

# Chapter 2

## Pillared Interlayered Clays as Adsorbents of Gases and Vapors

J. Pires and M.L. Pinto

**Abstract** This chapter reviews recent works where porous materials prepared from clays, particularly pillared interlayered clays (PILCs), were studied as gas phase adsorbents. It also includes the cases which used the adsorption of gases and vapors for the nanotextural characterization of the materials, other than the usual low temperature nitrogen adsorption. This is, for instance, the case of the adsorption of molecules of volatile organic compounds (VOCs), with various dimensions and shapes, which can be used as probe molecules for the characterization of the porosity or concerning the topic of the VOCs abatement. A similar situation occurs with water adsorption, whose results can be informative not only on the desiccant properties of the materials but also on their surface chemistry. A more recent line of studies of adsorption by materials prepared from clays, namely, the hydrocarbon purification from natural gas or biogas, was also addressed.

**Keywords** Adsorption · PILCs · PCHs · Purification · Separation · Volatile organic compounds · Landfill gases

### 2.1 Introduction

Pillared interlayered clays (PILCs) are far more studied concerning their preparation methodologies and their catalytic properties [1, 2] than what concerns their possibilities as adsorbents, particularly as selective adsorbents. PILCs present, in general, lower structural regularity than, for instance, the more usual zeolites, but PILCs structural regularity is higher than other important classes of adsorbent materials, such as activated carbons. Therefore, the lack of a precise regular structure cannot be regarded as a major drawback for PILC applications as adsorbents. Furthermore, these materials can be prepared from soils, creating added value materials from

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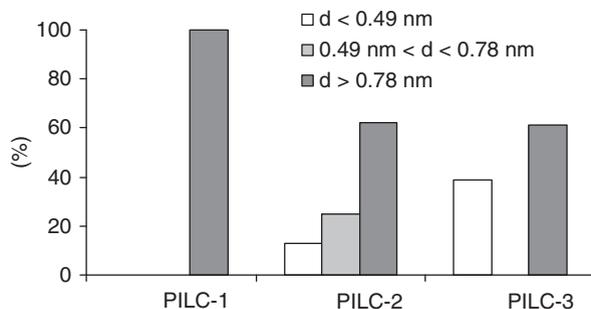
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natural products. This review intends to be a contribution for the study of PILCs as adsorbents of gases and vapors. And, in a certain extent also, for the use of adsorption methodologies in the study of properties of PILCs, other than the well-known and well-documented low temperature nitrogen adsorption. In this way, the adsorption of volatile organic compounds (VOCs) is studied both for textural characterization using selected VOCs as probe molecules as well as for the abatement of noxious VOCs. Also water adsorption in PILCs can be studied from the view of the characterization of the surface chemistry, namely, their hydrophobic–hydrophilic properties, and as adsorbents for water removal. Particular attention is devoted also to the potentialities of PILCs as selective adsorbents of natural and biogas components, such as carbon dioxide, methane, ethane, and nitrogen. In this work we avoided to refer data from the literature where the units for adsorbed amounts were not clear, particularly in cases where, at least apparently, some confusion could be made between the units of  $\text{cm}^3/\text{g}$  and  $\text{cm}^3\text{STP}/\text{g}$ .

## 2.2 Adsorption of Volatile Organic Compounds (VOCs)

### 2.2.1 As Probe Molecules

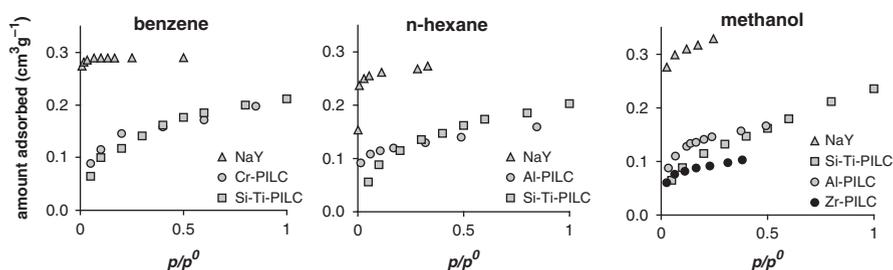
Concerning the characterization of the porosity of PILCs, while the gallery heights can usually be known with high accuracy from X-ray diffraction, the knowledge of the space between the pillars poses more difficulties. Micropore size distributions, evaluated from the adsorption of only one probe molecule, usually nitrogen at 77 K, have been obtained for PILCs [3–5]. The various methodologies have necessarily their advantages and drawbacks. The use of only nitrogen adsorption at 77 K is advantageous since few experiments are needed but quality data at very low pressures are mandatory. Furthermore, effects due to the surface chemistry can change the adsorption potential and, in this way, influence the obtained micropore size distribution. The use of the adsorption of various probe molecules has also been made in the characterization of the porosity of PILCs [6–10], but more experimental work is needed in this case, since several adsorbates are to be used. These adsorbates are usually organic molecules with different sizes and shapes. This methodology is also limited by the vapor pressure of the probe molecules to be used. In fact, since the experiments are normally performed at room temperature the organic molecules to be used need to have a measurable vapor pressure at this temperature. Another assumption of the use of various organic probe molecules for characterizing the porosity is that, since porous volumes are preferably expressed in liquid volume ( $\text{cm}^3/\text{g}$ ), the density of the adsorbed phase needs to be approached by the density of the liquid at same temperature. Nevertheless, this methodology was adopted by some authors who were able to propose micropore size distributions on the basis of the exclusion by molecular sizes [6, 8]. One illustrative example is given in Fig. 2.1 [8] where the micropore size distributions were proposed for three PILCs, prepared from starting clays with different origins, on the basis of the size exclusion effect of nitrogen, *n*-hexane, cyclohexane, and triethylamine [8]. This methodology can



**Fig. 2.1** Micropore size distributions proposed from the adsorption of various probe molecules in three different PILCs

also give useful information for the characterization and understanding of the catalytic properties of PILCs by knowing the precise amount of a particular reactant or reaction product that can be accommodated in the material structure.

