Equilibrium Isotherms of CH_4, C_2H_6, C_2H_4, N_2, and H_2 on Zeolite 5A Using a Static Volumetric Method

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Adsorption data for CH_4, C_2H_6, C_2H_4, H_2, and N_2 on the zeolite 5A adsorbent (W. R. Grace & Davision Co.) were obtained at 293 K, 303 K, and 313 K. The pressure range studied was 0 to 2 MPa, which covers the operating pressure range in pressure swing adsorption (PSA) units. Experimental data were correlated by the Langmuir and Langmuir−Freundlich (L−F) equations for several isotherm models. This paper compares the Langmuir and L−F equations. Despite the relative simplicity of both isotherms, the experimental data were fit very well. In addition, the Clausius−Clapeyron equation was employed to calculate the isosteric enthalpy of adsorption.

Introduction

A variety of molecular sieves are used for a wide range of purposes in different industries. The successful applications of these materials as industrial adsorbents depend on the proper development of adsorption cycles, the correct selection of the adsorbent, and suitable operating conditions. One necessary tool when choosing a selective adsorbent is the adsorption equilibrium data. In addition, adsorption equilibria are the key information for the design of practical separation processes based on adsorption mechanisms. Moreover, they are used to simulate the adsorption process. There are several reviews of adsorption equilibrium available in the literature.[1−9] However, there are few isotherm data for various adsorbents at high pressure.

Single and multicomponent adsorption equilibria data at high pressure are needed to design a separation system based on a PSA process. However, multicomponent adsorption equilibria data are difficult to obtain directly. The multicomponent adsorption equilibrium is usually predicted using single-component isotherm information.[10−13] Therefore, researchers require basic adsorption data (equilibrium and kinetic) for a wide range of experimental conditions.

In recent years, there has been renewed interest in high-purity hydrogen owing to environmental pollution, industrial development, the exhaustion of energy sources, and other factors. Hydrogen energy is spotlighted as one of the new, clean energy sources. Most industrial hydrogen is produced from steam reforming of light hydrocarbons, partial oxidation of heavy hydrocarbons, recovery from coke oven gas, and water electrolysis.[14] The conversion of methane/natural gas to hydrogen and elemental carbon by direct pyrolysis is attractive commercially because of the readily available supply of natural gas and because the hydrogen product is clean and pollution-free (CO and CO_2).[15]

This paper presents the adsorption equilibria of the single components of methane and hydrogen, which are the main products of natural gas pyrolysis, with minor products on the zeolite 5A adsorbent. This paper reports the single-component adsorption equilibria of CH_4, C_2H_6, C_2H_4, H_2, and N_2 at 293.15 K, 303.15 K, and 313.15 K and at pressures up to 2 MPa. Adsorption equilibria were measured using a volumetric technique.[1,14] The experimental data were correlated by the Langmuir and Langmuir-Freundlich (L−F) equations.

Table 1. Characteristics of Zeolite 5A Adsorbent

adsorbent	zeolite 5A[a]
form	sphere
nominal pellet size/mesh	4−8
average pellet size/mm	1.57
pellet density/$g \cdot cm^{-3}$	1.16
intravoid fraction	0.29
macrovoid fraction	0.36
average macropore radius/Å	986
average heat capacity/$J \cdot g^{-1} \cdot K^{-1}$	0.92
weight fraction of crystals	0.83

[a] W. R. Grace & Davision Co.

Experimental Section

Material. Zeolite 5A (W. R. Grace & Davision Co.) was used as the adsorbent. Table 1 shows the properties of zeolite 5A. Before the measurement, the adsorbent was activated at 623.15 K in an electronic furnace overnight and then dried at 473.15 K in a vacuum oven (<1 Pa) for more than 12 h to remove impurities. The purities of each adsorbate were 99.9% hydrogen, 99.99% methane, 99.999% nitrogen, 99.9% ethylene, and 99.5% ethane. The properties of zeolite 5A and the purities of each adsorbate were obtained from the manufacturers' reports.

