Adsorption of Propylene and Ethylene on 15 Activated Carbons

Pengcheng Ye, Zhaohua Fang, Baogen Su, Huabin Xing, Yiwen Yang, Yun Su, and Qilong Ren*

National Laboratory of Secondary Resources Chemical Engineering, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China

The adsorption equilibria of propylene and ethylene on 15 commercial activated carbons at 101.3 kPa and 313 K were investigated. The adsorption amount of propylene and ethylene on these adsorbents varied greatly from a minimum of 1.593 $\text{mmol}\cdot\text{g}^{-1}$ for propylene and 1.430 $\text{mmol}\cdot\text{g}^{-1}$ for ethylene to a maximum of 4.528 $\text{mmol}\cdot\text{g}^{-1}$ for propylene and 3.100 $\text{mmol}\cdot\text{g}^{-1}$ for ethylene. Characteristics of these activated carbon adsorbents such as the Brunauer−Emmett−Teller (BET) surface area, micropore area, external surface area, total pore volume, micropore volume, and average pore diameter were determined by a volumetric method. The adsorption amount of the two alkenes on these 15 carbon samples were correlated with their physical parameters. Both the BET surface area and micropore volume have an effect on their adsorption.

Introduction

Ethylene is a basic industrial organic chemical. With prices soaring, engineers are getting more interested in the recovery of ethylene from refinery dry gas and other gases which are usually burnt.[1] One efficient way is making ethyl benzene by using lean ethylene,[2] including the Mosanato−Lumus process, Alkar process,[3] and Mobil−Badger process.[4] However, propylene in the dry gas will impact the reaction to ethyl benzene.[5,6] According to some previous research, the side reaction can be inhibited if the mass concentration of propylene is below 0.7 % in the gas mixture.[7] Thus, it is essential to separate propylene and ethylene.

Activated carbon is a potential candidate in industrial applications such as water purification,[8] gas storage,[9] and separation.[10] It has a well-developed pore structure, unique surface, and large pore volume, resulting in a high adsorption capacity and selectivity.[11–15] Therefore, it is a promising adsorbent for the separation of propylene and ethylene from the dry gas, taking into account the low price, abundant source, and easy regeneration.

Pressure-swing adsorption (PSA) has gained great interest and wide industrial applications for gas separation.[16] Information on adsorption equilibria and the physical characteristics of adsorbents is essential for the design of adsorption separation processes. There has been a great amount of research on the separation of olefin and paraffin.[17,18] Only limited work has been carried out on the adsorption and separation of propylene and ethylene. Szepesy and Illes measured the adsorption isotherms of eight organic gases, including ethylene and propylene, on Nuixt-AL activated carbon by a static method.[19] Peng et al. measured the isotherms of propylene and ethylene on silicalite-1 using a gravimetric method.[20] It should be noted that there has been no comparative and systematic investigation on the adsorption of propylene and ethylene on a series of different activated carbons.

This paper presents the amount of ethylene and propylene adsorption on 15 commercial activated carbons and intends to evaluate the separation possibility of propylene and ethylene by activated carbon adsorption or chromatography. We also use the adsorption ratio to roughly characterize the separation efficiency of the investigated carbons. Furthermore, the physical parameters of these adsorbents, such as the Brunauer−Emmett−Teller (BET) surface area, micropore area, external surface area, total pore volume, micropore volume, and average pore diameter, were obtained by a volumetric method. The objective of this paper is to view the adsorption difference between the activated carbons and to help to select a suitable adsorbent for separation of propylene and ethylene. So the relationship between the adsorption amount and the physical parameters of the activated carbons were also correlated. These data will be important for further industrial applications.

Experimental Section

Materials. The 15 commercial activated carbons used in this work were purchased from five different corporations in China. They are referred to as AC-1 to AC-15. AC-1, AC-2, AC-6, and AC-9 were from the Beijing Guanghua-Jingke Activated Carbon Co., Ltd. AC-4 was from the Shanghai Activated Carbon Co., Ltd. AC-11 was from the Tangshan Huaneng Technology Carbon Co., Ltd. AC-14 was from the Huadong Medicine Group Co., Ltd. AC-15 was from the Hangzhou Wood Co., Ltd., and the seven remaining samples were from the Beijing Kecheng Guanghua New Technology Co., Ltd. The textural properties were determined by the adsorption of N_2 at 77 K with a Micrometritics ASAP2000 gas adsorption analyzer, which are summarized in Table 1.