It is obviously very difficult to generalize the results published in the literature for the adsorption of molecules with different sizes and shapes in different PILCs. Nevertheless, Fig.2.2 illustrates some interesting features. In this figure, the results obtained for the adsorption in PILCs, prepared from montmorillonites, are compared with those obtained in the well-known NaY zeolite. As expected, due to the differences in their total microporous volumes, the adsorbed amounts of the presented organic molecules are lower in the PILCs than in the NaY zeolite. Also, the shape of the isotherm is different. In the case of the NaY zeolite, the isotherm is normally more steeper for low relative pressures and a plateau is more clearly defined, as a consequence of its narrow pore sizes (0.74 nm) [11] and more uniform structure of the zeolite.



**Fig. 2.2** Adsorption isotherms of various organic molecules in PILCs and in the NaY zeolite at 298 K. Data from [7, 8, 12]

It is also interesting to note in Fig. 2.2 that PILCs prepared with rather different types of pillars, such as chromium oxide (Cr-PILC) and silicium–titanium oxides (Si–Ti-PILC), can have relatively similar adsorption isotherms in the case of benzene. Also for *n*-hexane adsorption the aluminum oxide-pillared material (Al-PILC)

presents an isotherm which is relatively similar to the Si–Ti-PILC. In the case of methanol (a zirconium oxide-pillared sample – Zr-PILC – was included in this case), probably because this is the smallest molecule of the series, the isotherms are now more different among the various solids.

When the adsorption of chlorinated or oxygenated VOCs is considered, the isotherms can be very different in the same PILC [9, 13, 14]. But, in this case and because these types of molecules have normally a high dipole moment or are highly polarizable, those differences can be entirely attributed not only to size exclusion affects but also, in a non-measurable way, to specific adsorbate–adsorbent interactions. In this way, the use of chlorinated or oxygenated VOCs as probe molecules for the characterization of the microporosity may not be adequate. The adsorption of organic gases and vapors in PILCs has been modeled according to the BET [7], Langmuir [7, 14] virial [15], Dubinin–Radushkevich [12], and Dubinin–Asthakov [14] equations.

### ***2.2.2 For Separation/Purification***

It is well known that a number of VOCs, liberated in various industrial activities, are toxic and contribute to the atmospheric pollution, with direct or indirect action on human tissues [16]. The abatement of VOCs can be made by thermal oxidation, an efficient but highly energy costly process that, additionally, is not entirely adequate for chlorinated VOCs [17]. The catalytic oxidation of VOCs is an important procedure but adsorption can, in the limit, make possible the re-use of a particular VOC [18]. Additionally, since VOCs are usually present in diluted air streams, adsorbents may be used to concentrate a diluted stream and therefore improving the efficiency of thermal or catalytic oxidation [18]. While activated carbons, due to their spread use and moderate-to-low cost, are usually considered as good candidates as adsorbents, in the field of the removal of VOCs these materials present some drawbacks since their flammability poses difficulties to their regeneration [19]. Zeolites are another family of adsorbents that can be considered for the VOCs abatement. Some limitations of zeolites, at least for the more common, are due to their hydrophilic nature, since humidity is also normally present in the streams where VOCs are to be removed. Zeolites can be prepared less hydrophilic [19], for instance, by dealumination processes [19, 20], but this is an additional preparative step and the limiting adsorbed amounts tend to be lower in the respective dealuminated samples [20]. Pillared clays have intermediate hydrophobic–hydrophilic properties between activated carbons and the more common zeolites [21] and could be an interesting alternative as adsorbents in the field of VOCs removal/abatement, at least if an appropriated methodology of making PILCs economically in large amounts is developed.

Since the removal of noxious volatile organic compounds is usually to be considered in the low pressure region, Table 2.1 includes the amounts of selected VOCs adsorbed in several PILCs at the relative pressure of 0.1.

**Table 2.1** Amounts of selected VOCs adsorbed in PILCs at the relative pressure of 0.1. When indicated in the original work, the structural formula of the clays, which were all montmorillonites, (per  $O_{10}(OH_2)$ ) is given

VOC	Type of pillars	Starting clay	Amount adsorbed ( $cm^3/g$ ) and reference
Benzene	SiO <sub>2</sub> -TiO <sub>2</sub>	(Si <sub>3.89</sub> Al <sub>0.11</sub> )(Al <sub>1.60</sub> Mg <sub>0.32</sub> Fe <sub>0.08</sub> )	0.1 [7]
Benzene	Chromium oxide		0.13 [12]
Benzene	Titanium oxide		0.14 [12]
Toluene	Aluminum oxide		0.12 [10]
Cyclohexane	SiO <sub>2</sub> -TiO <sub>2</sub>	(Si <sub>3.89</sub> Al <sub>0.11</sub> )(Al <sub>1.60</sub> Mg <sub>0.32</sub> Fe <sub>0.08</sub> )	0.065 [7]
<i>n</i> -Hexane	SiO <sub>2</sub> -TiO <sub>2</sub>	(Si <sub>3.89</sub> Al <sub>0.11</sub> )(Al <sub>1.60</sub> Mg <sub>0.32</sub> Fe <sub>0.08</sub> )	0.09 [7]
CCl <sub>4</sub>	Iron oxide-zirconium oxide	(Si <sub>4</sub> )(Al <sub>1.67</sub> Mg <sub>0.34</sub> Fe <sub>0.08</sub> )	0.31 [9]
CHCl <sub>3</sub>	Iron oxide-zirconium oxide	(Si <sub>4</sub> )(Al <sub>1.67</sub> Mg <sub>0.34</sub> Fe <sub>0.08</sub> )	0.28 [9]
Trichloroethane	Aluminum oxide		0.12 [10]
Trichloroethane	Zirconium oxide	(Si <sub>3.70</sub> Al <sub>0.30</sub> )(Al <sub>1.16</sub> Fe <sub>0.51</sub> Mg <sub>0.26</sub> )	0.07 [13]
Methanol	Aluminum oxide	(Si <sub>3.70</sub> Al <sub>0.30</sub> )(Al <sub>1.16</sub> Fe <sub>0.51</sub> Mg <sub>0.26</sub> )	0.12 [13]
Methanol	Zirconium oxide	(Si <sub>3.70</sub> Al <sub>0.30</sub> )(Al <sub>1.16</sub> Fe <sub>0.51</sub> Mg <sub>0.26</sub> )	0.08 [13]

Some studies addressed the separation of organic molecules using PILCs as selective adsorbents [13,22]. In dynamic experiments [22] separation factors for an aluminum oxide-pillared clay with values of 2.08 for *n*-hexane/benzene (at 523 K); 1.90 for *n*-hexane/*n*-heptane (at 594 K), and 2.68 for cyclohexane/benzene (at 624 K) were reported. The modeling of selective adsorption of VOCs, by a methodology based on the Dubinin-Radushkevich theory was also attempted in montmorillonites pillared with aluminum or zirconium oxide pillars [13]. Various VOCs were tested and separation factors near three (at a coverage of 0.5) for the methanol/propanone system and the methylethylketone/propanone system were obtained. The effects of the type of pillars in the separation factors were not entirely clear, although the total amounts adsorbed were highest for the aluminum oxide-pillared materials, in line with the highest specific surface area of these samples [13]. Chlorinated samples such as the 1,1,1-trichloroethane/trichloroethylene were also tested but the results were less promising in this case [13].