Apparatus. Adsorption equilibria data were obtained using a static volumetric method. Figure 1 shows a schematic representation of the apparatus. In this method, the amount of gas in the system is determined using appropriate pressure, volume, and temperature measurements. The pressure and temperature were recorded using a mobile recorder (MV 100, Yokogawa Co.). Moreover, the temperature in each cell was measured using K-type thermocouple operated within an accuracy of ±0.01 K; the pressure was measured using a pressure transducer with an accuracy of 0.1%. The adsorption cell, loading cell, and all connection tubes consisted of stainless steel. The volumes of the adsorption and loading cells were 521.61 ±

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10.1021/je0498309 CCC: $30.25

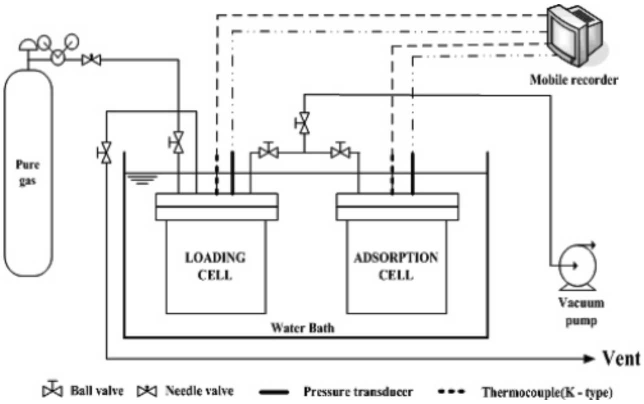

Figure 1. Apparatus of static volumetric method.

Table 2. Adsorption Isotherm Data for H_2 onto Zeolite 5A

T/K					
293.15		303.15		313.15	
P/ (kPa)	q/ (mol·kg^{-1})	P/ (kPa)	q/ (mol·kg^{-1})	P/ (kPa)	q/ (mol·kg^{-1})
171.710	0.036	156.634	0.032	164.860	0.031
323.131	0.069	362.575	0.063	329.567	0.049
554.432	0.100	580.272	0.093	492.266	0.065
727.135	0.130	770.538	0.122	633.224	0.085
984.796	0.162	976.094	0.143	774.893	0.107
1229.894	0.189	1260.246	0.166	913.401	0.118
1457.846	0.217	1503.302	0.188	1117.146	0.134
1692.801	0.244	1715.983	0.209	1346.451	0.151
1849.863	0.265	1854.667	0.222	1613.296	0.171
average deviation value					
Langmuir	L−F model	Langmuir	L−F model	Langmuir	L−F model
0.025507	0.028722	0.02373	0.031976	0.03966	0.053553

Table 3. Adsorption Isotherm Data for CH_4 onto Zeolite 5A

T/K					
293.15		303.15		313.15	
P/ (kPa)	q/ (mol·kg^{-1})	P/ (kPa)	q/ (mol·kg^{-1})	P/ (kPa)	q/ (mol·kg^{-1})
41.756	0.290	41.296	0.227	47.044	0.202
103.767	0.652	102.027	0.529	113.942	0.460
235.419	1.184	187.810	0.866	200.700	0.738
420.489	1.639	284.166	1.159	298.818	0.982
634.193	1.918	394.592	1.390	398.391	1.180
861.242	2.077	554.154	1.639	572.813	1.432
1091.149	2.170	747.186	1.833	756.763	1.615
1343.012	2.234	955.024	1.966	951.121	1.750
1621.575	2.275	1224.356	2.078	1219.171	1.879
		1513.713	2.138	1519.251	1.982
average deviation value					
Langmuir	L−F model	Langmuir	L−F model	Langmuir	L−F model
0.037393	0.014629	0.032952	0.010481	0.023865	0.006009

1 mL and 522.73 ± 1 mL, respectively, as determined from the expansion of helium gas. To minimize the dead volume, $^1/_8$ in. tubes and $^1/_8$ in. valves were used. During the experiments, the adsorption and the loading cells were immersed in a water bath (SWB-20, Jeio Tech.) maintained at a given temperature using a refrigeration circulator (RBC-11, Jeio Tech.). A vacuum pump was used to eliminate gaseous impurities from the adsorption and loading cells.

