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Controlled Gas Adsorption Properties of Various Pillared Clays

A. MOLINARD AND E.F. VANSANT
Laboratory of Inorganic Chemistry, University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium

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Abstract. Microporous pillared clays (PILC) were prepared by the intercalation of montmorillonite with particles of titania (Ti-PILC), zirconia (Zr-PILC), alumina (Al-PILC), iron oxide (Fe-PILC) and mixed lanthania/alumina (LaAl-PILC). Nitrogen adsorption isotherms (77 K) and XRD data provided information on the porosity, surface area, micropore volume and interlayer distance of these samples. The surface area varied between 198 and 266 m^2/g for Ti- and Fe-PILC, respectively. The titania pillared clay had also the highest micropore volume (0.142 cc/g) and interlayer spacing (16–20 Å), compared to the Zr-PILC, which had the smallest spacing between the layers (max. 4 Å). Despite this fact, Zr-PILC always showed a high adsorption capacity for gases such as N_2, O_2, Ar or CO_2, due to its high adsorption field in the very small micropores.

From gas adsorption experiments on these various PILCs, it became clear that their adsorption properties depend on the pillars in three ways: (i) the pillar height, (ii) the distribution of the pillars between the clay layers and (iii) the nature of the pillaring species.

The incorporation of other elements in the pillars leads to specific adsorption sites in the pores. This was demonstrated by the preparation of mixed Fe/Cr and Fe/Zr pillared clays. Compared to the parent Fe-PILC, the incorporation of chromium and zirconium in the iron oxide pillars had a positive influence on the adsorption capacity. Also the modification of a PILC with cations increases both capacity and selectivity for gases. This was confirmed by the increased adsorption of N_2, O_2 and CO_2 at 273 K on a Sr^{2+} exchanged Al-PILC.

Keywords: measurement method, mathematical model, zeolite, intraparticle diffusion

Introduction

As a result of the numerous adsorption processes that take place in industry, many scientists focused their work on the development of new porous materials. Activated carbon was probably one of the first adsorbents that were used for the adsorption of vapours, the purification of water and many other adsorption processes. While the capacity of these carbons is very high, they are not selective for specific gases due to their amorphous and extended mesoporous structure. For many applications, selectivity was needed and it seemed that the inorganic zeolites offered a complementary alternative. Besides their high adsorption capacity, their crystalline microporous network could exclude certain molecules from adsorption and they were soon called "molecular sieves".

Nowadays, the world-wide research on zeolites is still going on and they can be fine-tuned for almost any adsorption process. Zeolites are still extensively used for the separation of air components, although carbon molecular sieves (CMS) become more and more important for this purpose. The CMS have a very narrow micropore size distribution and show a kinetic preference for oxygen. The zeolites however have also two other properties which distinguishes them from the other porous materials. They have a good cation exchange capacity and show catalytic activity in many organic reactions.

During the oil crisis in the 70's however, there was a sudden demand for catalytic materials that could be used for the selective cracking of crude oils. Due to their limited pore size, zeolites failed and the quest for other substrates began. Alumina and crude clay minerals were used, but they had a poor selectivity towards the reaction products. In the late 70s, a brand new material was proposed which had a good catalytic activity, high adsorption capacity and pores that were large enough to admit the crude organic vapours, but also small enough to have selectivity towards the cracked

products. These potential useful materials are called "pillared interlayered clays" or PILCs. Due to several side effects and the development of large-pore zeolites however, the pillared clays were never commercially used as cracking catalysts. Research on these substrates is nevertheless very lively and the term "pillared clay" includes nowadays a variety of layered clay minerals, intercalated with organic or inorganic species that prop open the clay sheets (Burch, 1988; Mitchell, 1990; Izumi et al., 1992). As a result, a two-dimensional stable, microporous solid is obtained with a pore size between 2 and 20 Å. Most of these pillared clays have a high adsorption capacity and selectivity towards gases and vapours (Baksh and Yang, 1992), show catalytic activity for a variety of reactions (Adams, 1987) and seem to have both cation and anion exchange properties (Dyer and Gallardo, 1990; Molinard et al., 1994).

