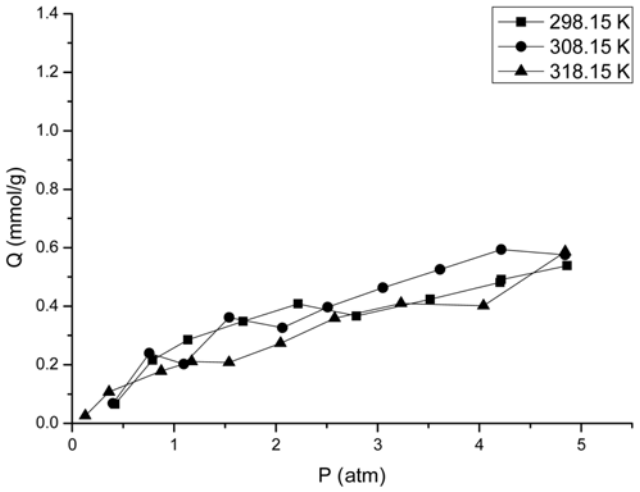

Fig. 7. Adsorption equilibriums of CO_2 on sample C (silica, 25 μm).

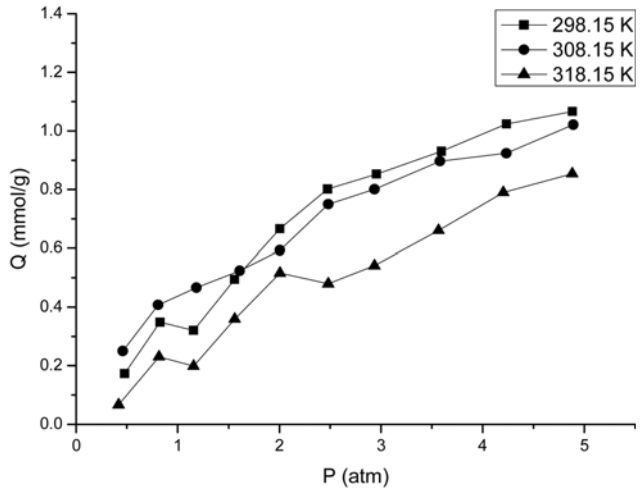

Fig. 6. Adsorption equilibriums of CO_2 on sample B (PEI-silica, 15 μm).

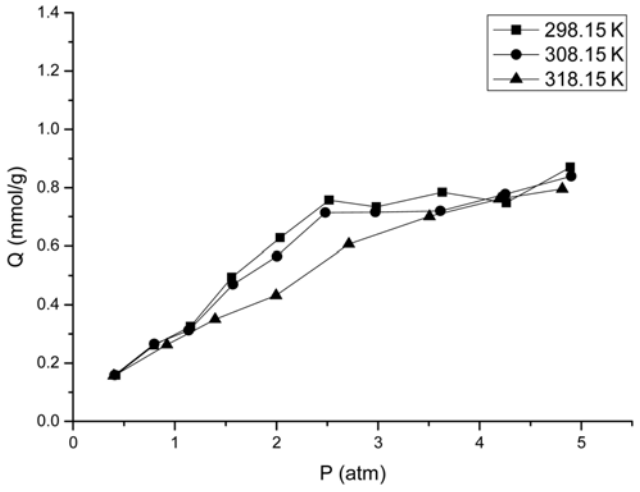

Fig. 8. Adsorption equilibriums of CO_2 on sample D (PEI-silica, 25 μm).

were between 1.536 and 4.88 atm. When the gas pressures are at around 4.88 atm, the adsorption amounts of various adsorbents are 1.0658, 0.87005, and 0.72192 mmol/g, respectively. The smaller particle size (15 μm) PEI modified silica gel had the largest adsorption capacity at 298.15 K. This is due to the higher surface area of the smaller particle size adsorbent. However, the CO_2 adsorption capacities are very similar at the lower gas pressure. The adsorption amounts of CO_2 on PEI-silica gel are shown in Table 1.

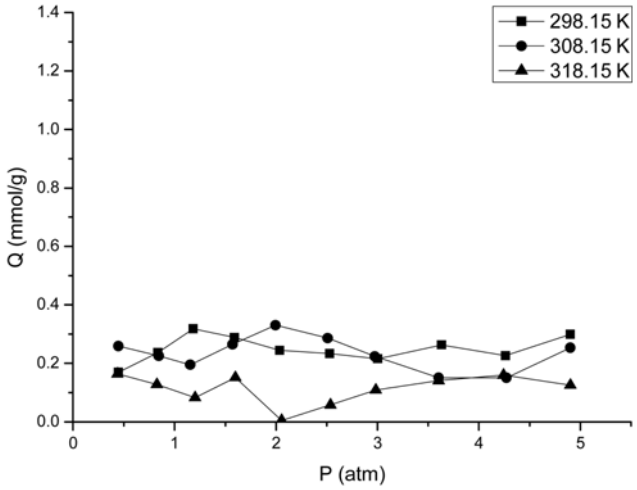

Fig. 9. Adsorption equilibriums of CO_2 on sample E (silica, 40-63 μm).