Table 4. Adsorption Isotherm Data for N_2 onto Zeolite 5A

T/K					
293.15		303.15		313.15	
P/ (kPa)	q/ (mol·kg^{-1})	P/ (kPa)	q/ (mol·kg^{-1})	P/ (kPa)	q/ (mol·kg^{-1})
122.149	0.246	116.720	0.208	124.164	0.166
235.057	0.487	224.866	0.417	216.020	0.322
333.933	0.652	345.769	0.601	328.875	0.481
446.690	0.799	474.178	0.758	435.853	0.615
543.487	0.939	644.533	0.925	540.843	0.719
693.430	1.090	773.642	1.029	660.919	0.845
857.928	1.217	864.716	1.096	761.366	0.922
1045.339	1.337	1051.503	1.222	876.719	0.991
1212.184	1.457	1228.146	1.329	1029.277	1.122
1367.507	1.589	1421.566	1.418	1198.957	1.237
1537.275	1.669	1558.689	1.488	1366.631	1.303
1707.392	1.742	1678.375	1.545	1567.364	1.373
				1831.217	1.469
average deviation value					
Langmuir	L−F model	Langmuir	L−F model	Langmuir	L−F model
0.020365	0.02066	0.016446	0.015805	0.034325	0.014357

Table 5. Adsorption Isotherm Data for C_2H_4 onto Zeolite 5A

T/K					
293.15		303.15		313.15	
P/ (kPa)	q/ (mol·kg^{-1})	P/ (kPa)	q/ (mol·kg^{-1})	P/ (kPa)	q/ (mol·kg^{-1})
43.667	0.699	57.564	0.591	68.423	0.634
55.642	1.596	73.342	1.441	89.312	1.478
103.079	2.470	150.807	2.381	161.268	2.240
223.654	2.769	321.918	2.704	332.889	2.491
390.447	2.891	516.209	2.765	478.304	2.604
539.669	2.941	767.176	2.808	608.125	2.657
710.841	2.967	955.199	2.836	770.337	2.692
903.151	2.977	1161.662	2.868	952.181	2.711
1124.106	2.979	1335.857	2.878	1128.760	2.727
1329.808	2.971	1519.224	2.890	1321.332	2.758
1531.600	2.959	1720.049	2.880	1523.283	2.779
1660.280	2.974	1892.931	2.870	1672.508	2.809
average deviation value					
Langmuir	L−F Model	Langmuir	L−F model	Langmuir	L−F model
0.119843	0.044135	0.127552	0.052418	0.114066	0.050332

Experimental Procedure. Before all operations, the adsorbent was regenerated to eliminate trace impurities. Therefore, the adsorbent was maintained in an electronic furnace at 623.15 K overnight and regenerated under vacuum (<1 Pa) at 473.15 K for at least 12 h using a drying vacuum oven. Then, the adsorbent was put into the adsorption cell. Traces impurities in the adsorption and loading cells were eliminated using a vacuum pump. Pure gas 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.[1,14]

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

$$\frac{PV}{ZRT}\bigg|_{l_1}+\frac{PV}{ZRT}\bigg|_{a_1}=\frac{PV}{ZRT}\bigg|_{l_2}+\frac{PV}{ZRT}\bigg|_{a_2}+qM \tag{1}$$

Table 6. Adsorption Isotherm Data for C_2H_6 onto Zeolite 5A

T/K					
293.15		303.15		313.15	
P/(kPa)	*q*/(mol·kg^{-1})	*P*/(kPa)	*q*/(mol·kg^{-1})	*P*/(kPa)	*q*/(mol·kg^{-1})
61.422	0.657	62.302	0.561	62.323	0.488
92.960	1.360	97.281	1.278	95.355	1.180
171.171	1.879	177.407	1.724	183.257	1.674
320.054	2.103	308.674	1.926	324.630	1.889
468.594	2.172	488.874	2.030	479.453	1.980
587.915	2.202	637.995	2.084	657.475	2.023
711.676	2.230	790.483	2.110	821.506	2.041
839.012	2.235	972.674	2.125	1065.781	2.046
982.332	2.240	1121.043	2.130	1197.172	2.047
1137.783	2.229	1294.779	2.143		
1293.141	2.212				
1391.825	2.222				
average deviation value					
Langmuir	L−F model	Langmuir	L−F model	Langmuir	L−F model
0.086003	0.020108	0.101202	0.036393	0.128774	0.040851

