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High Pressure Adsorption Studies of Ethane and Ethylene on Clay-Based Adsorbent Materials

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Bentonite clay is tailored in three different ways to produce porous materials viz. PCH1, PCH2, and PILC, where PCH1 and PCH2 are two different clay heterostructures and PILC is a Zr-oxide pillared clay. Surface characterization materials shows that both of PCHs have a higher surface area than PILC, and have micro and mesoporosity, where PILC is basically a microporous. DRIFT and X-ray techniques were used to investigate the surface-groups and height of micropores in PCHs and PILC, respectively. Adsorption isotherms of ethane and ethylene were measured on these materials up to high pressure (1000 kPa) under different temperatures, and by processing the obtained data these materials were evaluated for their aptness for ethane ethylene separation. Isosteric heats of adsorption were observed higher for ethylene than ethane during initial surface coverage for each material-gas system. Interaction in each material-gas system with gradual increase in pressure was elucidated with the help of isosteric heat curves. Adsorption performances of these materials were compared with already studied materials (reported by other workers for ethane/ethane separation). Comparison was based on selectivity and working capacity, which are the two decisive parameters for screening suitability of any adsorbent material (for PSA application).

Keywords adsorption; adsorption heats; ethane and ethylene; pillared clays; porous clay heterostructures; selectivity

INTRODUCTION

Separation of light olefins from analogous paraffins, such as ethane/ethylene or propane/propylene, by adsorption processes has been recognized as an imperative challenge (1), as ethylene and propylene are important building blocks in the petrochemical industry. For instance, the worldwide annual demand of ethylene is more than 90 million tons, which makes it one of the largest commodities in the plastics and rubber industries (2–4). Generally, the separation of ethylene from an ethane/ethylene mixture is carried out by a low-temperature/high pressure distillation technique, but due to proximity in the volatilities of these two gases this process becomes highly energy consuming, which ultimately raises the price of ethylene by 75% (2–4). Eventually, for such separations one more promising and cost-effective alternative process is separation via adsorption on porous adsorbents. In the past few years, various studies have been reported in the literature which focused on this subject with the help of several types of adsorbents and methodologies (2–14). Some studies show that with such a process olefins may be separated and then recovered by displacement desorption or temperature swing (15), but there is a risk in the later process as the polymerization reaction of the olefins may occur. However, this risk can be avoided if a process of pressure swing adsorption (PSA) (15,16) could be used, where the shape of the adsorption isotherm plays an important role. As for example, in PSA, the regeneration is made by lowering pressure and therefore, an isotherm which is too steep at low pressures, i.e., type I in the IUPAC classification (17), would not reflect the desired characteristics even if the olefin/paraffin separation is favorable. Generally, with PSA or TSA processes the separation is attained on the basis of either equilibrium selectivity or kinetic selectivity. There are only few studies on kinetic selectivity for the ethane/ethylene systems have been reported (6,14), since separations based on equilibrium selectivity are more common and easy to operate (16). Further, the majority of the studies available in literature are based on the adsorption experimental data, which is up to ambient pressure (1 atm), and as obvious such studies are usually not sufficient to predict the separation conditions in the PSA process, where adsorption takes place at higher pressure.

Several classes of adsorbents have been considered for the ethane/ethylene separation viz. porous materials such as zeolites (13,18), activated carbons (8,11), silica (19), titanosilicates (4,7), or non-porous materials (3). It has been observed that the surface modification of various types of materials can improve the adsorption selectivity to a larger extent. For example modification of material surface with silver or copper enhances the adsorption of the ethylene,

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and consequently the adsorbent selectivity, due to the π-complexation by the double bond of the olefin (2,5,12). However, the presence of silver may always increase the risk of explosion, particularly when the gaseous mixture to be separated is contaminated, for instance with acetylene. Another class of modified material is porous clays heterostructures (PCHs), which are obtained from clays by the gallery templated approach, as discussed elsewhere (20). In brief, to obtain PCHs the clay layers are first expanded by long-chain cations, such as cetyltrimethylammonium, and then the polymerization of a silica source, in the presence of a long-chain amine occurs between the clay layers. Commonly, tetraethoxysilane is the most used silica source (20,21), but we have noticed and demonstrated it in our previous work (22) that surface modification by polymerization of other silica sources, (such as phenyltriethoxysilane) is also an important methodology for changing the adsorption properties (selectivity) of materials. Likewise pillared interlayered clays (23) (PILCs) also represent clay based modified material, which are obtained from the intercalation of clays with oligomeric polyoxications. After calcination these polyoxications decompose into the respective oxides which form pillars within the clay layers. An important difference between both materials is that PILCs are essentially microporous materials (pore widths less than 2 nm) (17) whereas PCHs have pores in the range of the micropores as well as mesopores (pore widths between 2 and 50 nm) (17).

From what was briefly exposed above, the olefin/paraffin separation by adsorption is an important topic of research, and a number of issues are still under study. Therefore, in this work we studied the adsorption of ethane and ethylene up to high pressure (1000 kPa) on three modified porous materials (prepared from natural clay) at different temperatures. Isosteric heats of adsorption for each adsorbent-gas system were estimated. Two PSA related applied parameters (Selectivity and Working capacity) of these three porous materials were estimated and compared with some other studied materials. The novelty of this work is inherent in high pressure adsorption studies of ethane and ethylene on these clay based materials, which (to the best of our knowledge) has not been studied before.