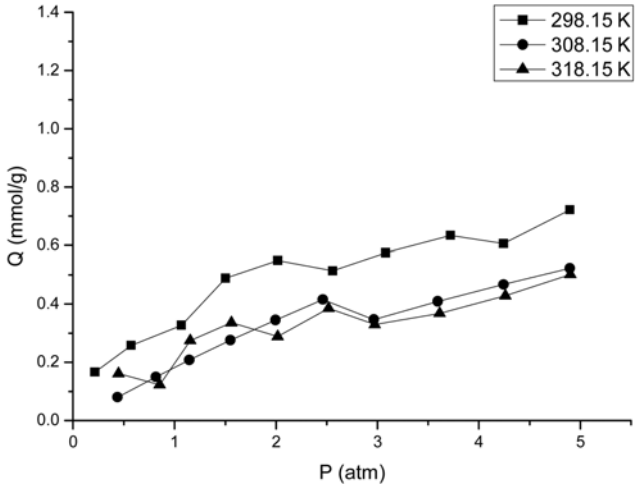

Fig. 10. Adsorption equilibriums of CO_2 on sample F (PEI-silica, 40-63 μm).

The adsorption isotherms of CO_2 on various adsorbents are shown in Fig. 5 to 10. The figures show that the CO_2 adsorption capacity of PEI modified silica gel was better than non-modified silica gel. This is due to the high concentration of amino groups on the line-type macromolecular chains of PEI: these groups have a stronger attraction to CO_2 gas molecules.

2-3. Effect of Gas Pressure

The adsorbent was regenerated to eliminate trace impurities under vacuum for at least 12 h using a vacuum pump, and then CO_2 was introduced into the loading cell and adsorption cell. Figs. 5 to 10 show a general trend of adsorption amounts of CO_2 on adsorbents increasing with increasing CO_2 gas pressure, due to the increased concentration of CO_2 in the adsorption cell with increased gas pressure, during which the CO_2 contacted not only contact the surface of the adsorbent, but also the internal pores.

2-4. Effect of Temperature

The effect of various temperatures (298.15, 308.15 and 318.15 K) was also investigated, and adsorption isotherms are shown from Figs. 5 to 10. Generally, the adsorbed amounts of PEI-silica increased with the increasing CO_2 pressure at various temperatures as a consistent trend. But the adsorbed amount decreased with increasing the temperature. This can be explained by desorption of CO_2 at relatively high temperatures. Meanwhile, physical adsorptions usually have a lower adsorbed amount at relative higher temperature. In this situation, this adsorption preferred relative low temperature.

3. Adsorption Isotherm Model

This experiment data of PEI-silica gel at 298.15 K were fitted to the following adsorption isotherm models:

$$Q=aP+b \tag{2}$$

$$Q=\frac{aP}{1+bP} \tag{3}$$

$$Q=aP^{1/c} \tag{4}$$

Where P (atm) is the gas pressure and Q (mmol/g) is the CO_2 adsorption amount on the adsorbent, a in Eq. (2) and (3) is the maximum adsorption capacity, and b is the apparent dissociation constant, which represents the affinity between the CO_2 and adsorbent. a and c are the parameters in Eq. (4). These adsorption isotherm models are the linear, Langmuir, and Freundlich models, respectively. The parameters fitted by three adsorption isotherm models can be seen in Table 1.

Among these adsorption isotherms, the Langmuir model is perhaps the most robust used model due to its simplicity and the strong theoretical reasoning underlying it. Three essential premises of the Langmuir isotherm are monolayer coverage, adsorption site equivalence and independence. Table 1 shows that the Langmuir Eq. (3) has better correlation results than the other two isotherm equations (Eq. (2) and Eq. (4)). The regression coefficients (r^2) of Langmuir adsorption model are 0.9791, 0.9485 and 0.9479 for various particle sizes PEI-silica (15, 25 and 40-63 μm), respectively. This shows that the Langmuir isotherm model is the most suitable for the adsorption amounts of various particle sizes of PEI-silica.

According to the International Union of Pure Theory and Applied Chemistry (IUPAC), the majority of adsorption isotherms may be grouped into six types. These six types of adsorption isotherms have the common characteristic that adsorption capacity is a monotone increasing function of adsorption pressure. Type I isotherms of IUPAC are given by microporous solids having relatively small external surfaces, the limiting uptake being governed by the accessible micropore volume rather than by the internal surface area, which are sometimes referred to as Langmuir isotherms [24]. Therefore, the adsorption isotherms of developed adsorbents belong to the type I isotherms of IUPAC.

CONCLUSIONS

A new PEI modified silica gel material has been synthesized with a simple procedure. Three silica gel materials with various particle sizes (15, 25 and 40-63 μm) were prepared and functionalized with PEI, and FE-SEM was used to evaluate the characterization of these adsorbents. The CO_2 adsorption amounts of PEI modified silica gel and non-modified silica gel were calculated by using a mass balance equation at three different temperatures (298.15, 308.15 and 318.15 K), respectively, and the influences of particle size, gas pres-

sure and temperature on adsorption were discussed. The results showed that the CO_2 adsorption capacity of modified silica gel was better than non-modified silica gel, and the adsorption capacity gradually decreased with increasing particle size. The smaller particle size (15 μm) PEI modified silica gel had the largest adsorption capacity at 298.15 K, and the adsorption amounts of various particle sizes PEI-silica better fit the Langmuir isotherm model than the other two isotherm models do. Compared to conventional adsorbents, the PEI modified silica gel procedure for silica gel was much simpler in terms of experimental step and lower cost. The developed adsorbents had an acceptable adsorption capacity for CO_2, and can be as a potential material for future CO_2 capture.

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