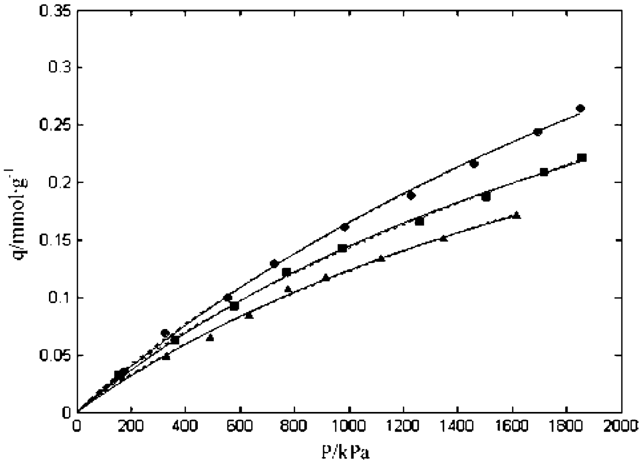

Figure 2. Hydrogen adsorption equilibria on zeolite 5A: ●, 293.15 K; ■, 303.15 K; ▲, 313.15 K; · · ·, Langmuir model; —, L−F model.

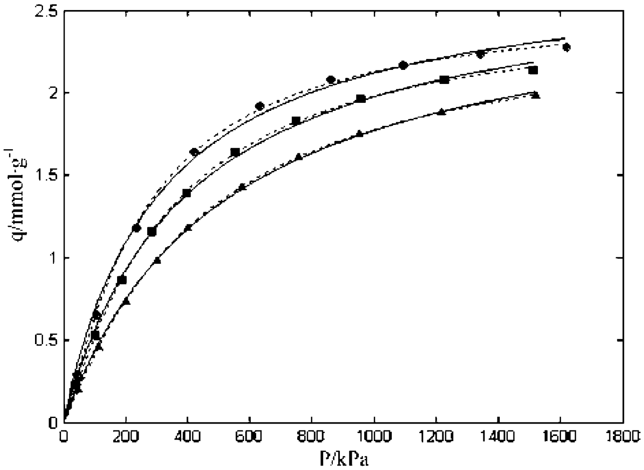

Figure 3. Methane adsorption equilibria on zeolite 5A: ●, 293.15 K; ■, 303.15 K; ▲, 313.15 K; · · ·, Langmuir model; —, L−F model.

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.

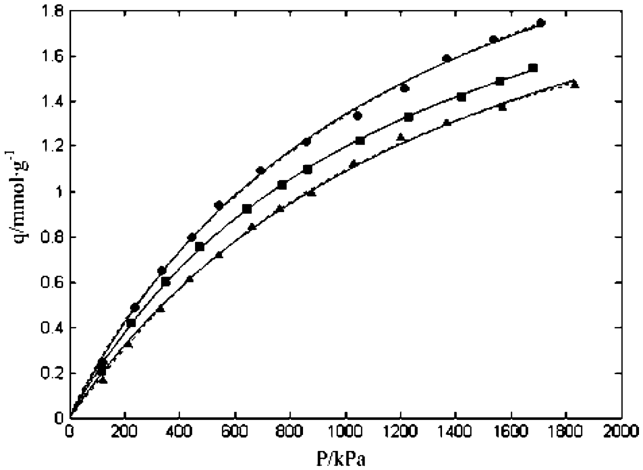

Figure 4. Nitrogen adsorption equilibria on zeolite 5A: ●, 293.15 K; ■, 303.15 K; ▲, 313.15 K; · · ·, Langmuir model; —, L−F model.