Pure ethylene gas (purity ≥ 99.99 %) and hydrogen gas (purity ≥ 99.99 %) were purchased from the Hangzhou Jingong Gas Industry Corporation. Pure propylene gas (purity ≥ 99.9 %) was purchased from the Foshan Kedi Gas Chemical Industry Corporation.

Apparatus and Procedure. The adsorption amount of ethylene and propylene were measured by a chromatographic method. The experiments were carried out in an apparatus, as shown in Figure 1, which was previously used and described in detail in refs 21 to 23. The mass flow controller (SevenStar Inc., CS-200A) provided a flow precision of ± 1.5 % of full scale. Pressure was measured using a pressure sensor (Kangyu Inc.,

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* To whom correspondence should be addressed. E-mail: renql@zju.edu.cn. Tel.: 86-571-8795-2773. Fax: 86-571-8795-2773.

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Table 1. Textural Properties of the Activated Carbons Investigated[a]

adsorbent	S_{BET} $m^2 \cdot g^{-1}$	S_{micro} $m^2 \cdot g^{-1}$	S_{exter} $m^2 \cdot g^{-1}$	V_{total} $mL \cdot g^{-1}$	V_{micro} $mL \cdot g^{-1}$	$D_{average}$ Å
AC-1	1274.5	684.4	590.1	0.8084	0.2783	25.37
AC-2	1218.1	939.7	278.3	0.5372	0.3761	17.64
AC-3	1127.9	851.7	276.2	0.5837	0.3414	20.70
AC-4	1027.8	614.5	413.3	0.6591	0.2803	19.38
AC-5	1009.3	638.3	371.0	0.6275	0.2566	24.87
AC-6	1008.2	709.9	298.4	0.5236	0.2844	20.77
AC-7	994.1	676.2	318.0	0.5493	0.2716	22.10
AC-8	971.1	679.1	292.0	0.5216	0.2710	21.48
AC-9	970.8	524.0	446.8	0.4687	0.2125	19.31
AC-10	937.8	777.4	160.4	0.4047	0.3089	17.26
AC-11	923.9	573.7	350.3	0.4294	0.2302	18.59
AC-12	883.6	404.0	479.6	0.4222	0.1650	19.11
AC-13	830.0	661.8	168.2	0.4105	0.3090	14.91
AC-14	778.4	512.8	265.6	0.4683	0.2374	18.11
AC-15	352.1	276.7	75.3	0.1803	0.1293	15.40

[a] S_{BET} = BET surface area = $S_{micro} + S_{exter}$; S_{micro} = micropore area; S_{exter} = external surface area; V_{total} = total pore volume; V_{micro} = micropore volume; $D_{average}$ = average pore diameter.

KYB18G05) providing a precision of ± 0.25 %. The incubator controlled the temperature within 0.5 K.

Prior to the adsorption measurement, the (150 to 180) μm adsorbent samples were degassed at 403 K for 12 h. Then they were packed into a stainless steel adsorption column (0.3 cm inner diameter × 25 cm). The flow rate was 20.0 $mL \cdot min^{-1}$, and the column pressure drop was less than 2 kPa in all processes according to previous experimental surveys. The exit gas first went through a Shimadzu GC-8A thermal conductivity detector (TCD), which was a good way to guide researchers to sample accordingly, especially during the breakthrough time. Then the exit gas was introduced intermittently by a six-way valve to a Shimadzu GC-8A flame ionization detector (FID) to analyze the concentration, using a Porapak Q analytical column (carrier gas: N_2, injector and detector temperature of 393 K, column temperature of 363 K). The breakthrough curves were drawn out, and then the adsorption amount of ethylene or propylene can be calculated by eqs 1 and 2 according to ref 22.

$$\tau_a = \int_0^{t^\infty} \left(1 - \frac{X_{ae}(1 - X_{ai})}{X_{ai}(1 - X_{ae})}\right) dt \tag{1}$$

$$Q = \left(\frac{(v_i \tau_a)}{L} - 1\right) \frac{\varepsilon}{1 - \varepsilon} \frac{P X_{ai}}{\rho_p R T} \tag{2}$$

where τ_a is the mean residence time; X_{ai} and X_{ae} are the inlet and outlet adsorbate mole fractions, respectively; Q is the adsorption amount; v_i is the interstitial gas velocity; L is the bed length; ε is the bed voidage; and ρ_p is the particle density; P is the bed pressure; T is the column temperature.