Depending on the type of pillars that are used, the pore size distribution and physicochemical properties of PILCs can be altered in an easy way. All these flexible characteristics make pillared clays interesting materials to investigate and already many applications are found. Only a few articles describe the gas adsorption properties of PILCs. Nevertheless, some nice results were reported which illustrate the adsorption on various PILCs, their potential energy profiles (Baksh and Yang, 1992) and the N_2/O_2 selectivity of cation modified PILC (Molinard and Vansant, 1994).

In this paper we describe the adsorption of some organic and inorganic gases on various pillared clays. It will become clear that the type of pillar that was used to intercalate the clay layers, has a huge influence on the adsorption properties of the PILC. Not only does the porosity change, and therefore the adsorption capacity, but also the physicochemical nature of the PILC, which has an effect on the selectivity of adsorption.

The presented work deals with pillared montmorillonites. This type of clay is well-investigated and can easily be pillared with different species. The alumina pillared montmorillonite (Al-PILC) is most famous in PILC-research (Butruille, 1992). In order to prepare an Al-PILC, the exchangeable Na^+ cations between the clay layers of natural montmorillonite are replaced by a hydrolysed Al^{3+}-complex. This pillaring precursor (mainly $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$) (Schoonheydt et al., 1993) props open the clay sheets and is converted into rigid alumina pillars after calcination. Other PILCs that we have used are montmorillonite pillared with titania (Ti-PILC), iron oxide (Fe-PILC), zirconia (Zr-PILC) and mixed oxide pillars of LaAl, Fe/Cr, Fe/Zr, etc. The principle of intercalation is the same for all the PILCs and is schematically represented in Fig. 1.

Experimental

Techniques

Interlayer distances were obtained from spectra, recorded on a Philips PW1840 Powder Diffractometer using CuKα-radiation. Oriented films were prepared by slow evaporation of an aqueous suspension of the sample on a glass microscope slide. The thickness of a montmorillonite layer (9.6 Å) was subtracted from the d_{001} spacing, to obtain the mean pillar height.

Surface areas were calculated from the nitrogen adsorption isotherms at 77 K, recorded on a Digisorb 2600 (Micromeritics). Before the measurement, the samples were degassed at 573 K during 3 hours under high vacuum. The micropore volume was determined according to the α_s-method (Gregg and Sing, 1982).

Elemental analysis was done by X-ray fluorescence on a JEOL JCXA 733 Electron Microprobe Analyzer (EPMA).

Adsorption experiments were performed in a glass volumetrical adsorption apparatus. The samples were degassed at 473 K (vacuum, overnight) prior to adsorption. An isothermal period of 1 hour was maintained to equilibrate the sample at the desired temperature.

Samples

The parent smectite clay was provided by ECC International as a purified and sodium exchanged montmorillonite with a cation exchange capacity of 90 meq/100 g and a mean particle size smaller than 2 μm.

The pillaring solution for the alumina pillared clay (Al-PILC) was prepared by diluting 4.4 ml Locron L® (Hoechst) into 275 ml water. While stirring, 10 g clay were dispersed in the pillaring solution. After 2 hours, the intercalated clay was separated by filtration and washed until Cl^--free. The solid was dried in air at 333 K during 19 hours and subsequently calcined at 723 K for 3 hours. Another sample, labelled Al-PILC.f, was freeze-dried and subsequently calcined in the same way.

A combined pillaring precursor of La^{3+} and alumina (Sterte, 1991) was prepared by refluxing 20 ml Locron L®, 4.55 g $LaCl_3$ and 17 ml water for 100 h.