MATERIAL AND METHODS

Materials

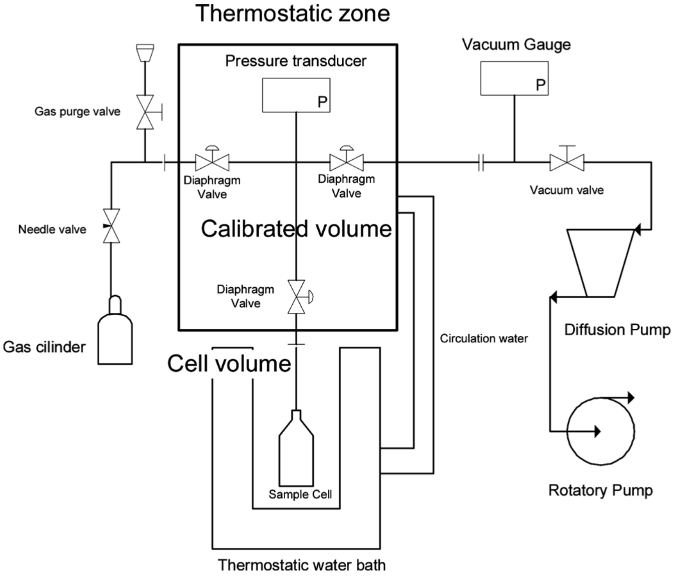
Three different materials (two different PCHs and a PILC) were prepared from Bentonite clay, which was obtained from Benavila, Portugal. In the following text these materials are being referred to as PCH1, PCH2, and PILC. The method of preparing PCH1 was adopted from literature (20,21), in which a suspension of 1 g clay and 100 ml distilled water was mixed with 4.8 ml solution of 0.5 M cetyltrimethylammonium bromide (CTAB) (Aldrich) solution. The solution was stirred overnight at 50°C and then centrifuged-washed repeatedly until pH $\approx$ 7 to separate the solid from the solution. The solid so obtained was air dried and stirred with 5.3 ml of decylamine (Aldrich, 95%) for 20 minutes, after that 35.5 ml of TEOS (Aldrich, 98%) was added and stirred for more than 3 h. The obtained suspension was then centrifuged and left for drying for some days, after which the sample was calcined at 650°C for 5 h with a slow ramp (1°C/min). Similarly, PCH2 was also prepared by an already optimized method which is reported in several reports (22,24). In this method a suspension of 1 g clay was prepared in 100 ml distilled water and it was stirred with 4.8 ml of 0.5 M CTAB (Aldrich) solution overnight, at 50°C. Now, to separate the solid from the solution it was centrifuged-washed repeatedly until pH $\approx$ 7. Further, the solid was added to 5.3 ml of decylamine (Aldrich, 95%), the same amine used for PCH1, and stirred for 20 min. Then a mixture of two silica sources i.e., TEOS (Aldrich, 98%), 32.3 ml and 3.2 ml of phenyltriethoxysilane, PhOS (Flucka, 98%) was added to it. The mixture was stirred for 3 h and then centrifuged and air-dried overnight. In the end, to remove CTAB and decylamine molecules from the porous structure, the dried sample was refluxed with 75 ml of 1 M HCl/ethanol. The resulted sample was then dried in an oven at 100°C for overnight.

PILC was prepared by following a procedure which has already been optimized and discussed in our previous work (25). In this procedure, a solution of 0.1 M in $ZrOCl_2$ (Merck, 99%) was added, dropwise and under continuous stirring, to a suspension of 1.0 g of clay in 100 ml of water. The relation of Zr and clay in $mmol \cdot g^{-1}$ was 2.5. The intercalation occurred for 2 h at 40°C, after which it was centrifuged and the solid was washed by dialysis until its conductivity reached to $<1\,mS \cdot m^{-1}$. The intercalated clay was then calcined for 2 h at 350°C.

Methods

In the present study, nitrogen (Air Liquide, 99.999%) physicsorption experiments were performed at −196°C using a volumetric apparatus (NOVA 2200e, from Quantachrome). For each experiment the samples (about 0.2 g each) have been degassed for 2.5 h at 200°C under a pressure lower than 0.133 Pa. Micro and mesopores volumes were obtained from the nitrogen adsorption isotherms by the α_S-method using nonporous hydroxylated silica as reference material (26).

The Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra were collected to confirm organic moieties inside PCHs, with the help of Nicolet 6700 FTIR spectrometer at $2\,cm^{-1}$ resolution at room temperature. The spectrometer was equipped with smart diffuse reflectance accessory and a DTGS TEC detector. XRD data of PILC (oriented mounts) were determined between 3° and 10°



SCH. 1. Representation of the volumetric apparatus (setup) used to carry out high pressure adsorption experiments.

with the help of a Philips PX 1820 instrument using the Cu Kα radiation.

Pure gas isotherms with ethane (Air Liquide, 99.995%) and ethylene (Gasin, 99.99%) were measured on each material. A conventional volumetric apparatus (Scheme 1) was used to carry out adsorption experiments. The apparatus was equipped with a pressure transducer (Pfeiffer Vacuum, APR 266) equipped and a vacuum system, which can maintain a vacuum better than 10^{-2} Pa. Different adsorption temperature was maintained with a stirred thermostatic water bath (Grant Instrument, GD-120). Before experiments, each sample was degassed for 2.5 h at 300°C. In the calculation of the adsorbed amounts, the non-ideality of the gas phase has been taken into account, by using the second virial coefficients.

THEORY/CALCULATION

Isosteric Heats

Isosteric heat of adsorption (q^{st}) is a key thermodynamic variable, particularly for the design of practical gas separation processes such as pressure swing and thermal swing adsorption. The q^{st} of a pure gas, at a given specific surface (n^{ads}) can be calculated from the adsorption isotherms of that gas at different temperatures using the Clausius-Clapeyron equation:

$$ln\left(\frac{p_1}{p_2}\right) = \frac{q_{st}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{1}$$

Where R is the gas constant, T_1 and T_2 are the two different temperatures, and P_1 and P_2 are the corresponding pressures.

Separation Parameters

The materials prepared in this work were studied for their possible application in ethane/ethylene separation by the determination of the pure gases adsorption isotherms, up to 1000 kPa. Information on the binary mixture separation was obtained from these isotherms using a method presented elsewhere (27), with calculation details described in our previous work (22). The main step of this method is the determination of the equation of state for the Gibbs free energy of desorption (27), calculated from the pure gas adsorption isotherms. For these calculations it is useful to have the experimental data described by analytical expressions and in the present work, the virial equation was used:

$$p = \frac{n^{ads}}{K}\exp(C_1 n^{ads} + C_2 n^{ads^2} + C_3 n^{ads^3}) \tag{2}$$

The integration of Eq. (2) give the free Gibbs energy of desorption,

$$\begin{aligned} G &= RT\int_0^p \frac{n^{ads}}{p}dp \\ &= RT\left(n^{ads} + \frac{1}{2}C_1 n^{ads^2} + \frac{2}{3}C_2 n^{ads^3} + \frac{3}{4}C_3 n^{ads^4}\right) \end{aligned} \tag{3}$$

Although in using this method different phase diagrams may be calculated (22), in the present case only selectivity vs. pressure was estimated, since it is the more significant and straightforward parameter when comparing different materials. For this, the evolution of the gas phase composition with the adsorbed phase composition was obtained by numerically solving Eq. (3) to determine the standard-state loadings (n_i^0) at a given value of G, for each one of the two pure gases (1 and 2). The components molar fraction in the gas (y) and adsorbed phases (x) were determined by solving the two-equation system:

$$py_1 = p_1(n_1^0)x_1 \tag{4a}$$

$$py_2 = p_2(n_2^0)x_2 \tag{4b}$$

The selectivity values, for a given gas phase composition and pressure, could then be calculated as:

$$S_{1,2} = \frac{(x_1/y_1)}{(x_2/y_2)} \tag{5}$$

The values obtained for the various studied materials were compared, and put forward variations in separation behavior that are related to the textural and chemical differences among the materials.