Results and Discussion

Table 2 shows the single-component adsorption data of ethylene and propylene on 15 activated carbons at 313 K and 101.3 kPa. The uncertainty of the results for at least three measurements was less than 2.0 %. To evaluate the separation potential of the investigated carbons, we define the adsorption ratio AR as the following equation, and the calculated data are also presented in Table 2,

$$\mathrm{AR} = \frac{Q_{propylene}}{Q_{ethylene}} \tag{3}$$

where $Q_{propylene}$ and $Q_{ethylene}$ are the adsorption amounts of propylene and ethylene, respectively. From the results, we found that the adsorption amount of propylene was larger than that of ethylene for the same activated carbon. That is because the main interaction between alkenes and activated carbons may be through the van der Waals forces. Propylene has a larger molecular weight and a longer carbon chain than that of ethylene, so it has stronger van der Waals forces with activated carbons, resulting in a larger adsorption amount. On the other hand, the adsorption amount of propylene and ethylene on these adsorbents varied greatly, from a minimum of 1.593 $mmol \cdot g^{-1}$ for propylene and 1.430 $mmol \cdot g^{-1}$ for ethylene on AC-15 to a maximum of 4.528 $mmol \cdot g^{-1}$ for propylene and 3.100 $mmol \cdot g^{-1}$ for ethylene on AC-2.

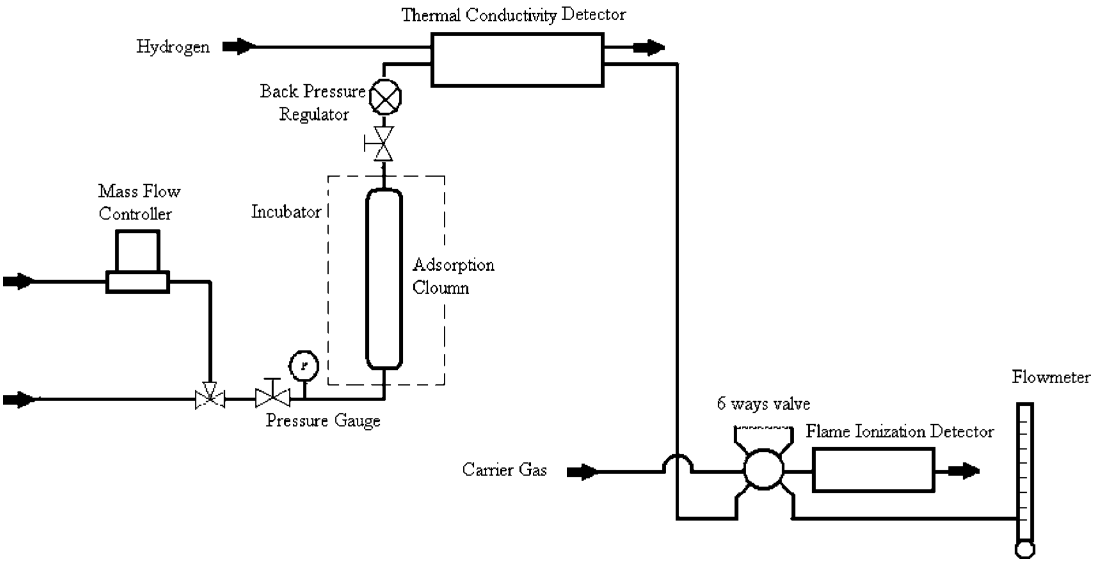

Figure 1. Laboratory setup for the adsorption of ethylene and propylene.

Table 2. Single-Component Adsorption Amount and Adsorption Ratios for Propylene and Ethylene at 313 K and 101.3 kPa