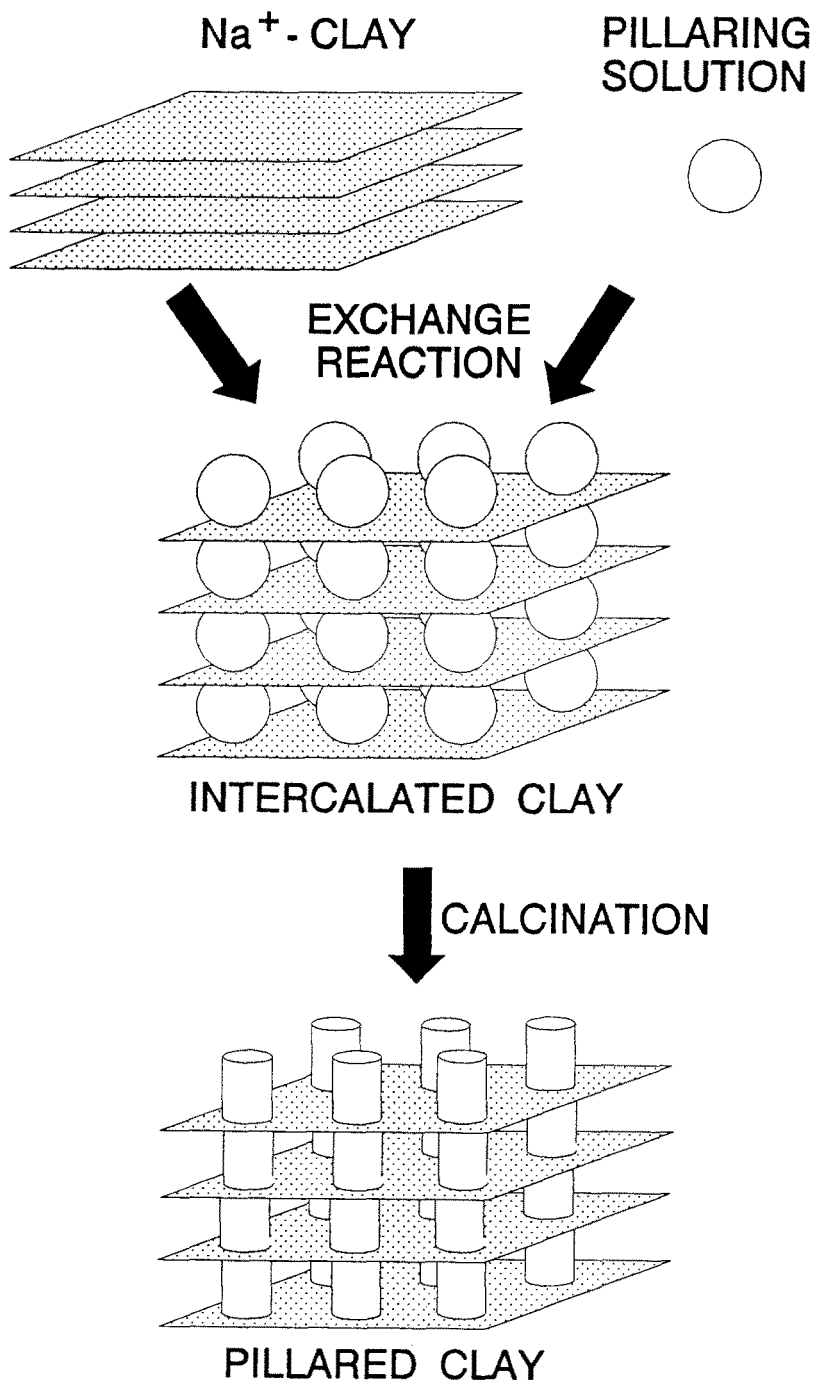

Fig. 1. The principle of the preparation of a pillared clay.

2 grams of montmorillonite were dispersed in 350 ml water and 40 ml of the pillaring solution were added to the suspension. After stirring for 2 hours, the solid was separated from the excess of pillaring solution, washed and dried and calcined at 773 K for 2 hours.

Titania pillared montmorillonite or Ti-PILC (Sterte, 1991) was prepared by adding a 0.4% clay suspension into a Ti-sol (2.3 ml saturated $TiCl_4$-solution and 4.2 ml (6 M) HCl, diluted with demiwater until $[Ti^{4+}] = 0.82$ M). After exchange, the sample was

separated from the pillaring solution, washed and air dried. Calcination took place at 723 K during 3 hours.

Iron pillared clays (Fe-PILC) were prepared according to the method of Rightor et al. (1991), by the reaction of a 1 wt% suspension of montmorillonite with an hydrolysed Fe-complex (clay/Fe = 70 mmol/meq). This Fe-pillaring precursor was made by adding anhydrous sodium carbonate to a rapidly stirred solution of 0.2 M iron(III)nitrate until a ratio of 2 equivalents base per mol metal was reached. This solution was aged overnight before the intercalation reaction. After the exchange, the solid was separated by centrifugation and washed until a pH of 3.5 was achieved. The intercalated product was then air-dried and calcined in vacuum at 625 K for 3 hours.

The pillaring of montmorillonite with zirconia (Zr-PILC) was performed by a refluxed (5 hours) solution of 0.1 M zirconylchloride (Burch and Warburton, 1986). 8.5 g clay were added to 250 ml of the pillaring solution. After refluxing 1 hour, the intercalated clay was separated, washed and dried at room temperature. Calcination took place at 773 K in air.