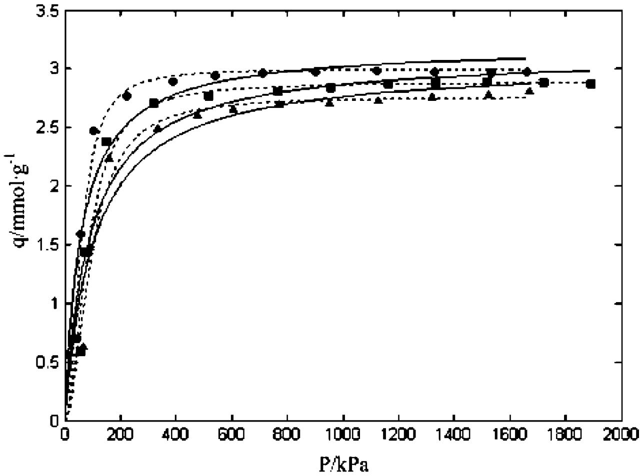

Figure 5. Ethylene adsorption equilibria on zeolite 5A: ●, 293.15 K; ■, 303.15 K; ▲, 313.15 K; · · ·, Langmuir model; —, L−F model.

Results and Discussion

Equilibrium data for hydrogen, methane, nitrogen, ethylene, and ethane onto zeolite 5A were obtained at 293.15 K, 303.15 K, and 313.15 K and at pressures up to 2 MPa. Experimental data are summarized in Tables 2 to 6 and presented graphically in Figures 2 to 6. In these Figures, solid and dotted lines show the fitted curves using the Langmuir and Langmuir−Freundlich equations, respectively.

For each set of equilibrium data, rigorous assessments were performed and correlated by several pure-species equilibrium models. The isotherm equations used in this study were the Langmuir (eq 2) and Langmuir−Freundlich (eq 3) equations.[1,16]

The mathematical forms of each model are

$$\text{Langmuir} \qquad q = \frac{q_m BP}{1 + BP} \tag{2}$$

$$\text{Langmuir−Freundlich} \qquad q = \frac{q_m BP^{1/t}}{1 + BP^{1/t}} \tag{3}$$

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

The Langmuir equation is widely used for physical adsorption from either gas or liquid solution. This expression is obtained from the assumed rate expressions of both

Table 7. Langmuir Adsorption Isotherm Parameters for CH_4, C_2H_6, C_2H_4, N_2, and H_2 onto Zeolite 5A

	q_m/(mmol·g^{-1})			B/(Mpa^{-1})		
adsorbate	293.15 K	303.15 K	313.15 K	293.15 K	303.15 K	313.15 K
H_2	0.79481	0.54464	0.45723	0.262423	0.360819	0.370688
CH_4	2.7703	2.75403	2.68604	3.257242	2.53511	1.935258
N_2	2.96689	2.62543	2.70452	0.823291	0.837207	0.671601
C_2H_4	3.19835	3.12487	3.04976	16.79319	11.1021	9.634444
C_2H_6	2.46492	2.38894	2.34239	11.84851	10.04194	9.259215

Table 8. Langmuir−Freundlich Adsorption Isotherm Parameters for CH_4, C_2H_6, C_2H_4, N_2, and H_2 onto Zeolite 5A

	q_m/(mmol·g^{-1})			B/(Mpa^{-1})			t^{-1}		
adsorbate	293.15 K	303.15 K	313.15 K	293.15 K	303.15 K	313.15 K	293.15 K	303.15 K	313.15 K
H_2	0.69627	0.44963	0.30114	0.292425	0.396941	0.440365	1.03012	1.0817	1.21089
CH_4	2.55718	2.52621	2.47325	3.281619	2.56906	1.972958	1.17977	1.14962	1.11123
N_2	3.01897	2.50749	2.17567	0.818159	0.849346	0.69055	0.9883	1.03329	1.17215
C_2H_4	2.93703	2.83657	2.70153	63.52213	20.02428	13.48502	3.24435	2.9608	3.02911
C_2H_6	2.21825	2.10668	2.0248	16.87856	13.57316	13.08088	2.56611	2.3493	2.5134

adsorption and desorption. The Langmuir−Freundlich equation simply combines the Langmuir and Freundlich equations. However, the Langmuir−Freundlich equation with three parameters should produce a better fit than does the Langmuir isotherm, which has only two parameters.