	$Q_{\text{propylene}}$	Q_{ethylene}	
adsorbent	$\text{mmol}\cdot\text{g}^{-1}$	$\text{mmol}\cdot\text{g}^{-1}$	AR
AC-1	4.249 ± 0.048	2.735 ± 0.030	1.553 ± 0.088
AC-2	4.528 ± 0.001	3.100 ± 0.018	1.461 ± 0.026
AC-3	3.941 ± 0.039	2.784 ± 0.042	1.416 ± 0.081
AC-4	3.602 ± 0.013	2.531 ± 0.016	1.424 ± 0.029
AC-5	3.445 ± 0.037	2.438 ± 0.042	1.413 ± 0.079
AC-6	3.281 ± 0.037	2.584 ± 0.010	1.270 ± 0.049
AC-7	3.296 ± 0.013	2.717 ± 0.010	1.213 ± 0.020
AC-8	3.428 ± 0.027	2.584 ± 0.010	1.327 ± 0.038
AC-9	2.998 ± 0.010	1.882 ± 0.013	1.593 ± 0.026
AC-10	3.769 ± 0.038	2.984 ± 0.042	1.263 ± 0.072
AC-11	3.025 ± 0.016	2.185 ± 0.035	1.385 ± 0.053
AC-12	2.890 ± 0.004	1.707 ± 0.004	1.693 ± 0.010
AC-13	3.368 ± 0.020	2.714 ± 0.045	1.241 ± 0.061
AC-14	2.756 ± 0.035	2.466 ± 0.050	1.118 ± 0.068
AC-15	1.593 ± 0.017	1.430 ± 0.013	1.113 ± 0.024

Table 3. Correlation Coefficients between Adsorption Data and Physical Parameters

	S_{BET}	S_{micro}	S_{exter}	V_{total}	V_{micro}	D_{average}
	$\text{m}^2\cdot\text{g}^{-1}$	$\text{m}^2\cdot\text{g}^{-1}$	$\text{m}^2\cdot\text{g}^{-1}$	$\text{mL}\cdot\text{g}^{-1}$	$\text{mL}\cdot\text{g}^{-1}$	Å
$Q_{\text{propylene}}/\text{mmol}\cdot\text{g}^{-1}$	0.9300	0.9029	0.3611	0.7520	0.8809	0.4050
$Q_{\text{ethylene}}/\text{mmol}\cdot\text{g}^{-1}$	0.6950	0.9259	−0.0465	0.5556	0.9510	0.2178
AR	0.5624	0.0854	0.7988	0.4371	−0.0004	0.3725

The R Program[24] was used for the statistical analysis of the experimental results to obtain the relationship between the adsorption data and the physical parameters of the activated carbons. The correlation coefficients are listed in Table 3. Figures 2 and 3 are presented for a better understanding. It can be verified that both the BET surface area and micropore volume have an effect on propylene and ethylene adsorption, although propylene adsorption capacities correlate a little better with the BET surface area and ethylene adsorption capacities with the micropore volume. The BET surface area has the greatest influence on the propylene adsorption amount with a correlation coefficient of 0.9300. Data from previous literature (at 313 K and 101.3 kPa) are also shown in Figure 2 for comparison. The adsorption amount of propylene on Nuxit-Al with a 1100 $\text{m}^2\cdot\text{g}^{-1}$ BET surface area was 3.8203 $\text{mmol}\cdot\text{g}^{-1}$,[19] while the adsorption amount of propylene on Black Pearl I with a 705 $\text{m}^2\cdot\text{g}^{-1}$ BET surface area was 2.667 $\text{mmol}\cdot\text{g}^{-1}$.[25] They are very close to the line fitted in this work. It is comprehensible that a larger surface area means more activated adsorption sites for propylene. Similar results were found by Chakraborty et al. that the amount of both hydrogen and methane adsorption varied linearly with the surface area of various porous materials.[26] Chakraborty et al. thought adsorbents with high surface areas tended to possess lower heats of adsorption (ΔH^{o}) in the Henry regime, resulting in a larger amount of adsorption. Micropore volume has a comparatively greater effect on the ethylene adsorption amount with a correlation coefficient of 0.9510, while the adsorption ratio has the closest relationship with the external surface area with a coefficient of 0.7988. Maybe this is due to the molecular volume and shape. The diameter of ethylene is 3.9 Å, while the diameter of propylene is 4.5 Å,[27] and the carbon chain of ethylene molecule is linear while that of propylene is a "V" shape, which allows ethylene molecules to more easily fill into micropores; therefore, propylene molecules are relatively more likely to lie on open surfaces. This means that the external surface area, defined as the BET surface area minus micropore area, to some degree, can influence the difference of propylene and ethylene adsorption. Anyway, both the BET surface area and micropore volume have an effect on both propylene adsorption and ethylene adsorption.