Results and Discussion

1 Surface Area and Porosity

The surface area of a parent montmorillonite, if calculated by summation of the surface of the individual clay particles, is about 750 m^2/g. This theoretical value does not agree at all with the surface area as determined by nitrogen adsorption at 77 K, which is about 50 m^2/g. This low value is due to a collapse of the clay layers when they are dried and degassed. The experimental value therefore represents the external surface area and the available surface in meso- and macropores. Due to this fact, surface areas always depend on the conditions of drying. If the clay is air dried, the layers settle down very slowly and all of them are oriented in the same parallel direction. Freeze-drying on the other hand is a fast drying technique. Now, the clay sheets are randomly oriented and the dried product has a so-called "card house" structure with many mesopores. Therefore, a freeze-dried clay frequently has a higher surface area than the air-dried sample (Fig. 2).

If a clay is pillared, however, the pillars support the sheets and prevent them from collapsing during the drying process. Moreover, the galleries that are formed by the pillars serve as micropores and the final PILC has always a high surface area and micropore volume.

Table 1 gives an overview of the surface area (SA), micropore volume (μPV) and interlayer distance (ID) of several pillared clays. All PILCs were well intercalated by the various pillaring species. This is reflected by the SA and μPV, but also by EPMA analysis of the samples. All of them contain a rather high amount of the pillaring element, although there is a mutual difference for the various PILCs.

The interlayer distance varies with the nature of the pillars. The largest species seem to be the titania pillars. As a result, this Ti-PILC also has large galleries and therefore a very high micropore volume. The exact structure of these pillars is not elucidated yet, but some variations in pillar height might take place and interlayer distances between 15 and 20 Å are frequently found. The same counts for the Fe-PILC. Although their d_{001} distance is rather high, the micropore volume of this substrate is small. Therefore, not only the height of the pillars results in a good microporous material, also their distribution between the clay sheets influences the porosity. In the case of Fe-PILC, the pillaring precursor has a low charge and many pillaring species are intercalated. As a result, the interlayer space is stuffed with pillars which occupy a large part of the available micropore volume. This is also reflected in the high amount of iron in the Fe-PILC. The iron content is almost one third of the total mass, while for the other PILCs, the pillaring element is only responsible for one fifth of the weight.

Both Al-PILCs exhibit the same interlayer distance since they differ only in the way they were dried. An alumina pillared montmorillonite normally has an interlayer distance around 9 Å, when calcined at 673 K. These substrates were calcined at 773 K however, which in fact results in a stronger bond between the alumina pillars and the clay layers, but also in a bending of the clay sheets and therefore a lower d_{001} spacing. This is also the reason why this air-dried PILC has a higher BET surface area than the freeze-dried one. The homogeneous stacked layers of Al-PILC support better a thermal treatment than the card house structure of Al-PILC.f. The main difference between these two substrates is still seen in the higher micropore volume of air-dried Al-PILC. A completely delaminated structure, as presented in Fig. 2, seems not to be true for this freeze-dried sample, since we will show that Al-PILC.f still exhibits a well defined XRD pattern. Probably this sample is only slightly delaminated as a result of the experimental conditions we have used, especially the extended filtration and washing procedure.