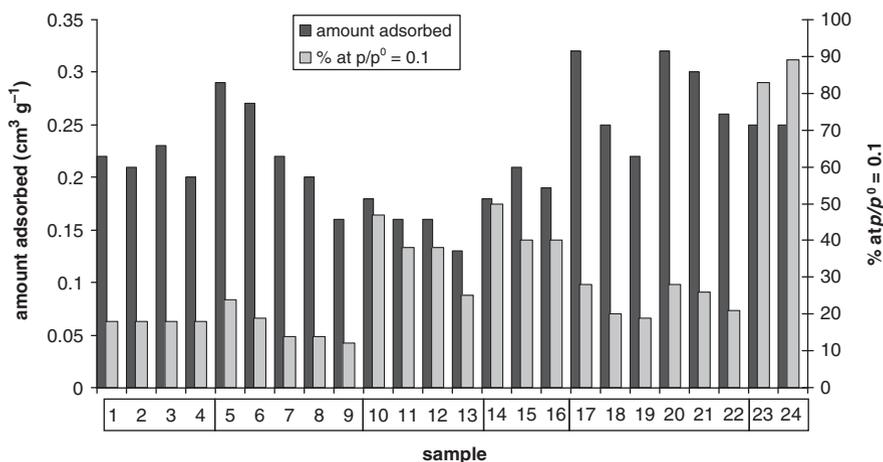
A limited number of studies were made considering the adsorption of H<sub>2</sub>S, which is also a noxious gaseous pollutant. These considered either the study of the effect of the pillaring with different oxide pillars, mainly of aluminum or iron [23] or the particular case of H<sub>2</sub>S removal related to the conservation of works of art [24]. In the latter case, a montmorillonite from Wyoming pillared with aluminum oxide pillars resulted to be more efficient in the removal of H<sub>2</sub>S at very low relative pressures, in spite of its lowest total microporous volume when considered with other more common adsorbents, such as sodium X or Y zeolites.

## 2.3 Adsorption of Water

Water adsorption studies in pillared clays have been made by various authors, essentially with a twofold objective: the potential use of these adsorbents in moisture removal and also the characterization of the surface of PILCs. In this section, we considered the analysis of published water adsorption results in terms of their potentialities as desiccants, using some indications in the literature that materials should have, in particular, if the envisage use is as desiccants in gas-fired cooling systems and dehumidification [25]. For this, one important criterion, although of course not the only one, is that the water adsorption isotherm must be of a “moderate” type I. Roughly, the amount adsorbed at a relative pressure of 0.1 should be about 50% the total amount adsorbed [25, 26].

Figure 2.3 collects the maximum water adsorbed amounts, estimated from the published data for relative pressures between 0.85 and 0.95 and the respective percentage of amount adsorbed at the relative pressure of 0.1. In this figure, the data for samples 1–4 are from [26], for samples 5–9 from [27], for samples 10–13 from [28], for samples 14–16 from [29], and for samples 17–22 from [12]. Samples 23 and 24 [8] are not PILCs, they are, respectively, Y and A zeolites. The latter samples were include in Fig. 2.3 to illustrate the effect of a steep type I isotherm, which is usually obtained for water adsorption in these hydrophilic zeolitic materials. In fact, for these zeolites, the amount adsorbed at a relative pressure of 0.1 is more than 80% (almost 90% for A zeolite) of the total adsorbed volume.

All materials in Fig. 2.3 have alumina-based pillars except samples 17–19 [12], which have chromium oxide pillars, and samples 20–22 [12] that have titanium



**Fig. 2.3** Adsorption capacities for water and respective adsorption at  $p/p^0 = 0.1$  for various pillared clays and zeolites (see text for references)

oxide pillars. As can be seen in Fig. 2.3, the highest water adsorption amounts seem to be registered not for PILCs that have aluminum oxide pillars but for those that have chromium or titanium oxide pillars.

In the series of samples 5–9 [27], samples 5 and 6 are also among those with the highest water adsorbed amounts. In that work the authors study the effect of the progressive increase of the calcination temperature, in steps of 100 °C between 200 °C, for sample 5, and 600 °C, for sample 9, and observed that the maximum adsorbed amount of water decreases as the calcinations temperature increases. In the case of the lowest calcination temperature (200 °C), the highest adsorbed amount observed may also be due to the fact that the oligomeric cationic species that are the precursors of the pillars can be not entirely transformed into the respective oxide and the residual OH groups may then increase the adsorption via specific interaction with the water molecules. For all samples of this series (samples 5–9) the percentage adsorbed at  $p/p^0 = 0.1$  is always well below 50%, putting in evidence the relatively low hydrophilicity of the studied samples.

In the case of the samples 1–4, the authors [26] tried to improve the properties of the PILCs for water adsorption by increasing the percentage of the amount adsorbed at  $p/p^0 = 0.1$  by varying the aging conditions of the pillaring solution. A slightly better result was obtained in the same study in a PILC, where  $\text{Ca}^{2+}$  cations were introduced after the pillaring/calcination process, where that percentage increases to 32%. Other authors have also studied the effect on water adsorption properties of PILCs by introducing cations after the preparation of the PILCs [28], by direct cation exchange at high pH, namely,  $\text{Ca}^{2+}$ ,  $\text{Na}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Li}^+$  (samples 10, 11, 12, and 13, respectively). As can be seen in Fig. 2.3, the most favorable results were obtained for  $\text{Ca}^{2+}$ , while  $\text{Li}^+$  and  $\text{Mg}^{2+}$  resulted only in a modest improvement. The authors [28] interpreted the latter fact as due to the migration of the smallest  $\text{Li}^+$  and  $\text{Mg}^{2+}$  cations into the octahedral layers of the clay sheets, according to the known Hoffmann–Klemen effect.