During cyclic adsorption processes, the gases are consecutively pressurized and depressurized on the material surface.

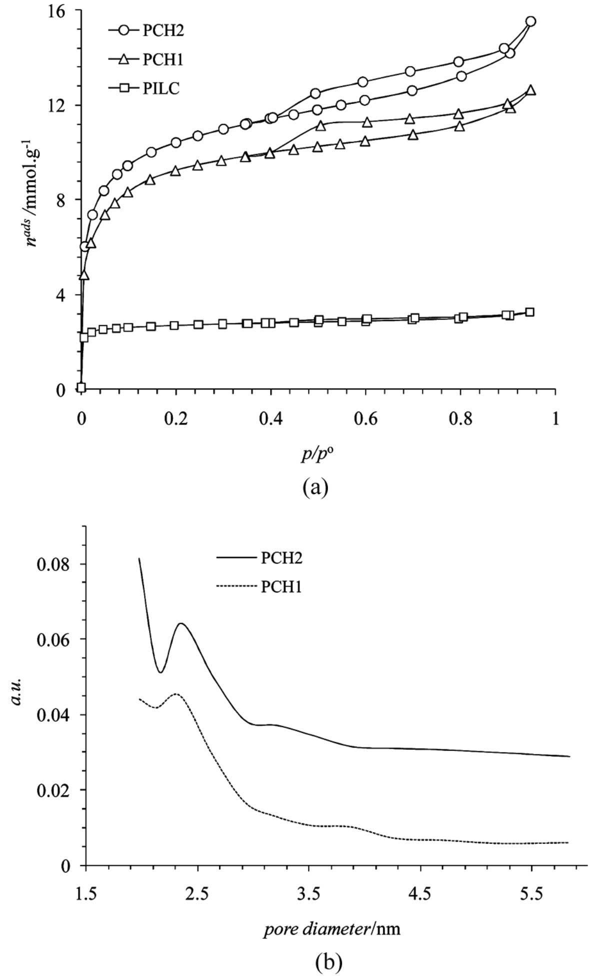
The later step (depressurization) is also known as the desorption step, during this step there is always some amount of gas that remains adsorbed, which is directly related to the magnitude of pressure at that point. The amount of gas, which was successfully desorbed, out of the total adsorbed amount is forwarded in successive cyclic steps for further purification. Therefore, the amount of gas desorbed from a unit mass of material during the desorption step of the cyclic adsorption process is known as the working capacity of the material in the respective process. In other words, the working capacity at a given equilibrium pressure is a definite fraction of the total amount of gas adsorbed on that pressure. It is calculated via subtracting the amount of gas that remains adsorbed during the desorption step of the cycle from the total adsorbed amount.

These methodologies may be regarded as approximate in nature, but they are essential tools for screening adsorbent materials as it helps in pointing out important directions for the appropriate synthesis and physical-chemical modifications of the materials (for further improvement in adsorption/separation characteristics).

RESULTS AND DISCUSSION

Characterization of Adsorbent Material

Nitrogen adsorption isotherms of PCH1, PCH2, and PILC are given in Fig. 1(a). It is apparent that the shape of the isotherms for both PCHs are similar, (type I+II, as per Brunauer, Deming, Deming, and Teller i.e., BDDT classification (17)), however, for the PILC isotherm it is of typical type I. The amounts adsorbed by PCHs are higher than PILC, and the order of amount adsorbed is PCH2 > PCH1 > PILC. Isotherms of both PCHs show a hysteresis loop (see Fig. 1a), which generally reflects the presence of mesoporosity, besides the microporous structure (which is due to type I shape). The presence of sufficient mesopore volumes in both PCH was again confirmed from the results obtained via α_s-method (Table 1). To further characterize the mesoporosity in these materials, the mesopore size distributions were calculated (Fig. 1b) from nitrogen adsorption isotherm data by the Broekhoff de Boer method with the Frenkel-Halsey-Hill equation (BdB-FHH) (28). This method is a well recognized and frequently used method to determine pore dimensions for the mesoporous materials, particularly where the pores are not cylindrical or well defined. The distribution shows a broad peak between 2.1–2.9 nm, and confirms the presence of mesoporosity in both PCHs. On the other hand type I shape of PILC a isotherm with a negligible hysteresis loop, confirms its predominantly microporous structure. Additional textural parameters of these materials were calculated from nitrogen isotherms and are compiled in Table 1. PCHs have more specific surface area (A_{BET}) than PILC and it decreases as PCH2 > PCH1 > PILC.



(a)

(b)

FIG. 1. (a) Nitrogen adsorption isotherms of studied materials (at −196°C); (b) Pore size distribution in PCH1 and PCH2.

DRIFT spectra of both, PCH1 and PCH2 are shown in Fig. 2. It shows a broad absorption band between 2800 and 3800 cm^{-1} which corresponds to the fundamental stretching vibrations of different types of hydroxyl groups, for example Si-OH. On comparing both spectra, the bands in PCH2 observed at 2950–3100 cm^{-1} correspond to the C−H stretching, and the bands at 1433, 1514, and 1400 cm^{-1} are due to C=C stretching and C-H bending

TABLE 1
Surface parameters of studied materials measured from nitrogen adsorption at −196°C

Material	A_{BET} (m$^2\cdot$g^{-1})	V_{micro} (cm$^3\cdot$g^{-1})	V_{meso} (cm$^3\cdot$g^{-1})	V_{total} (cm$^3\cdot$g^{-1})
PCH1	766	0.26	0.18	0.44
PCH2	859	0.26	0.35	0.61
PILC	216	0.08	0.03	0.11

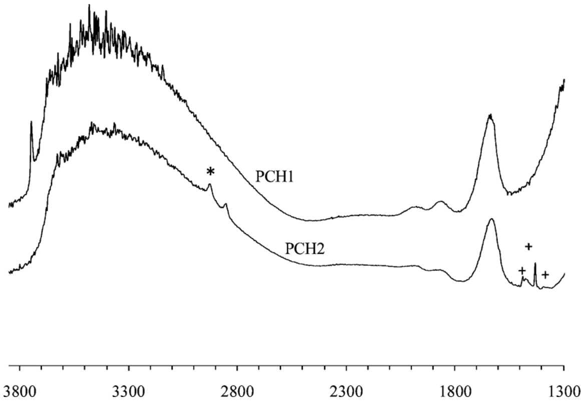


FIG. 2. DRIFT spectra of both PCH1 and PCH2.

modes (29,30), hence, confirming the existence of aromatic rings in PCH2, due to the use of phenyltriethoxysilane in this material.