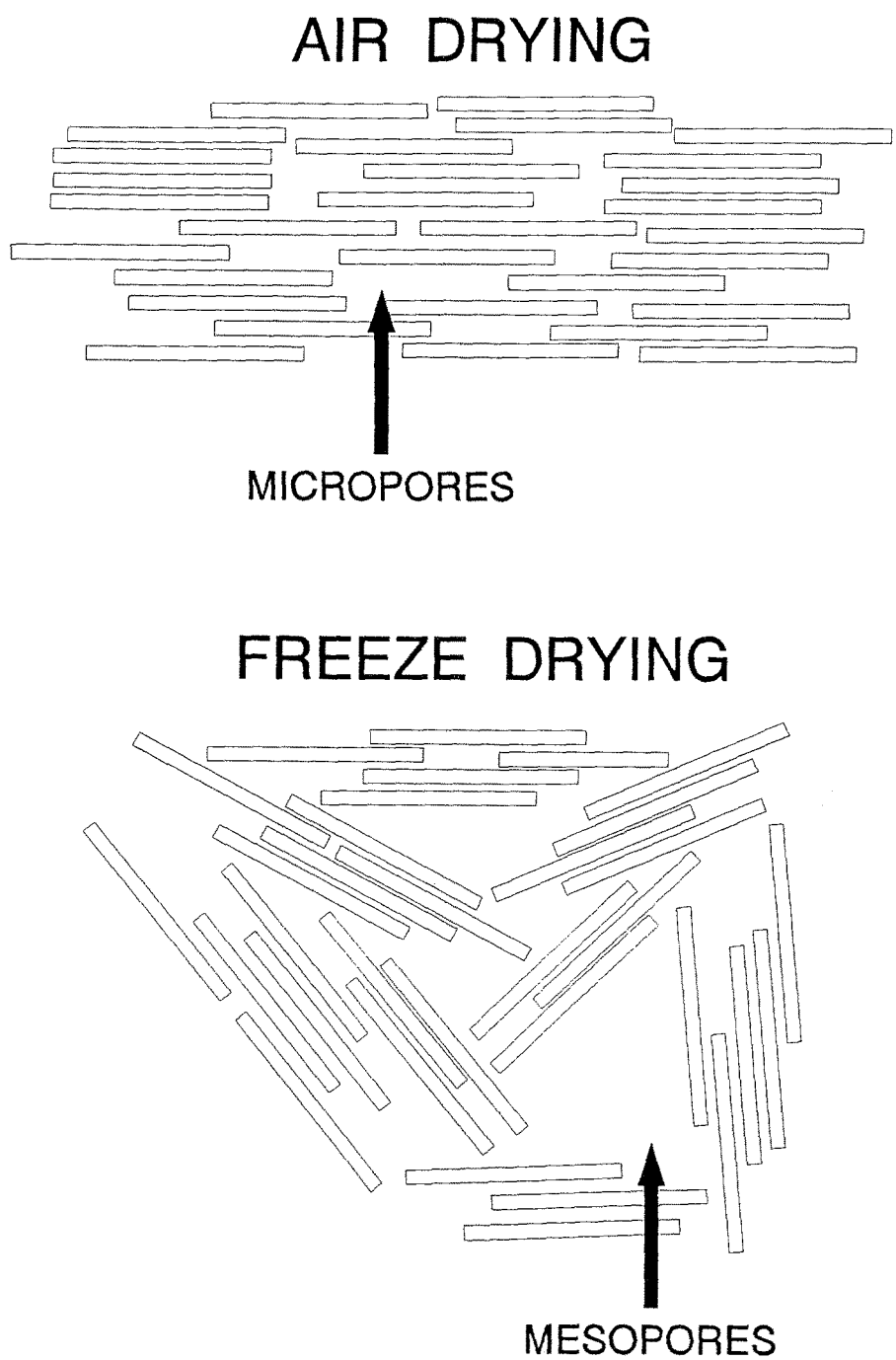

Fig. 2. Difference between an air-dried and freeze-dried clay on the final porosity.

Very small d_{001}-spacings are observed for Zr-PILC. In these micropores, only monolayers of nitrogen can be adsorbed. Since the calculation of the SA according to the Langmuir model is based on monolayer adsorption, the value of 280 m^2/g fits close to reality. The BET-value is based on multilayer adsorption and is therefore an underestimation for this sample. For Ti-PILC, the BET-surface area is probably more acceptable since mainly multilayers of N_2 are adsorbed in this porous material.

Table 1. Porosity data and elemental analysis of the various pillared clays.

	Al-PILC	Al-PILC.f	LaAl-PILC	Zr-PILC	Ti-PILC	Fe-PILC
SA_{BET} (m^2/g)	249	223	221	202	266	198
$SA_{Langmuir}$ (m^2/g)	341	327	344	280	401	–
μPV (cc/g)	0.102	0.091	0.105	0.089	0.142	0.082
ID (Å)	7.8	7.8	8.0 14.0	4.0	16.0– 19.6	16.0
EPMA analysis (wt.%)	18.7 (Al^{3+})	18.7 (Al^{3+})	19.0 (Al^{3+}) 0.3 (La^{3+})	19.1 (Zr^{4+})	20.0 (Ti^{4+})	33.1 ($Fe^{2+/3+}$)