The isotherm parameters were obtained from a nonlinear regression using the least-squares method. The program Matlab was used to determine the adsorption curve parameters of each adsorption system. The nonlinear least-squares programs were solved using Gauss−Newton or Levenberg−Marquardt methods.[17] In addition, the following objective function was used in this study:

$$\varphi = \min \sum_j (N_j^{\text{obsd}} - N_j^{\text{calcd}})^2 \tag{4}$$

where N_j^{obsd} represents the experimental data on the amount adsorbed and N_j^{calcd} represents the correlation results. Moreover, the deviation parameter (eq 5) for the amount adsorbed, D, was used to compare the correlation results with the experimental data, where k is the number of datum points. The average deviation parameters for each component are shown in Tables 2 to 6.

$$D = \frac{1}{k}\sum_i^k \left| \frac{N_i^{\text{obsd}} - N_i^{\text{calcd}}}{N_i^{\text{obsd}}} \right| \tag{5}$$

Of the five types of physical adsorption defined by Brunauer et al.,[18] the experimental isotherm data closely resembled the I-type Langmuir isotherm. The I type represents single molecular adsorption and applies to microporous adsorbents with small pore sizes.[1] This suggests that the adsorption equilibrium is dominated by adsorbent−adsorbate interactions rather than adsorbate−adsorbate interactions. For all of the systems, the isotherm curves showed nonlinearity, except for hydrogen, as stated previously. This is attributable to the pore sizes of the adsorbent and active sites. In addition, surface heterogeneity depends on the relative sizes of the adsorbate and active sites.

The amount of adsorbed ethane and ethylene increased dramatically at pressure of less than 0.2 MPa. Besides, the amounts of adsorbed methane and nitrogen are found to be smaller than the amounts of adsorbed ethane and ethylene at the same pressure. The data indicate that the molar amount of adsorbed methane exceeds that of ethane above 1.4 MPa.

Equations such as the Langmuir, Freundlich, Langmuir−Freundlich, Toth, Unilan, Dubinin−Radushkevich, and others are useful for describing the adsorption of gases and vapors.[1,2,9,14,19] We compared two of these equations and found that the L−F model showed better performance than the Langmuir model in terms of fit accuracy except for hydrogen. Although the Langmuir isotherm shows good fits for methane, nitrogen, and hydrogen, the L−F model shows excellent fits for all five components. The isotherm parameters for all of the gases studied are tabulated in Tables 7 and 8.

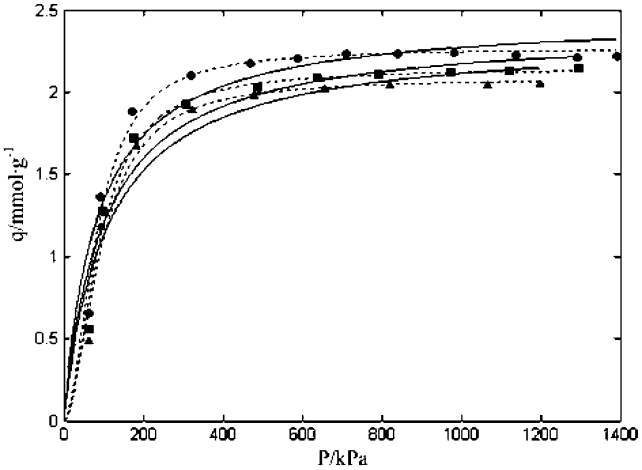

Figure 6. Ethane adsorption equilibria on zeolite 5A: ●, 293.15 K; ■, 303.15 K; ▲, 313.15 K; · · ·, Langmuir model; —, L−F model.

In this study, the isosteric enthalpy of adsorption[20,21] was calculated from the temperature dependence of the equilibrium capacity using the Clausius−Claypeyron equation (eq 9)[20] along with the Langmuir−Freundlich isotherm.

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

where q_{st} is the isosteric enthalpy of adsorption.