Water is a polar molecule, and as well stated in the literature for water adsorption, the contribution of the dispersion forces to adsorption is usually small when compared with the contribution from the interactions with the dipole [30]. Therefore, water adsorption has a high degree of specific interactions with the surface. In the present review it is difficult to disclose from the published results some aspects related namely with differences in the used starting clays that could also partially explain the variation of results in Fig. 2.3. For the preparation of the aluminum oxide-pillared clays corresponding to the samples 14–16 [29] the authors used three montmorillonites from three different soil deposits. From these materials, sample 14 presented the best results, particularly concerning the value of the amount adsorbed at  $p/p^0 = 0.1$ , which approached 50% of the total amount. This sample was prepared with a montmorillonite that had a high degree of substitutions in the tetrahedral substitutions (of silicon by aluminum), while the global silicon to aluminum ratio of the three samples was much similar. The tetrahedral sheets are, of course, more exposed to the interactions with the adsorbed molecules and so specific interactions can be developed with the adsorbed water molecules. This

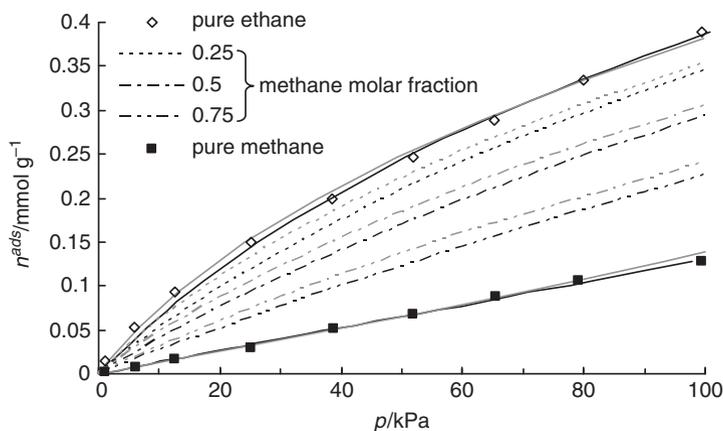
result seems to indicate that starting clays with high degree of tetrahedral substitutions may be beneficial when preparing PILCs for moisture adsorption, particularly for improving the adsorption properties in the initial portion of the adsorption isotherm.

## 2.4 Adsorption of Natural and Biogas Components

One important application of adsorbent materials is in gas separation processes, where a mixture of two or more gases is separated to obtain one or more purified components [31]. PILCs can be potentially used in such processes, provided that they present the adequate properties for an effective separation of a given mixture. However, comparing with other types of adsorbent materials, like activated carbons and zeolites, relatively few studies and experimental data can be found on the literature about the adsorption of permanent gases on PILCs. Works involving adsorption at pressures above the atmospheric pressure (high-pressure adsorption) are even scarcer. Nevertheless, some important and illustrative results were obtained, namely, in the study of PILCs for the purification of natural and biogas components. This section presents the published adsorption results on this topic along with a discussion and analysis of the results in the view of possible industrial applications.

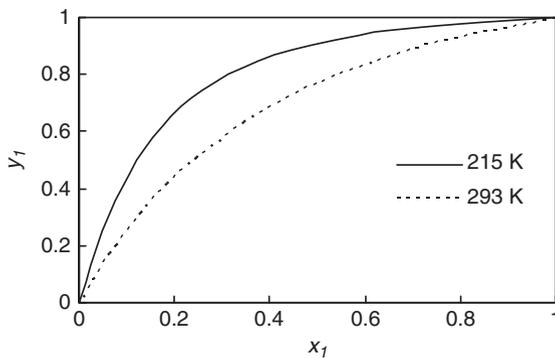
PILCs have been studied for the methane/ethane separation [32, 33]. This separation has importance in the context of the natural gas extraction, since these are the two main hydrocarbon components of natural gas [34]. Ethane may be separated for use as a feedstock for steam cracking for the production of ethylene. Other higher molecular weight hydrocarbons present in natural gases are important fuels as well as chemical feedstocks and are normally recovered as natural gas liquids. An example of the methane and ethane adsorption results is presented in Fig. 2.4 for the adsorption on a zirconium oxide PILC (Zr-PILC). As expected, ethane adsorbs considerably more than methane, since it is the heavier component, and at near atmospheric pressure the adsorbed amounts of ethane are more than three times higher than those of methane. The vacancy solution theory (VST) [35–37] was used to predict the adsorption isotherms of methane/ethane binary mixtures and successfully compared them with some experimental points [32]. In Fig. 2.4, the binary adsorption isotherms predicted by VST and by the ideal adsorbed solution theory (IAST) [38–41] are also presented and as may be observed agree fairly well for the gas phase compositions compared, although VST tends to predict higher adsorption values at the same composition. It is interesting to note that, for equal composition in the gas phase (0.5 methane molar fraction), the predicted isotherms are considerably more close to the pure ethane isotherm than to the pure methane. This is a first indication that the material selectively adsorbs ethane over methane.

For a better understanding of the adsorption behavior of mixtures in an adsorbent material, at a given fixed pressure, it is useful to compare the composition of the gas phase ( $y_i$ ) with the composition of the adsorbed phase ( $x_i$ ), by constructing



**Fig. 2.4** Comparison between IAST (*black*) and VST (*gray*) predictions of binary mixture isotherms of methane/ethane on a zirconium oxide-PILC, at 289 K. Experimental values taken from [32]