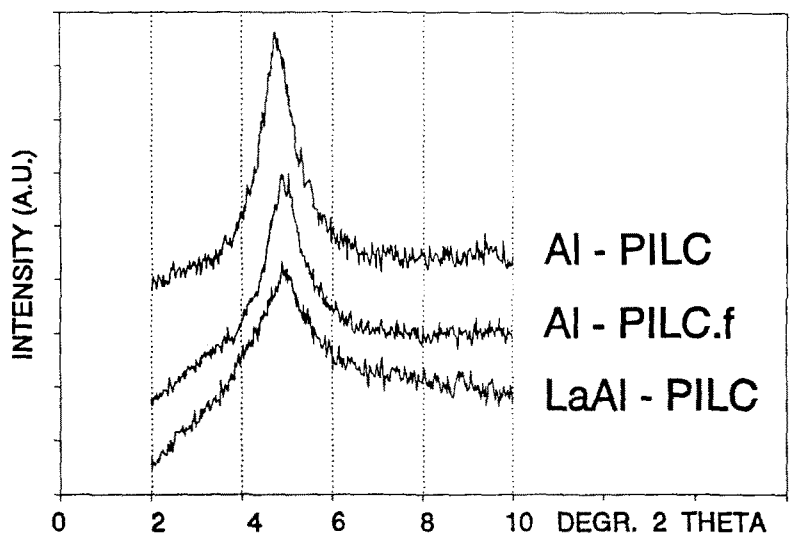

Fig. 3. XRD-spectra of alumina pillared clays.

The LaAl-PILC seems to have two main types of interlayer spacing. The one around 8 Å is due to alumina pillars while combined and larger pillars of La^{3+} and alumina are responsible for the larger interlayer spacing of 14 Å. The latter pillar complex is only responsible for a very small part of the pillaring species.

2 *XRD-Spectra*

In the first place, the XRD-spectra (Figs. 3 and 4) provide information on the interlayer distances, which can be correlated to the height of the pillaring species, as discussed before.

The calculation of the d_{001} spacing should be done with some precaution since we know from previous experiments that the observed peaks for Ti-, Fe- and LaAl-PILC are in fact second order peaks. Their first order peaks are located at very small 2θ angles. Since these spectra were recorded on an instrument with a variable slith width at changing diffraction angles, the intensity at small angels is very low and makes the first order peaks for these samples almost invisible. The first order peak of the Ti-PILC is only seen as a shoulder near $3°2\theta$. The same is true for the 14 Å-spacing in the LaAl-PILC. Moreover, the Ti-PILC exhibits a very broad peak, indicating that this sample has no uniform interlayer spacing. As said before, many pillaring ti-

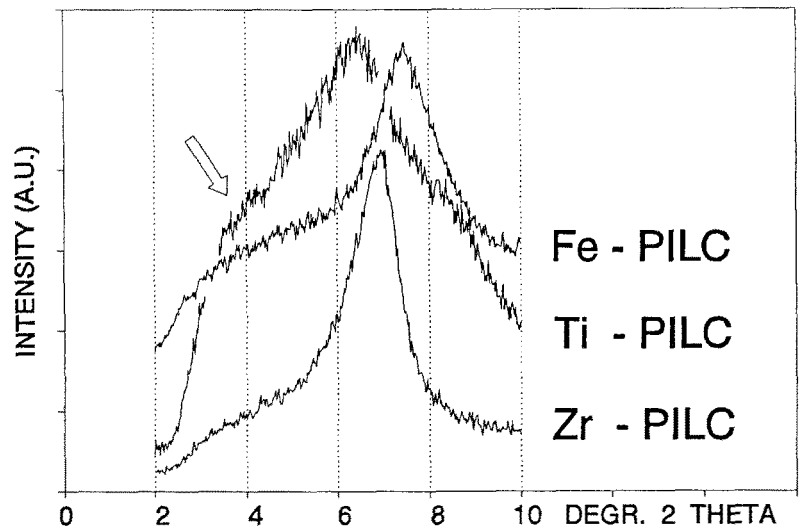

Fig. 4. XRD-spectra of iron oxide, titania and zirconia PILCs. The first order peak of the Ti-PILC is weakly seen as a shoulder in the pattern (indicated with the arrow).

tania species with different sizes are present in the Ti-PILC and this results in a varying interlayer distance between 15 and 20 Å. In the case of Fe-PILC, the background level is elevated by fluorescence radiation, due to large amounts of iron in the sample, which also hides the first order peak at small angles.