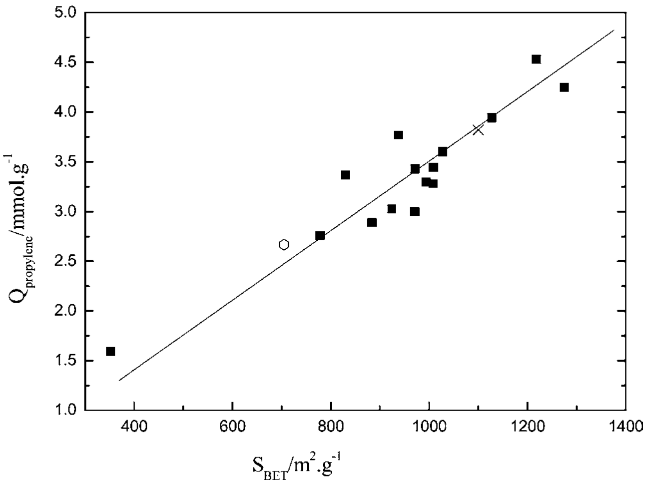

Figure 2. Relationship between the BET surface area and the propylene adsorption amount: ■, this work; ×, Szepesy and Illes;[19] ○, Lewis et al.;[25] the line represents best linear fits of data from this work.

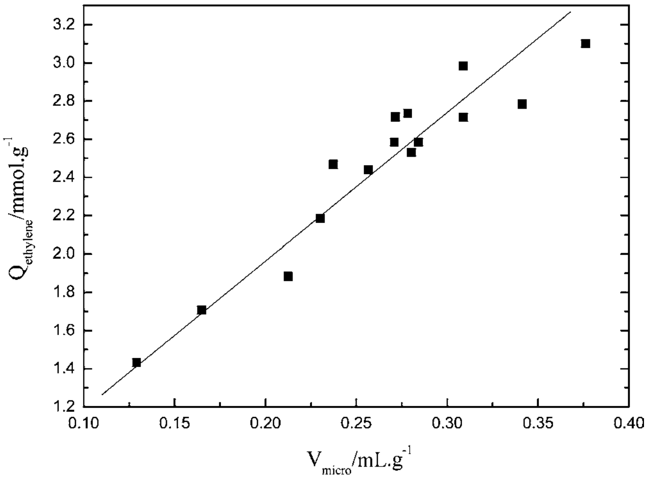

Figure 3. Relationship between the micropore volume and the ethylene adsorption amount. The line represents best linear fits of data from this work.

AC-2 has the largest adsorption amount for propylene (4.528 $\text{mmol}\cdot\text{g}^{-1}$), while AC-1 has the maximum adsorption ratio for propylene over ethylene (about 1.553). Actually AC-1 exhibits a considerable adsorption amount for propylene as well (4.249 $\text{mmol}\cdot\text{g}^{-1}$). As a result, AC-1 was selected as a suitable adsorbent candidate for the industrial separation process.

Conclusions

A total of 15 commercial activated carbons, with various BET surface areas, micropore areas, external surface areas, total pore volumes, micropore volumes, and average pore diameters, were investigated for the separation of propylene and ethylene by measuring the adsorption amount of the two alkenes at 101.3 kPa and 313 K, using a chromatographic method. For the same activated carbon, the adsorption amount of propylene was larger than that of ethylene. The adsorption amount of propylene and ethylene on these different carbon adsorbents varied greatly. The statistical analysis of the results show that the BET surface area and micropore volume are the key factors influencing propylene and ethylene adsorption. AC-1 had a large propylene adsorption amount (4.249 $\text{mmol}\cdot\text{g}^{-1}$) and the maximum adsorption ratio of 1.553 and was selected as the optimum adsorbent.

The present results are useful for further research of the industrial processes for ethylene reutilization.

Literature Cited

(1) Mehra, Y. R. Using Extraction to Treat Hydrocarbon Gases. *Chem. Eng.* **1996**, *93*, 53–55.

(2) Savage, P.; Brooks, K. Refinery Gases: A Quick Source of Ethylene. *Chem. Week* **1988**, *142*, 16.

(3) Grote, H. W. Introducing: Alkar and Butamer. *Oil Gas J.* **1958**, *56*, 73.

(4) Dwyer, F. G.; Lewis, P. J.; Schneider, F. H. Efficient Non-polluting Ethylbenzene Process. *Chem. Eng.* **1976**, *83*, 90–91.

(5) Porter, R. L.; Balinsky, A. M.; Weber, E. P. Process to Produce a Dilute Ethylene Stream and a Dilute Propylene Stream. U.S. Patent 6790342 B1, 2004.

(6) Netzer, D. Integrate Ethyl Benzene Production with an Olefins Plant. *Hydrocarbon Process.* **1999**, *78*, 77–88.