In both spectra the peaks around 1630–1650 and 3450–3404 cm^{-1} are attributed to water molecules (O−H and H−O−H vibrations, respectively). X-ray Diffraction patterns for the PILC shows (figure not given) basal spacing (d_{001}), is 16.4 Å and when we subtract the thickness of the clay layer (9.6 Å) from it, it gives the height of micropores in PILCs as 6.8 Å. For PCH materials it was not possible to detect diffraction peaks when using either oriented or non-oriented mounts (31). This difficulty can be related with the fact, noticed previously by the other authors (21,32), that these types of materials present a poor long-range order (33).

Ethane and Ethylene Adsorption

Pure gas isotherms were obtained on these materials at different temperatures, see Fig. 3. The experimental data was applied to Eq. (2), for the isotherm fitting and calculation for related virial coefficients, which are listed in Table 2.

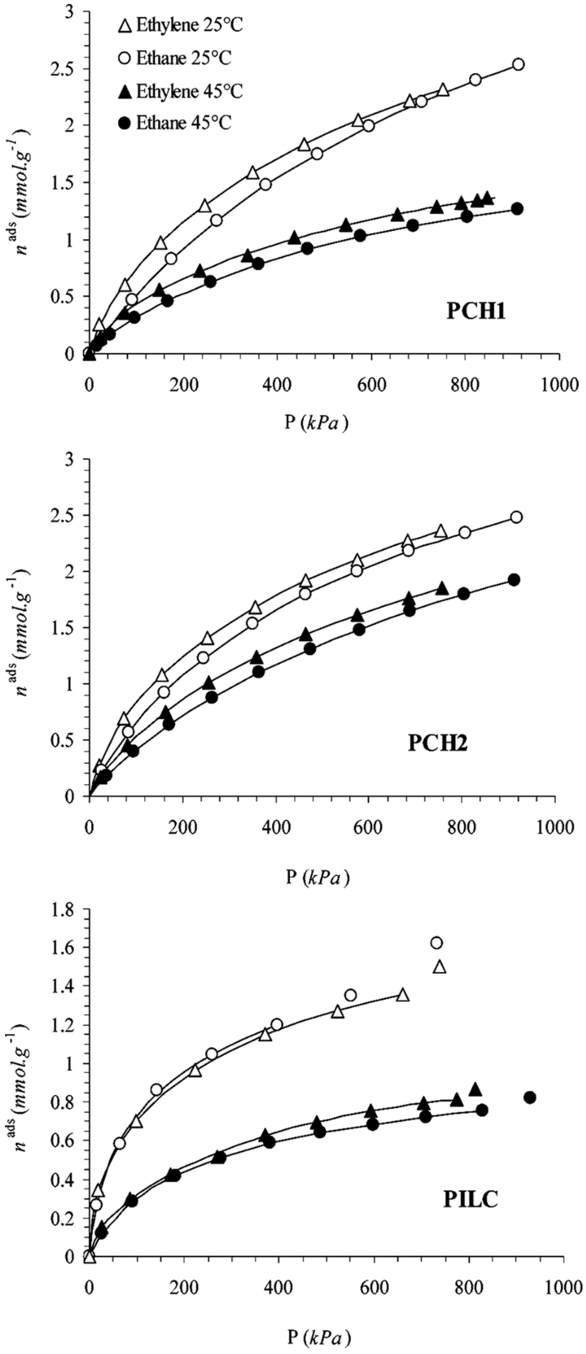


FIG. 3. Adsorption isotherm of ethane and ethylene on PCH1 and PCH2 at 25 and 45°C; on PILC at 0 and 45°C.

On both PCH the adsorption was studied at 25 and 45°C separately, however, on PILC the studies were made at 0 and 45°C separately, for both gases. At first glance it can be seen that the amount adsorbed with respect to pressure is of the same order in both PCHs but different (lower) in case of PILC. The isotherm studied on PCH1 shows that ethylene gets adsorbed to a greater extent than ethane. It is noteworthy here that the difference in the amount of ethane and ethylene adsorbed is more uniform at 45°C, though it decreases with pressure at 25°C. For further comparison, at equilibrium pressure of 750 kPa (common highest studied pressure), the ethylene and ethane get adsorbed 2.32 and 2.28 mmol · g^{-1} respectively at 25°C, and on increasing this temperature up to 45°C, these amounts fall to 1.29 and 1.17 mmol · g^{-1} for ethylene and ethane, respectively. Similarly, PCH2 is also showing more adsorption of ethylene than ethane. However, the mutual difference in the amount adsorbed for ethylene and ethane at the same pressure is constant after 100 kPa. At the common highest studied pressure, i.e., at 750 kPa, the ethylene and ethane get adsorbed 2.37 and 2.27 mmol · g^{-1} respectively, at 25°C, but 1.85 and 1.73 mmol · g^{-1} at 45°C for ethylene and ethane, respectively. PILC was found to be different towards these pairs of gases when compared with

TABLE 2
Parameters obtained from Langmuir virial fitting of experimental data

Material	Gas	Temp.	$K \times 10^2$ ($\mathrm{mmol \cdot g^{-1} \cdot kPa^{-1}}$)	C_1 ($\mathrm{g \cdot mmol^{-1}}$)	C_2* ($\mathrm{g^2 \cdot mmol^{-2}}$)	C_3* ($\mathrm{g^3 \cdot mmol^{-3}}$)
PCH1	C_2H_6	25°C	5.76	0.22	0.03	–
		45°C	0.48	1.63	−1.18	0.53
	C_2H_4	25°C	1.35	0.95	−0.23	0.04
		45°C	0.99	2.48	−1.58	0.54
PCH2	C_2H_6	25°C	0.94	0.64	−0.15	0.04
		45°C	0.55	0.77	−0.27	0.07
	C_2H_4	25°C	1.71	1.04	−0.24	0.04
		45°C	0.82	0.93	−0.26	0.06
PILC	C_2H_6	0°C	2.84	1.87	–	–
		45°C	0.45	0.94	1.57	–
	C_2H_4	0°C	9.76	6.15	−4.51	1.53
		45°C	1.52	7.64	−10.71	6.58

*For some isotherms, the values of second and third virial constants (C_2 and C_3) were neglected, for the sake of better fitting with experimental data.