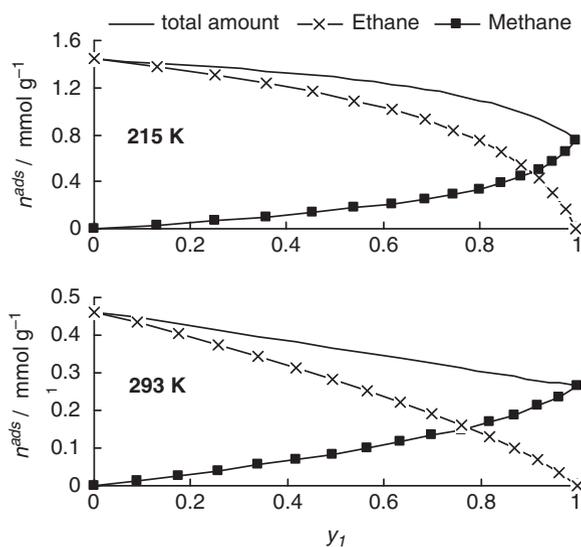
the so-called  $x$ - $y$  phase diagram [31]. For the same zirconium oxide-pillared clay presented in Figure 4.1, it is possible to obtain the diagram in Fig. 2.5 using the IAST model adjusted to the experimental results obtained at two temperatures. In this figure, the composition of methane (molar fractions) in the gas phase ( $y_1$ ) and adsorbed phase ( $x_1$ ) are represented in the axis. In this way, the composition of the adsorbed phase may be known for a given gas composition, which is a very useful information in the context of gas separation since it allows to estimate the expected purity of the separated gases. The two curves (one at each temperature) show that the gas phase is always richer in methane than the adsorbed phase, i.e., the ethane tends to adsorb on the material and the methane tends to stay in the gas phase. The sharper the knee of the curve, the more effective is the separation. In fact, if one



**Fig. 2.5**  $x$ - $y$  phase diagram of the methane/ethane adsorption (composition of the adsorbed and gas phases) on a Zr-PILC, at 215 and 293 K and 100 kPa

considers the gas mixture with 0.8 in methane ( $y_1$ ) it can be seen that the composition of the adsorbed phase at 215 K is about 0.3 in methane ( $x_1$ ) (i.e., about 0.7 in ethane), but increases to 0.55 in methane at 293 K. Therefore, Fig. 2.5 clearly shows that the separation is more effective at 215 K than at 293 K. Nevertheless, the results indicate that this PILC could be used for the methane/ethane separation.

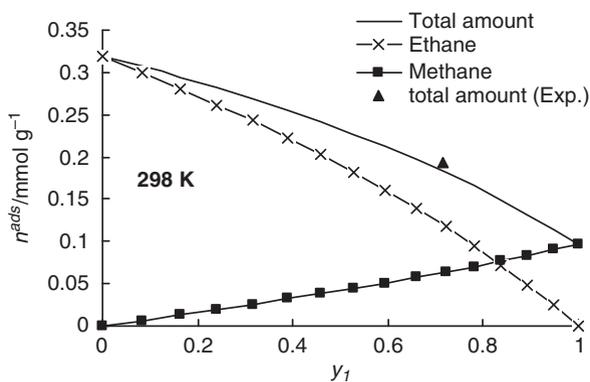
The  $x$ - $y$  diagrams are useful for the evaluation of a material for a specific separation, as shown by the preceding example, but they do not give any information on the adsorbed amounts in a given mass of adsorbent. This information is also important when designing the separation equipment for a particular application, namely, for calculating the maximum adsorbed amounts of a separation column. For this purpose, the representation of the adsorbed amounts as a function of the gas phase composition is more suited, by constructing a gas phase diagram of the adsorbed phase. When using such representation for the same Zr-PILC (shown in Fig. 2.6) it becomes evident that the adsorption capacities at 215 and 293 K are significantly different. The interception of the lines for the ethane and methane amounts indicates the composition of the gas phase at which the composition of the adsorbed phase is equal in the two components. This point moves to lower  $y_1$  values when the temperatures increase, indicating that the separation becomes less effective. The results at 293 K are more significant for possible applications, since they are close to ambient temperatures and separations are normally preformed near these temperatures. In these conditions, Fig. 2.6 shows that the amounts of ethane vary from about 0.45 mmol/g of the pure ethane adsorption to about 0.16 mmol/g, at 0.79 methane molar fraction, and for higher methane concentration on the gas phase the amounts of



**Fig. 2.6** Phase diagrams (amounts adsorbed) at two temperatures predicted by IAST at 100 kPa, as a function of the gas phase composition, for a Zr-PILC

methane adsorbed became higher than those of ethane. This indicates the amounts of ethane that could be recovered from mixtures under these conditions, using this Zr-PILC as the adsorbent material.

The predictions shown in Fig. 2.6 may be compared with experimental values obtained for the adsorption of methane/ethane mixtures. When the predictions made using the VST are compared with the total adsorbed amount and gas phase composition determined experimentally, deviations of about 2–3% in the adsorbed amount were found [32] which is a good result considering that the experimental values have about the same uncertainty. The predictions presented in 2.6 were made by the IAST may also be compared with the experimental data, and in Fig. 2.7 the experimental point is compared with the predictions. As can be seen, the experimental point is close to the solid line of the total adsorbed amount, with a deviation of 5%. This supports the predictions made by IAST and confirms that they are close to those made by VST (already seen in Fig. 2.4). Also very important is the indication that these theories are suitable for modeling the adsorption of binary mixtures in PILC, using the pure components adsorption isotherms. In fact, the measurements of isotherms for gas mixtures are much more complicated than for pure gases, due to equilibrium problems and to the analysis of the gas phase composition. Thus, IAST or VST are important tools to the analysis of the adsorption data, especially when comparing different PILC materials for an envisaged application. More recently, an adsorption model based on statistical mechanics for the prediction of mixture isotherms on PILCs was proposed [42] with higher accuracy at very high pressures, but for the range of pressures normally used on adsorption experiments it gives similar results to IAST.



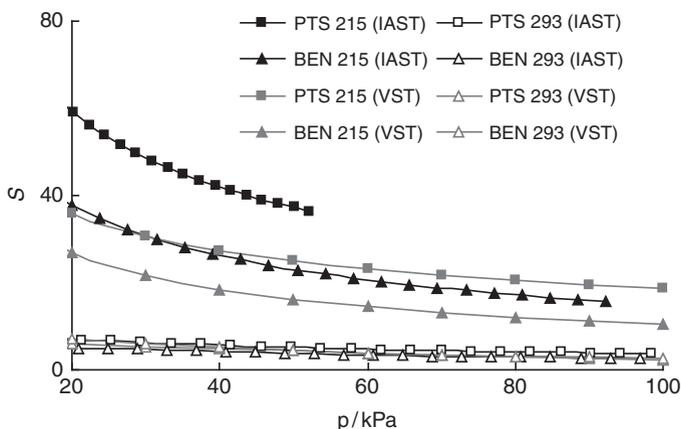
**Fig. 2.7** Comparison of the predicted adsorbed phase diagram at 73.84 kPa, with an experimental point, for a Zr-PILC