(7) Xie, C. L.; Fang, Y. D. Recovery and Application for Ethylene from Catalytic Cracking Dry Gas. *Petrochem. Ind. Technol.* **2005**, *12*, 63–66.

(8) Faust, S. D.; Aly, O. M. *Chemistry of Water Treatment*; Butterworths: Boston, 1983.

(9) Ahmadpour, A.; Wang, K.; Do, D. D. Comparison of Models on the Prediction of Binary Equilibrium Data of Activated Carbons. *AIChE J.* **1998**, *44*, 740–752.

(10) Dabrowski, A. Adsorption-from Theory to Practice. *Adv. Colloid Interface Sci.* **2001**, *93*, 135–224.

(11) Bagreev, A.; Menendez, J. A.; Dukhno, I. Bituminous Coal-based Activated Carbons Modified with Nitrogen as Adsorbents of Hydrogen Sulfide. *Carbon* **2004**, *42*, 469–476.

(12) Wigmans, T. Industrial Aspects of Production and Use of Activated Carbon. *Carbon* **1989**, *27*, 13–22.

(13) Mofarahi, M.; Sadrameli, M.; Towfighi, J. Characterization of Activated Carbon by Propane and Propylene Adsorption. *J. Chem. Eng. Data* **2003**, *48*, 1256–1261.

(14) Choi, B. U.; Choi, D. K.; Lee, Y. W.; Lee, B. K. Adsorption Equlibria of Methane, Ethane, Ethylene, Nitrogen, and Hydrogen onto Activated Carbon. *J. Chem. Eng. Data* **2003**, *48*, 603–607.

(15) Al-Muhtaseb, S. A. Adsorption and Desorption Equilibria of Nitrogen, Methane, Ethane, and Ethylene on Date-Pit Activated Carbon. *J. Chem. Eng. Data* **2010**, *55*, 313–319.

(16) Yang, R. T. *Gas Separation by Adsorption Processes*; Imperial College Press: London, 1997.

(17) Rege, S. U.; Padin, J.; Yang, R. T. Olefin/Paraffin Separations by Adsorption: π-complexation vs Kinetic Separation. *AIChE J.* **1988**, *44*, 799–809.

(18) Yang, R. T.; Kikkinides, E. S. New Sorbents for Olefin/Paraffin Separations by Adsorption via π-complexation. *AIChE J.* **1995**, *41*, 509–517.

(19) Szepesy, L.; Illes, V. Adsorption of Gases and Gas Mixtures I. *Acta Chim. Hung. Tomus* **1963**, *35*, 37–51.

(20) Peng, J.; Ban, H. Y.; Zhang, X. T. Binary Adsorption Equilibrium of Propylene and Ethylene on Silicalite-1: Prediction and Experiment. *Chem. Phys. Lett.* **2005**, *40*, 94–98.

(21) Siddiqi, K. S.; Thomas, W. J. The Adsorption of Methane-Ethane Mixtures on Activated Carbon. *Carbon* **1982**, *20*, 473–479.

(22) Malek, A.; Farooq, S. Determination of Equilibrium Isotherms Using Dynamic Column Breakthrough and Constant Flow Equilibrium Desorption. *J. Chem. Eng. Data* **1996**, *41*, 25–32.

(23) Wu, Q.; Zhou, Li.; Wu, J. Q.; Zhou, Y. P. Adsorption Equilibrium of Mixture $CH_4 + N_2 + H_2$ on Activated Carbon. *J. Chem. Eng. Data* **2005**, *5*, 635–642.

(24) Ihaka, R.; Gentleman, R. A Language for Data Analysis and Graphics. *J. Comput. Graph. Stat.* **1996**, *5*, 299–314.

(25) Lewis, W. K.; Gilliland, E. R.; Chertow, B.; Hoffman, W. Adsorption Isotherms of Hydrocarbons and Carbon Dioxide on Activated Carbon. *J. Am. Chem. Soc.* **1950**, *72*, 1153.

(26) Chakraborty, A.; Shaha, B. B.; Ng, K. C.; Koyama, S.; Srinivasan, K. Theoretical Insight of Physical Adsorption for a Single Component Adsorbent + Adsorbate System: II. The Henry Region. *Langmuir* **2009**, *25*, 7359–7367.

(27) Breck, D. W. *Zeolite Molecular Sieves*; Wiley: New York, 1974.

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