PCHs. The extent of adsorption for both the materials was very close to each other, up to 400 kPa and 200 kPa at 0°C and 45°C respectively. It is interesting to note here that at the high pressure (beyond 500 kPa) and 0°C, the PILC was found to adsorb more ethane than ethylene at the same pressure. However, at 45°C, it is inversed at high pressure. In case of PILC the amount adsorbed at the highest studied pressure (733 kPa) for ethylene and ethane is 1.49 and 1.62 $\mathrm{mmol \cdot g^{-1}}$ at 0°C and 0.81 and 0.73 $\mathrm{mmol \cdot g^{-1}}$ at 45°C for ethylene and ethane, respectively.

To further compare adsorption tendencies (affinity for materials), the values of the amount adsorbed on each material at the highest studied common pressure are compiled in Table 3. Results are shown as $\mathrm{mmol \cdot g^{-1}}$ and $\mathrm{mmol \cdot m^{-2}}$, the later unit was chosen to compare the affinity of the material's surface for individual gas. It is evident from Table 3, that although, the adsorption capacity of PCHs are higher than PILC in terms of $\mathrm{mmol \cdot g^{-1}}$(due to their high surface area), but PILC has more affinity to adsorb ethane and ethylene as compared to PCH, which is clear from the higher adsorption capacity of PILC in terms of $\mathrm{mmol \cdot m^{-2}}$ (see Table 2).

Isosteric Heats of Adsorption

Isosteric heats of adsorption, q^{st}, were estimated from adsorption isotherms by the Clausius-Clapeyron

TABLE 3
Amount adsorbed by different material at highest common studied pressure on different temperature

Material	Gas	Temp.	Amount Adsorbed n_a in ($\mathrm{mmol \times g^{-1}}$)	$\times 10^3$ in ($\mathrm{mmol \times m^{-2}}$)	Respective pressure (kPa)
PCH1	C_2H_6	25°C	2.28	2.98	750
		45°C	1.17	1.53	750
	C_2H_4	25°C	2.32	3.03	750
		45°C	1.29	1.68	750
PCH2	C_2H_6	25°C	2.27	2.64	754
		45°C	1.73	2.01	754
	C_2H_4	25°C	2.37	2.76	754
		45°C	1.85	2.15	754
PILC	C_2H_6	0°C	1.62	7.5	733
		45°C	0.73	3.38	733
	C_2H_4	0°C	1.49	6.9	733
		45°C	0.81	3.75	733

equation (1). The variation in q^{st} with the surface coverage (amount adsorbed) is presented in Fig. 4. Heats measured in case of ethylene are always higher than that of ethane, except for PILC, where it falls below ethane after some extent of coverage.

In PCH1, (Fig. 4a) q^{st} was found increasing continuously with coverage, which can be ascribed to continuous increase in molecule-molecule interaction with a gradual filling of pores with gas molecules (13,34). During the adsorption of both gases, initially the total heat of adsorption is caused by a combination of surface-molecule and molecule-molecule interaction, but with gradual covering of the surface the previous interaction reduces, and only mutual interaction of molecules contributes to q^{st}, that initially causes a more steep plot which later (after $0.4\,\text{mmol}\cdot\text{g}^{-1}$) becomes less steep. Furthermore, due to the presence of π electrons, ethylene interacts with the surface more strongly than ethane, which resulted in a high heat, for ethylene ($20.3\,\text{kJ}\cdot\text{mol}^{-1}$) than for ethane ($14.1\,\text{kJ}\cdot\text{mol}^{-1}$). Evidently, both plots get aligned with an increase in the surface coverage (decrease in surface-molecule interaction). In case of PCH2 (Fig. 4b), the walls of the pores are functionalized with phenyl group, which interacts more strongly with ethylene than PCH1, and thereby causes high initial heats of adsorption for ethylene ($28.3\,\text{kJ}\cdot\text{mol}^{-1}$) than ethane ($21.3\,\text{kJ}\cdot\text{mol}^{-1}$). Here again, the high initial contribution of phenyl group and π electron clouds interaction decreases with coverage. It is noteworthy here that a strong interaction of ethylene with the surface prevents its further possibility for the molecule-molecule interaction. Therefore, contrary to PCH1 here the molecule-molecule interactions are not frequent enough and strong, to contribute significantly in total q^{st}. Most probably this could be the reason why the q^{st} values were not found to vary too much with the coverage in case of ethane adsorption.

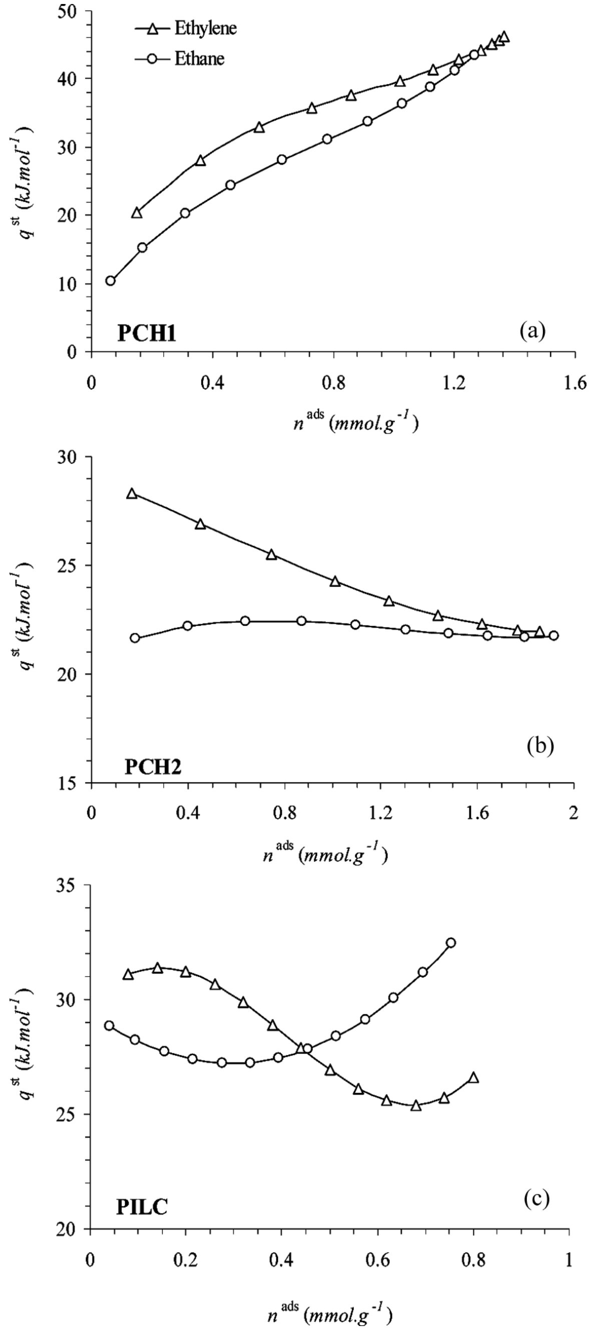


FIG. 4. Isosteric heats of ethane and ethylene adsorption (a) on PCH1 and (b) PCH2 (calculated between 25 and 45°C); (c) on PILC (calculated between 0 and 45°C).