Most times, there is an interest to study the separation of a gas mixture with a specific composition and the temperature or pressure effects on the separation performance of the adsorbent materials. One way is to use the selectivity of the separation, defined as

$$S_{2,1} = \frac{x_2/y_2}{x_1/y_1} \quad (2.1)$$

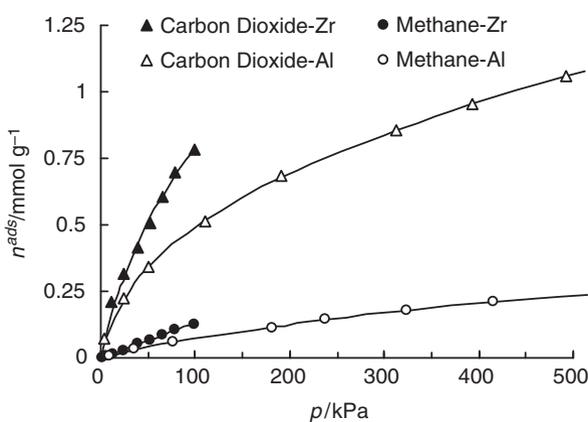
and evaluate this parameter as a function of pressure or temperature. Usually a separation with selectivity higher than three is considered appropriate for industrial applications [31].

In the methane/ethane separation applied to natural gas, the abundance of ethane in the distribution gas is only about 8% (i.e.,  $y_1 = 0.92$ ), and this value can be used as reference to the evaluation of the selectivity of PILC. Figure 2.8 shows the selectivity for the separation of ethane from methane, at this reference composition, using zirconium oxide-pillared clays synthesized from two different clays [32]. One clay, labeled as PTS, is from Porto Santo (Madeira archipelago, Portugal), and the other, labeled as BEN, is from Benavila (Alentejo, Portugal). It is evident from Fig. 2.8 that selectivity toward ethane decreases, as pressures and temperatures increase, although at the higher temperature (293 K) the selectivity is almost insensitive to the pressure. It is interesting to notice that the selectivity values for BEN and PTS-pillared clays are not very different. Nevertheless, in the majority of conditions, selectivity is higher for the PTS sample, a fact that is related, most probably, to the higher heat of adsorption of ethane on this pillared clay [32]. The selectivity values calculated using IAST and VST present some discrepancies at 215 K for the same materials, being the IAST values higher than those calculated by VST. However, they qualitatively agree in the order of the expected selectivity for the separation, and at 293 K the values are identical. From the practical point of view, the potential application of pillared clays in the separation of the major hydrocarbon components of natural gas (methane and ethane) is confirmed, since the selectivity coefficients, between six and eight at 293 K, compare well with those obtained with other adsorbents [43].



**Fig. 2.8** Selectivity of Zr-PILC (PTS and BEN) predicted by IAST (*black*) and VST (*gray*), at two temperatures, for the methane/ethane separation, at 0.92 methane molar fraction

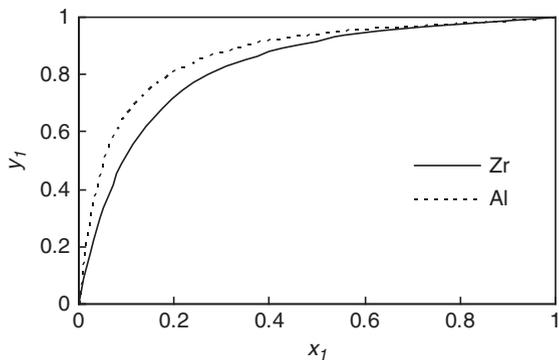
Another important gas separation, which has also been studied using PILCs as adsorbents, is the carbon dioxide/methane separation. This separation can be applied for the purification of natural gas, biogas, and landfill gas, which are formed with a considerable amount of carbon dioxide along with the combustible part [34, 44–46]. In Fig. 2.9 the adsorption results on two PILCs using the same Porto Santo clay (PTS), but different pillars, are presented [47, 48]. The Zr-PTS present higher adsorption capacity for methane and carbon dioxide in the range of comparable values (0–100 kPa), although the two materials have about the same surface area. This indicates that the nature of the pillars strongly influences the adsorption behavior of these gases, either by differences on the chemical nature of the surface (surface charges, acidity, etc.), or by differences in the pillar's density and size (i.e., the size of the micropores). In a recent work, aluminum and zirconium oxide-PILCs prepared using Wyoming (WYO) and Benavila (BEN) clays have been studied for carbon dioxide/methane separation, up to 1,000 kPa [33]. The results showed that the zirconium PILCs presented the highest carbon dioxide adsorbed amounts per unit surface area of the studied materials, due to the more acidic nature of Zr oxide-PILCs and their interaction with the quadrupole of the carbon dioxide. However, when the comparison is made by the adsorbed amount in terms of the mass of material only, the comparison is not be so evident. In fact, some aluminum-PILC presented higher adsorbed amounts than another zirconium-PILC (Zr-BEN), due to their higher surface areas and microporous volumes. Therefore, the work concludes that the more favorable results obtained for Zr-WYO PILC is an outcome of the chemistry of  $ZrO_2$  pillars in the Wyoming clay host. This points out the difficulties of drawing some general conclusions about the pillars that are more suitable for a given separation, since they will also depend on the parent clay used in the preparation. This subject will be further discussed with more detail hereafter.



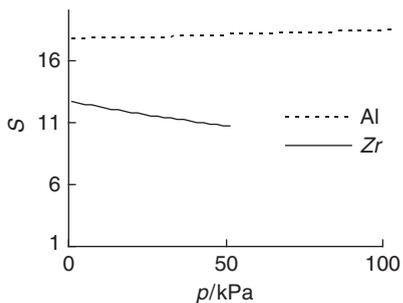
**Fig. 2.9** Carbon dioxide and methane adsorption isotherms, on PILCs obtained with Al and Zr oxide pillars at 298 K

Considering applications using pressure swing adsorption [31], which is the most used type of cyclic gas adsorption separation, the materials used in this process should be easily regenerated in the end of the adsorption step, preferably by a simple decompression of the system. The fact that the adsorption isotherms of carbon dioxide and methane on PILCs are most times slow rising curves, like those presented in Fig. 2.9, is favorable from this viewpoint. This is an advantage over many zeolites, since these usually have rectangular shaped isotherms and become almost saturated with carbon dioxide below atmospheric pressure, hampering the effective regeneration by a simple decompression step. Taking into account the example for the aluminum oxide-PILC in Fig. 2.9, one can see that the adsorption amount rises from about 0.5 mmol/g at 100 kPa (atmospheric pressure) to more than 1 mmol/g at 500 kPa, giving a working capacity of 0.5 mmol/g for that pressure cycle. Similar working capacity for pressure swing adsorption and vacuum swing adsorption results were also reposted for other PILCs, supporting the possible application of PILCs for carbon dioxide/methane separation [33].