To obtain the enthalpy of adsorption, an accurate pressure and temperature for a given adsorption capacity are necessary. In this study, the Langmuir−Freundlich model was used because it fit the data more accurately than the Langmuir model did.

As shown in Figure 8, the isosteric enthalpies of adsorption varied with the surface loading on zeolite 5A. For methane, ethane, and ethylene, the isosteric enthalpy of adsorption increased gradually and then dramatically. In addition, hydrogen and nitrogen showed different tendencies. As stated by Hill,[20] when the surfaces are energetically homogeneous and there is no interaction between adsorbed

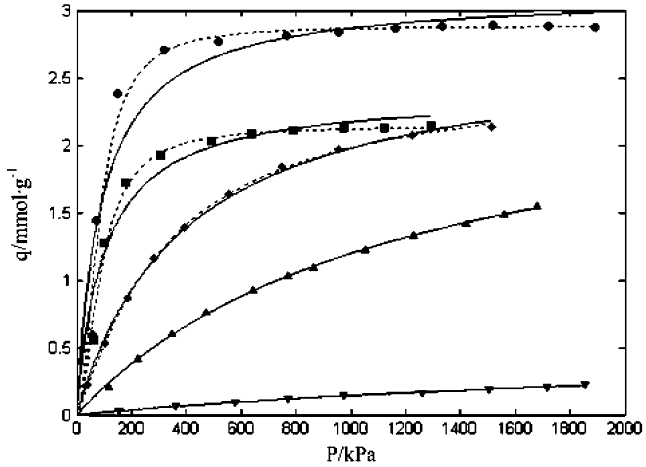

Figure 7. Measured and fitted isotherms of H_2, CH_4, N_2, C_2H_4, and C_2H_6 on zeolite 5A at 303.15 K: ▼, H_2; ◆, CH_4; ▲, N_2; ●, C_2H_4; ■, C_2H_6; · · ·, Langmuir model; —, L−F model.

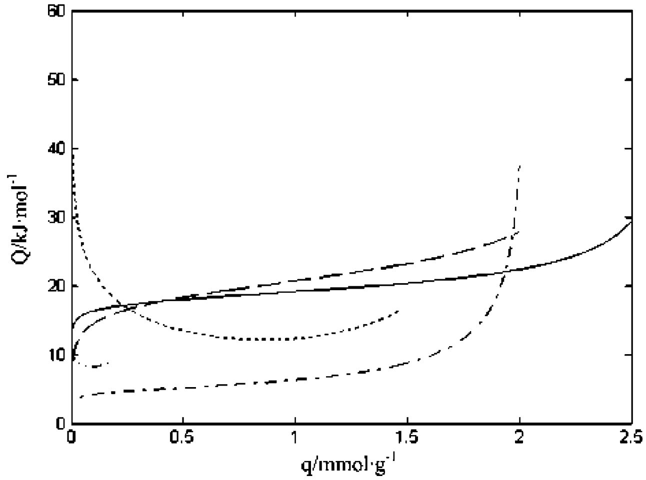

Figure 8. Isosteric enthalpy of adsorption with respect to surface loading on zeolite 5A: - - -, CH_4; -·-, C_2H_6; —, C_2H_4; · · ·, N_2; -··-, H_2.

molecules, the isosteric enthalpy of adsorption is independent of the amount adsorbed. However, if different levels of surface energy exist and the interactions between adsorbed molecules cannot be neglected, then the isosteric heat of adsorption varies with the surface coverage.

Conclusions

This study measured the adsorption equilibria of the pure gases hydrogen, methane, nitrogen, ethylene, and ethane onto zeolite 5A in the pressure range of 0 to 2 MPa at 293.15 K, 313.15 K, and 313.15 K using a static volumetric method. The Langmuir and Langmuir−Freundlich equations for correlating experimental data were compared. The Langmuir−Freundlich equation was more accurate than the Langmuir equation for all species. The Clausius−Clapeyron equation was used to calculate the isosteric enthalpy of adsorption and indicated that zeolite 5A has an energetically heterogeneous surface.

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Received for review May 3, 2004. Accepted September 16, 2004.

JE0498309