PILC (Fig. 4c) show a different trend in heats plots. In the first part of the curve higher heats in ethylene adsorption were observed than for ethane, which is due to π electron clouds interaction, a situation that is similar to what was described for the PCHs. Since in ethane adsorption more molecules interact with each other as the coverage increases, therefore the heats of adsorption were found to increase as well. In contrast to it, ethylene molecules were initially being attached to the surface and do not interact mutually, therefore there is a decrease in heats with the surface coverage. However, after certain coverage the molecules are abundant enough for interaction, and they would cause a small increase in the latter part of curve.

Further, a comparison has been made in Table 4 between isosteric heat data from these materials and from those reported in literature for a similar pair of gases. The comparison shows that the results on these materials are within the results reported for various other clay based and inorganic synthetic materials. The high values of q^{st} for ethylene compared to ethane, indicates π interaction with the material surface, especially at low coverage.

Selectivity and Working Capacity

As already stated, these materials were also studied to investigate their suitability for separation applications

TABLE 4
Comparision of isosteric heats of adsorption on PCH1, PCH2, and PILC with other materials, reported in literature

	q_{st} (kJ/mol)		
adsorbent[a]	ethane	ethylene	ref
CuCl/TiO_2-PILC	20.08	57.32	35
CuCl/Al_2O_3-LP	22.59	51.04	35
CuCl/Al_2O_3-PILC	23.01	47.70	35
CuCl/ZrO_2-PILC	23.85	46.02	35
CuCl/Fe_2O_3-PILC	23.01	46.86	35
Ag^+resin	20.08	41.84	36
CuCl/Al_2O_3	22.18	48.95	36
Ag^+-Amberlyst 35	19.25	39.33	37
Ag^+-Amberlyst 15	23.43	37.66	37
Ag^+-Dowex 88	24.69	27.61	37
Olesorb-1	19.66	46.03	38
PCH1	16.21	23.02	present work
PCH2	21.89	28.25	present work
(Bentonite-ZrO_2)-PILC	29.48	31.45	present work

[a] PILC = pillared clay; LP = Laporte pillared clay; q^{st} values from the current work and literature are being reported at an adsorption loading of 0.2 mmol · g^{-1} of ethane or ethylene.

which can be made for instance by Vacuum Swing Adsoprtion (VSA) or Pressure Swing Adsorption, depending if the regeneration of the adsorbent is to be made by vacuum or by pressure decrease, respectively. The selectivity and working capacity of materials, that is, the remaining adsorption capacity after the regeneration step, are amongst the most important properties which determine the merit of any material for such a process. Therefore, these properties of PCHs and PILC were estimated and then compared with some already reported materials for ethane/ethylene adsorption in literature (4,11,13). Due to the reasons pointed out in the Introduction section, we did not compare our results with literature values obtained with adsorbents modified with silver or copper.

Selectivity of PCHs, PILC, and other reported materials, which are representative of different classes of adsorbents (molecular sieves, zeolite, and activated carbon), were calculated with Eq. (5). For such calculation raw isotherm data on reported materials was processed, along with current experimental data of present study. The plots of selectivity are shown in Fig. 5, where variation in selectivity with an increase in pressure (up to 100 kPa) has been reported at a fixed (0.5) binary composition of ethane\ethylene. Figure 5 shows that a molecular sieve in sodium form, i.e., ETS 10 (Na) (4) is highly selective and BPL activated carbon (11) was least selective.

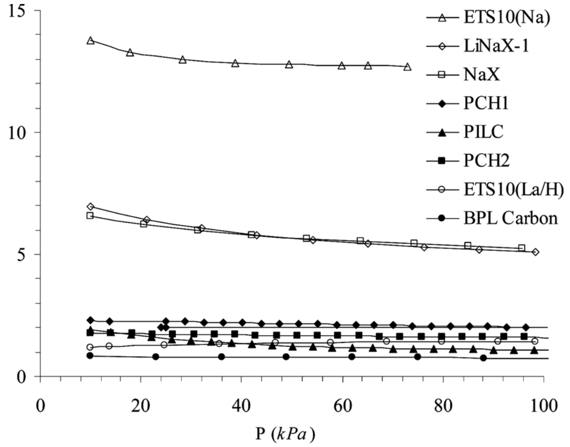


FIG. 5. Comparison in Selectivity of currently studied and previously reported materials (4,11,13) (for ethane\ethylene separation) with fixed (0.5) binary composition.

Among presently studied materials the PCH1 is more selective (range 2.3–2.0) than PCH2 (1.8–1.6) and PILC (1.9–1.1). At lower pressure PILC has selectivity comparable to PCH2 which decreases with increasing pressure. Therefore, on this parameter (selectivity) alone, our materials appear between the low selective materials.

The working capacity of these materials was calculated by subtracting the amount adsorbed by the respective material at a given regeneration pressure (1 Torr or 100 kPa), from the successive amount adsorbed at different equilibrium pressures. In Fig. 6, adsorption isotherms and working capacities of these materials have been compared. A comparative figure of adsorption isotherms on different materials up to various equilibrium pressures is shown in Fig. 6(a). Besides, the working capacity of these materials at a regeneration pressure of 1 Torr (0.133 kPa) is also shown (Fig. 6b). At a regeneration pressure of 1 torr, the working capacity of NaX and LiNaX-1 fall by only 1–19% and 1–29% of adsorption capacity. Similarly, this fall in case of BPL carbon, ETS 10 (Na), and ETS 10 (La/H) was 0.3–2.2%, 45–65%, and 0.6–3.1%, respectively. However, with PCHs and PILC this fall is negligible, i.e., 0.1–0.8% of adsorption capacity.