For a better analysis of the adsorption results presented in Fig. 2.9,  $x$ - $y$  phase diagrams and selectivity coefficients were calculated using the IAST and are presented in Figs. 2.10 and 2.11. Both figures show that the PILC with aluminum oxide pillars is more effective for the separation under study, since it allows obtaining methane



**Fig. 2.10** Zr-PTS and Al-PTS  $x$ - $y$  phase diagrams of carbon dioxide/methane mixture, at 100 kPa and 298 K (component 1 – methane)

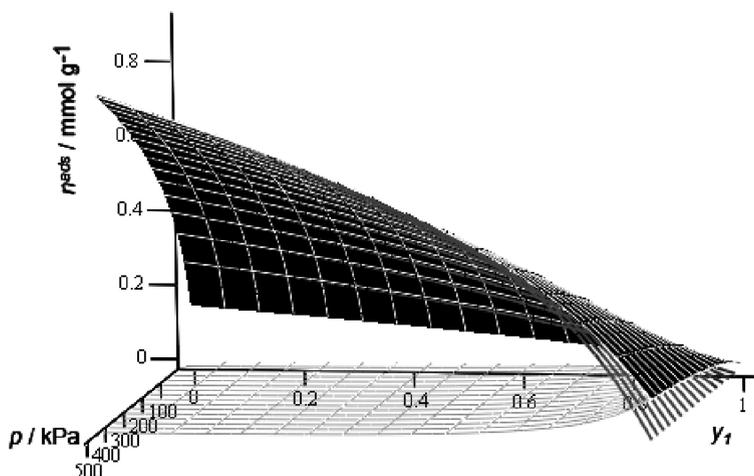


**Fig. 2.11** Selectivity coefficients as function of pressure, at  $y_1 = 0.5$  (methane), for the two PILCs prepared from PTS clay, at 298 K

with a slightly higher purity. It is interesting to note that the simple comparison of the isotherms would clearly lead to this conclusion. In fact, Zr-PTS presented the highest adsorption amounts for both methane and carbon dioxide. However, it is the relation between these two amounts that influences the selectivity of the separation. The results presented in Figs. 2.10 and 2.11 are inline with those obtained with the same type of pillars in other clays [33].

As already mentioned, most gas separations are carried at pressures above atmospheric, and there is much interest to study the adsorption of gases in this pressure range. However, there is scarce data in the literature on high-pressure adsorption of gases on PILCs. Recently, the first comparison work on the high-pressure adsorption of methane, ethane, carbon dioxide, and nitrogen on different aluminum and zirconium PILCs [33] was presented. This work was a contribution to evaluate the real applicability of PILCs for the separation of binary mixtures of the studied gases, which is important in the context of the natural, bio, and landfill gas upgrade. For the studied binary mixtures, the presented results indicate the possible application in the separation of methane/ethane, methane/carbon dioxide, nitrogen/ethane, and nitrogen/carbon dioxide. The latter separation has also interest for applications in carbon dioxide emissions abatement.

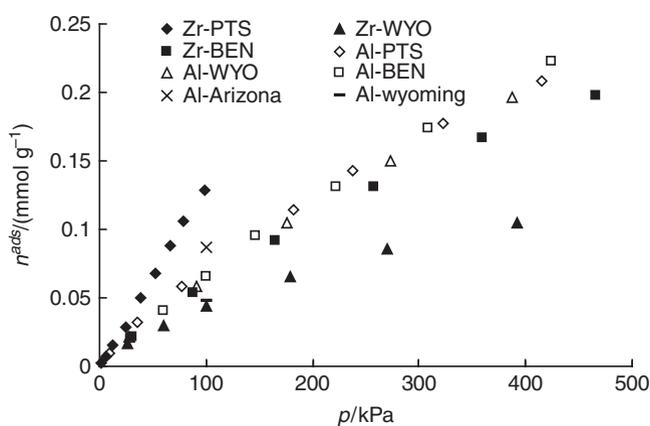
In addition to the applicability evaluation, the results obtained in a broad pressure range also give the opportunity to study the evolution of the phase diagrams, similar to those in Figs. 2.6 and 2.7, but now as function of pressure. This approach leads to tri-dimensional representation of the phase diagrams as in Fig. 2.12. This figure shows the phase diagram for a zirconium oxide-pillared clay, which presented the best results of the studied PILCs for the methane/carbon dioxide separation. The



**Fig. 2.12** Phase diagram (composition of the adsorbed phase) predicted by IAST, as a function of the gas phase composition and pressure for a zirconium oxide-PILC. The *black* surface represents the total amount adsorbed, the lower *gray* mesh represents the adsorbed methane amounts and the upper *gray* mesh represents the adsorbed carbon dioxide amount

lines formed by the interception of the surfaces with the vertical  $p$ ,  $n^{\text{ads}}$  planes at  $y_1 = 0$  and  $y_1 = 1$  (methane molar fraction in the gas phase) correspond to the pure components adsorption isotherms of carbon dioxide and methane, respectively. Similarly, the lines contained in the  $p$ ,  $n^{\text{ads}}$  planes, but at intermediate compositions ( $0 < y_1 < 1$ ), correspond to the isotherms of each component and the total amount adsorbed at a given gas phase composition. The cuts obtained from the  $n^{\text{ads}}$ ,  $y_1$  plane are phase diagram representations analogous to those in Figs. 2.6 and 2.7. Observing the effect of pressure on the adsorbed amounts, Fig. 2.12 clearly shows that the increasing of the pressure favors the adsorption of  $\text{CO}_2$  and so the separation at higher pressures becomes more effective. In fact, at a gas phase composition between 0.4 and 0.6 in methane (typical of biogas and landfill gas), the composition of the adsorbed phase is about 0.05 in methane at 500 kPa, that is, the adsorbed phase is about 95% rich in carbon dioxide. This is a strong indication that these materials could be used for the upgrade of biogas or landfill gas.