Also the peak intensity should be handled with care since it is very dependent on the pretreatment of the XRD-sample (drying process on the glass slide, particle size, concentration of the slurry, etc.). XRD-spectra of Al-PILC and Al-PILC.f are comparable since a reference peak, due to a quartz impurity in the clay, appeared for both samples at the same position and with the same intensity (at 23°2θ, not shown in these spectra). One can see that freeze-drying has no influence on the size of the alumina pillars (same d_{001} position) but affects somewhat the homogeneous stacking of the clay layers. This is reflected in the lower intensity of the d_{001} peak of the freeze dried Al-PILC. It is clear however, that our preparation procedure did not result in a completely delaminated freeze-dried PILC, since the XRD spectrum of Al-PILC.f still shows some semi-crystallinity in the sample.

3 *Nitrogen Adsorption Isotherms (77 K)*

Figure 5 shows the N_2 adsorption isotherms at 77 K for the various pillared clay samples.

The equality in the shapes is striking for the isotherms of Al-, Zr-, LaAl- and Al-PILC.f. In fact, these four samples exhibit a typical Type I adsorption isotherm, which is correlated with Langmuir adsorption. The Fe-PILC and especially the Ti-PILC have an isotherm of Type II (BET-like). Especially the high interlayer spacing of these two samples is responsible for this kind of multilayer adsorption. The low capacity for Fe-PILC is due to its dense pillar system and therefore low micropore volume. Recently, we have found that this problem can be solved by controlling the pillaring process of Fe-PILC. A good procedure seems to be the preadsorption of butylamine between the clay sheets prior to pillaring with the Fe-complex. As a result, the pillar density decreases since a part of the interlayer space is occupied by the amine. Calcination results in the formation of rigid iron oxide pillars, but also in the desorption of the amine species. Thus, more micropore volume becomes available again. If the clay is first dispersed in a solution of butylamine (0.1 M) which is half the CEC-value of the clay, and successively pillared with the Fe-complex, than the surface area and micropore volume are 2.5 times larger than without the preadsorption of the amine.

Although a very small interlayer spacing was observed for the Zr-PILC, a high adsorption capacity is seen. This might be attributed to the overlapping potential energy fields of two adjacent layers (Baksh and Yang, 1992). This cumulative effect induces a very high adsorption field in the small pores of the Zr-PILC,

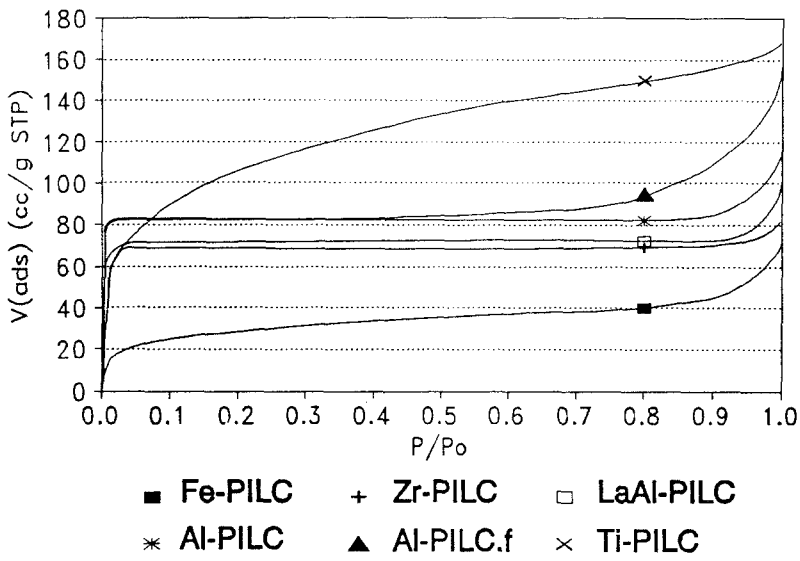

Fig. 5. N_2 adsorption isotherms at 77 K of various PILCs.

which results in a high adsorption capacity.