Further, a regeneration pressure of 1 Torr was selected to simulate the condition of VSA, where such low pressure is maintained during the vent off of the adsorbed gas. Nonetheless, VSA is a more expensive process than PSA. Besides, its operation is often more tedious due to the involvement of the extra pressure drop (with vacuum production). Conversely, in PSA, regeneration is made at ambient pressure, i.e., 1 atm (100 kPa). Therefore, the working capacity of all materials with a regeneration pressure of 100 kPa were also calculated and presented in Fig. 6(c). It is clear from this figure that under such conditions, only

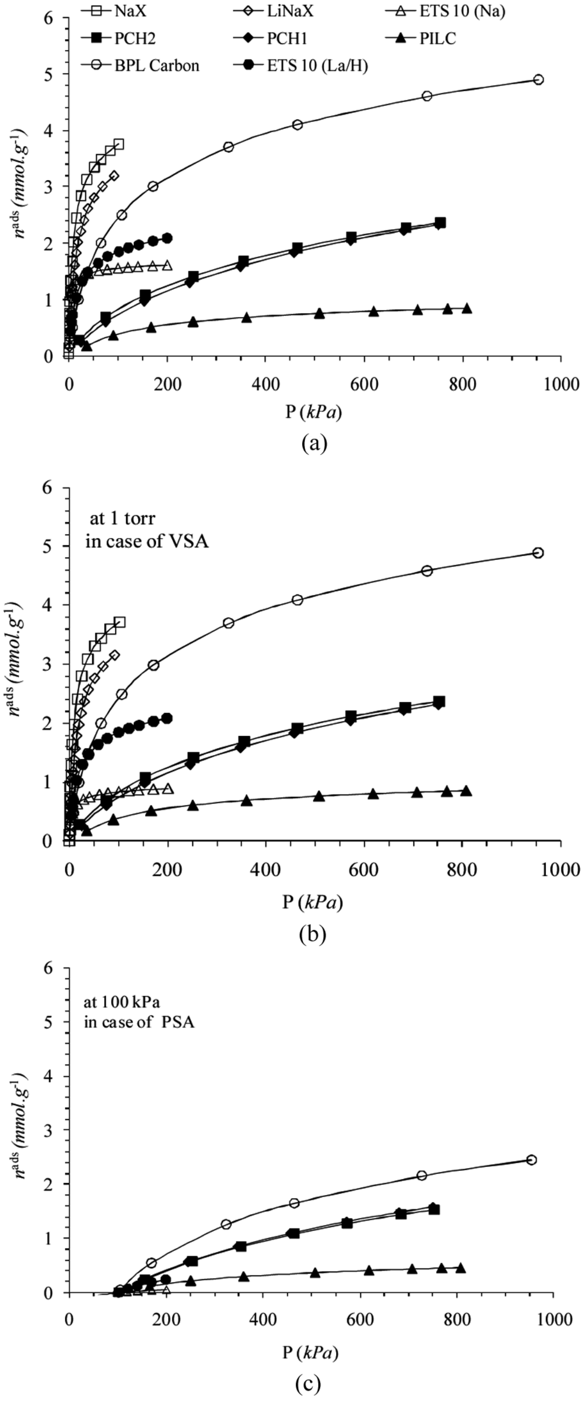


FIG. 6. A Comparison of working capacities of currently studied materials with other reported materials (4,11,13) under different regeneration conditions. (a) Simple ethylene adsorption isotherms reported/studied on different materials at 25°C; (b) working capacities of these materials at a regenerating pressure of 1 Torr; (c) at a regenerating pressure of 100 kPa.

BPL carbon, PCHs, and PILC has measurable working capacities. But the working capacity of BPL carbon get more decreased (60%) than with PCHs and PILC (32–46%). This decrease is much more in other materials, for example with ETS 10 (Na) and ETS 10 (La/H) this is 96 and 89%, respectively. Besides, the NaX and LiNaX1 were only reported up to 100 kPa (see Fig. 6a), therefore their working capacity could not be measured with this regeneration. Nevertheless, in the case of the latter materials, due to the high type I (IUPAC) character of the isotherms, it could be anticipated that the working capacity would not be favorable.

Finally, it is clear from the above results that instead of being highly selective, molecular sieves and zeolites are less suitable materials for PSA applications regarding the ethane/ethylene separation than BPL carbon, PCHs, and PILCs. It is important to note here that currently studied (our) materials did not show the type I (IUPAC) shape of isotherms like other materials, which in turn resulted in less capacity drop after the regeneration process.

CONCLUSIONS

To be a suitable adsorbent material for ethane/ethylene separation a material must be investigated from various aspects of the technology, used for their separation. In this way, retaining the adsorption capacity after regeneration and also increasing the selectivity are two important aspects. The material studied in this work can successfully retain their adsorption capacity by 68–54%, particularly under vacuum regeneration (Fig. 6), it is fairly a large value when compared with other reported material, though these materials possess relatively low selectivity values (ranged from 2.3–1.1). The surface modification of the porous clay heterostructures with phenyl groups (PCH2) changes the interactions between the adsorbed molecules and the surface, which is observed in isosteric heat curves but it could not increase the selectivity of the material. In fact PCH1, which have the lowest initial heats of adsorption shows fluid-fluid (adsorbate-adsorbate) interactions and thus reflects the highest selectivity values among the prepared samples.

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REFERENCES

1. Ruthven, D.M. (2000) Past progress and future challenges in adsorption research. *Industrial Engineering and Chemistry Research*, 39: 2127.
2. Choudary, N.V.; Kumar, P. (2002) Adsorption of light hydrocarbon gases on alkene-selective adsorbent. *Industrial Engineering and Chemistry Research*, 41: 2728.
3. Uchida, S.; Kawamoto, R.; Tagami, H.; Nakagawa, Y.; Mizuno, N. (2008) Highly selective sorption of small unsaturated hydrocarbons by non-porous flexible framework with silver ion. *Journal of American Chemical Society*, 130 (33): 12370.