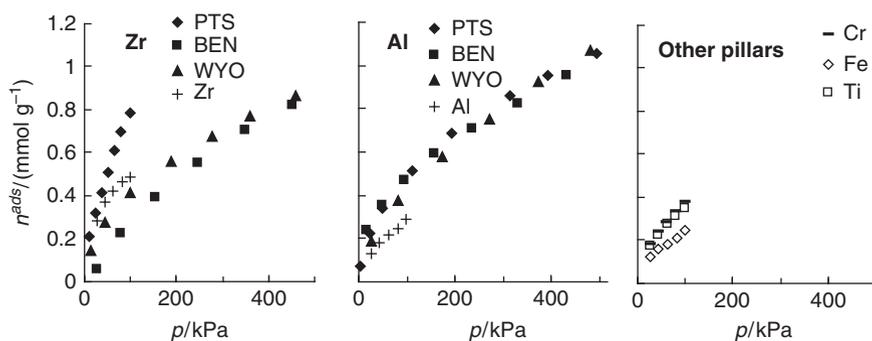
Another separation that was studied using PILCs is the methane/nitrogen [33, 49, 50]. Selectivity values of 2.35 were reported for an  $\text{Al}_2\text{O}_3$ -PILC from Arizona montmorillonite [49] and for a series of Wyoming-based PILCs reported values were slightly above 5 for Al-PILC, about 2 for Ti-PILC and Fe-PILC, and close to 1 (no separation) for Cr-PILC and Zr-PILC [50]. Other results obtained at higher pressures revealed selectivity above 10 for best case (Zr-WYO) and about 2–3 in the other cases [33]. Although these values seem encouraging for the applications of PILCs in the methane/nitrogen separation, it must be taken in to account that the methane adsorbed amounts are quite low. Figure 2.13 presents adsorption isotherms of methane, at 298 K, on different PILCs, and show that the amounts are only about 0.2 mmol/g at 500 kPa. It can be observed that the amounts are relatively similar and independent of the pillars and clays used in the preparation of the materials. This is more or less expected since the methane adsorption is due to non-specific



**Fig. 2.13** Adsorption isotherms of methane, at 298 K, in different pillared clays (different clays with different metal oxide pillars). Experimental results collected from the literature [33, 48, 49]

dispersion forces, and thus the chemical nature of the adsorbents surface is much less relevant. Nevertheless, some significant differences are noticed, namely, among the Zr PILCs, since these presented the lowest (Zr-WYO) and the highest amounts (Zr-PTS) in the pressure range where they are comparable. Some values reported in the literature [50] were not included in Fig. 2.13 because they seem to be inconsistent with the values for carbon dioxide adsorption and also with the values obtained by the same authors in following works. Values for methane adsorption on iron–zirconium oxide-PILC, and on an amine-modified iron oxide-PILC, higher than those presented in Fig. 2.13, but at 273 K, were reported also [9]. The small adsorption capacity of PILCs for methane stems from its relatively low surface area, when compared to other clay-based adsorbents like the porous clays heterostructures [48], which have surface areas around 1,000 m<sup>2</sup>/g. This disadvantage imposes the use of quite large amounts of adsorbent in the separation columns to achieve a minimum adsorption capacity of the separation systems.

On the contrary, PILCs usually present a considerable adsorption capacity for the adsorption of carbon dioxide. Figure 2.14 presents the adsorption isotherms obtained on different PILCs, at 298 K. In this case, the carbon dioxide molecule has a quadrupole moment (about  $3.3 \times 10^{-16}$  cm<sup>2</sup> [51]) that is capable of specific interaction with surface charges or dipoles and is expected that its adsorption is more sensitive to differences in the surface chemistry of the different PILCs. However, Fig. 2.14 does not give a clear distinction of the pillars or clays that are more suited to prepare PILCs with high adsorption capacity for carbon dioxide. In the case of the Al-PILCs, it is noticed that the adsorption of this gas is almost insensitive to the clay used in the PILC preparation. The Zr-PILCs are known to have higher acidity than Al-PILCs, but this property seems not to strongly influence the carbon dioxide adsorption. Although, Zr-PTS presented the highest adsorption capacity of the PILCs, in the comparable pressure range, the other Zr-PILCs show lower adsorption capacities than Al-PILCs. The Cr and Ti-PILCs results indicate that these materials have adsorption capacities for carbon dioxide comparable to those of Zr or Al-PILCs. The lowest values obtained for Fe-PILCs could be explained by the low



**Fig. 2.14** Adsorption isotherms of CO<sub>2</sub>, at 298 K, in different pillared clays (different clays with different metal oxide pillars). Experimental results collected from the literature [33, 48–50]

surface areas and porous volumes usually obtained in these PILCs [9]. Considering the above, the results in Fig. 2.14 strongly suggest that the variations in the surface chemistry of PILCs are not sufficient to explain the carbon dioxide adsorption. In fact, other textural parameters, like the surface area and porous volumes, are also important to explain the differences between the carbon dioxide adsorption [33]. In the preparation of PILCs, the size and charge of the oligomeric cations and the cation-exchange capacity of the clay influence the pillar's size and density. Thus is very difficult, if not impossible, to obtain PILCs from the same clay with different pillars but with the same pore size and pore volume, i.e., the same pore size distribution. This impairs any attempt of prediction on the best clay or type of pillar to use for the adsorption of carbon dioxide, since ultimately the results will depend on the particular combination of both factors.

## 2.5 Conclusion

As said in the introduction the number of published works where PILCs are considered as adsorbent materials is not very large. Therefore, the systematic of effects such as the composition of the pillars, the nature of the parent clays, or the surface chemistry versus porosity in the selective adsorption properties of PILCs is still difficult. Nevertheless, the materials prepared from natural montmorillonites, with aluminum or zirconium oxide pillars, have important adsorption properties for the adsorption of VOCs, water, and natural gas or biogas components. Having in mind the importance of preparing adsorbent materials from natural, low-added value products, in a sustainable development the study of PILCs as adsorbents surely has its place in the general field of nanoporous materials.

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