4. Anson, A.; Wang, Y.; Lin, C.C.H.; Kuznicki, T.M.; Kuznicki, S.M. (2008) Adsorption of ethane and ethylene on modified ETS-10. *Chemical Engineering Science*, 63: 4171.
5. Padin, J.; Yang, R.T. (2000) New Sorbents for olefin/paraffin separations by adsorption via π-complexation: synthesis and effects of substrates. *Chemical Engineering Science*, 55 (14): 2607.
6. Ruthven, D.M.; Reyes, S.C. (2007) Adsorptive separation of light olefins from paraffins. *Microporous Mesoporous Mater*, 104: 59.
7. Al-Baghli, N.A.; Loughlin, K.F. (2006) Binary and ternary adsorption of methane, ethane, and ethylene on ETS-10 zeolite. *Journal of Chemical and Engineering Data*, 51: 248.
8. Zhu, W.; Groen, J.C. (2005) Comparison of adsorption behavior of light alkanes and alkanes on Kureha activated carbon. *Carbon*, 43 (7): 1416.
9. Dewitt, A.C.; Herwig, K.W. (2005) Adsorption and diffusion behaviour of ethane and ethylene in sol-gel derived microporous silica. *Adsorption*, 11: 491.
10. Zuech, J.L.; Hines, A.L.; Sloan, E.D. (1983) Adsorption of methane on 5 a molecular sieve in the pressure range 4 to 690 kPa. *Industrial and Engineering Chemistry Process Design and Development*, 22: 172.
11. Reich, R.; Ziegler, W.T. (1980) Adsorption of methane, ethane and ethylene gases and their binary and ternary mixtures and carbon dioxide on activated carbon at 201–301 K and pressures to 35 atmospheres. *Industrial Enginerring and Chemistry Research*, 19: 336.
12. Jiang, D.E.; Sumpter, B.G. (2006) Olefin adsorption on silica-supported silver salts – A DFT study. *Langmuir*, 22: 5716.
13. Bezus, A.G.; Kiselev, A.V. (1971) Adsorption of ethane and ethylene on X-zeolites containing Li^+, Na^+, K^+, Rb^+ and Cs^+ cations. *Transactions of the Faraday Society*, 67: 468.
14. Teramoto, M.; Shimizu, S.; Matsuyama, H.; Matsumiya, N. (2005) Ethylene/ethane separation and concentration by hollow fiber facilitated transport membrane module with permeation of silver nitrate solution. *Separation and Purification Technology*, 44: 19.
15. Yang, R.T. (1987) *Gas Separation by Adsorption Processes*; Butterworth Publications: USA.
16. Ruthven, D.M.; Farooq, S.; Knaebel, K.S. (1994) *Pressure Swing Adsorption*; VCH: NY.
17. Sing, K.S.W.; Everett, D.H.; Haul, R.A.W.; Moscou, L.; Pierotti, R.A.; Rouquerol, J.; Siemieniewska, T. (1985) Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure and Applied Chemistry*, 57: 603.
18. Olson, D.H.; Camblor, M.A.; Villaescusa, L.A.; Kuehl, G.H. (2004) Light hydrocarbon sorption properties of pure silica Si-CHA and ITQ-3 and high silica ZSM-58. *Microporous Mesoporous Mater*, 67: 27.
19. Grande, C.A.; Araujo, J.D.P.; Cavenati, S.; Firpo, N.; Basaldella, E.; Rodrigues, A.E. (2004) New complexation adsorbents for propane—propylene separation. *Langmuir*, 20: 5291.
20. Galarneau, A.; Barodawalla, A.; Pinnavaia, T.J. (1995) Porous clay heterostructures formed by gallery-templated synthesis. *Nature*, 374: 529.
21. Pires, J.; Araújo, A.C.; Carvalho, A.P.; Pinto, M.L.; González-Calbet, J.M.; Ramírez-Castellanos, J. (2004) Porous materials from clays by the gallery template approach: synthesis, characterization and adsorption properties. *Microporous Mesoporous Mater*, 73: 175.
22. Pinto, M.L.; Pires, J.; Rocha, J. (2008) Porous materials prepared from clays for the upgrade of landfill gas. *Journal of Physical Chemistry C*, 112: 14394.
23. Gil, A.; Korili, S.A.; Vicente, M.A. (2008) Recent advances in the control and characterization of the porous structure of pillared clay catalysts. *Catalysis Reviews*, 50: 153.
24. Ishii, R.; Nakatsuji, M.; Ooi, K. (2005) Preparation of highly porous silica nanocomposites from clay mineral: a new approach using pillaring method combined with selective leaching. *Microporous Mesoporous Mater*, 79: 111.
25. Pereira, P.R.; Pires, J.; de Carvalho, M.B. (1998) Zirconium pillared clays for carbon dioxide methane separation. 1. Preparation of adsorbent materials and pure gas adsorption. *Langmuir*, 14: 4584.
26. Gregg, S.J.; Sing, K.S.W. (1982) *Adsorption, Surface Area and Porosity*; Academic Press: London.
27. Myers, A.L. (2003) Equation of state for *adsorption* of gases and their mixtures in porous materials. *Adsorption*, 9: 9.
28. Lukens, Jr. W.W.; Schmidt-Winkel, P.; Zhao, D.; Feng, J.; Stucky, D.D. (1999) Evaluating pore sizes in mesoporous materials: A simplified standard adsorption method and a simplified Broekhoff-de Boer method. *Langmuir*, 15: 5403.
29. Chong, A.S.M.; Zhao, X.S. (2003) Functionalization of SBA-15 with APTES and characterization of functionalized materials. *Journal of Physical Chemistry B*, 107: 12650.
30. Bourlinos, A.B.; Jiang, D.D.; Giannelis, E.P. (2004) Clay-organosiloxane hybrids: A route to cross-linked clay particles and clay monoliths. *Chemistry of Materials*, 16: 2404.
31. Velde, B. (1992) *Introduction to Clay Minerarals—Chemistry, Origin, Uses and Environmental Significance*; Chapman & Hall: London.
32. Polverejan, M.; Pauly, T.R.; Pinnavaia, T.J. (2002) Acidic porous clay heterostructures (PCH): Intragallery assembly of mesoporous silica in synthetic saponite clays. *Chemistry of Materials*, 12: 2698.
33. Zhu, H.Y.; Ding, Z.; Barry, J.C. (2002) Porous solids from layered clays by combined pillaring and templating approaches. *Journal of Physical Chemistry B*, 106: 11420.
34. Parsonage, N.G. (1970) Contribution to the variation with coverage of the isosteric heat of adsorption on a square lattice and in incompletely separated cells. *Journal of Chemical Society*, A: 2859.
35. Cheng, L.S.; Yang, R.T. (1995) Monolayer cuprous chloride dispersed on pillared clays for alkene-alkane separations by π-complexation. *Adsorption*, 1: 61.
36. Yang, R.T.; Kikkinides, E.S. (1995) New sorbents for alkene/alkane separations by adsorption via π-complexation. *AIChE J.*, 41: 509.
37. Wu, Z.; Han, S.S.; Cho, S.H.; Kim, J.N.; Chue, K.T.; Yang, R.T. (1997) Modification of resin-type adsorbents for ethane/ethylene separation. *Industrial Engineering and Chemistry Research*, 36: 2749.
38. Choudary, N.V.; Kumar, P.; Bhat, T.S.G. (2002) Adsorption of light hydrocarbon gases on alkene-selective adsorbent. *Industrial Engineering and Chemistry Research*, 41: 2728.