The differences between the nitrogen isotherms of Al-PILC and Al-PILC.f are a nice example of the information that can be obtained from these data about the porosity of the samples. As said before, the Al-PILC.f differs from Al-PILC by the larger amount of mesopores, resulting from the random card house structure. In the low pressure region ($0 < p/p_0 < 0.4$), both isotherms are exactly equal. This area represents the adsorption in the micropores. At pressures above $p/p_0 = 0.4$, condensation in mesopores starts and the isotherms deviate from each other. Only the Al-PILC.f curve becomes more steep now as a result form the multilayer condensation in the mesopores.

4 *Influence of the Pillars on the Adsorption Properties*

Besides the nitrogen isotherms, the adsorption of other gases can give some interesting information on the influence of the pillaring species on the adsorption behaviour of the PILC. It is also important to examine the adsorption at other temperatures. At low temperature (77 K), mainly non-localized adsorption occurs by condensation of the gases in the pores of the pillared clay. Specific adsorption sites (OH-groups, cations, ...) or other specific electrical adsorption fields have only a small contribution in the adsorption phenomenon. At higher temperatures, however, these localized adsorption effects gain in importance. The higher the electrical field, the better the interaction with the adsorbed molecules.

Table 2. Adsorption capacities (mmol/g) at 77 K and 0.45 atm, on three pillared clays with varing pore sizes.

Gas	Al-PILC	Zr-PILC	Ti-PILC
Nitrogen	2.50	3.50	2.80
Oxygen	3.38	5.00	5.90
Argon	3.04	4.40	5.20

Table 2 compares the adsorption of several gases at 77 K on three pillared clays. These substrates were chosen since they differ totally in their pore structure, as discussed before.

It can be seen that both Ti-PILC and Zr-PILC have a higher adsorption capacity than Al-PILC. Ti-PILC has the largest micropore volume and can therefore adsorb most gas in its pore system. Although the Zr-PILC has the smallest interlayer spacing, the substrate still adsorbs more gas than the Al-PILC, which has larger galleries. This can only be explained by the increased electrical field from two adjacent clay layers that are close together in the Zr-PILC.

At higher temperatures (194 K), the adsorption capacity of all the samples decreases significantly, compared to adsorption at 77 K (Table 3).

Now, especially for nitrogen and oxygen, mainly localized adsorption forces are responsible for the uptake of gas in the pores. Except for CO_2 where, again, the

Table 3. Adsorption capacities (mmol/g) at 194 K and 0.45 atm, on various pillared clays.

Gas	Al-PILC	LaAl-PILC	Zr-PILC	Ti-PILC	Fe-PILC
N_2	0.05	0.05	0.09	0.16	0.03
O_2	0.02	0.03	0.07	0.07	0.01
CO_2	0.95	n.m.	2.40	1.46	0.29

n.m. = not measured.

high interaction field in the small pores of Zr-PILC becomes important. Since adsorption under these conditions of pressure and temperature are close to the p_0-value of this gas, also condensation effects are responsible here for the high uptake.

The capacity of LaAl- and Al-PILC is almost equal for both nitrogen and oxygen. Although the La^{3+} had a small influence on the pillaring species, this element almost not influences the interaction field in the pores.

The Fe-PILC has a higher interlayer spacing than Al-PILC, but a lower adsorption capacity. In this case, it is not the higher adsorption field in the Al-PILC that is responsible for this result, but the dense pillar system of the Fe-PILC that decreases the available adsorption volume.

From these examples, it becomes clear that the type of pillar in the PILC influences the adsorption in three ways. First of all, the size of the pillaring species, and therefore the interlayer distance, is of importance. Large pillars result in large galleries in which much space is available for adsorption (e.g. Ti-PILC). Small pillars however, make the potential energy fields of the top and the bottom clay layer overlap. As a result, an increased adsorption field is present in these pores, which has a positive influence on the capacity (e.g. Zr-PILC). It is evident that the pillar height should not be too small, in such a way that molecules are excluded from adsorption by their size.

Secondly, the distribution of the pillars between the clay layers is of importance. It is supposed that all the PILCs that are described here, have a good distribution in such a way that they support the clay layers and prevent them from collapsing. As a result, high SA and μPV are observed. Sometimes (e.g. Fe-PILC), the pillars are too close to each other and the available pore volume is occupied by them. If interpillar distances are extremely small, than this results also in the exclusion of gas molecules for adsorption.

Thirdly, since adsorption is a process of electrical interaction between the substrate and the gas molecule, the nature of the pillar and its induced electrical field are of importance. In the following section, we will discuss the influence of this adsorption field in the pillars and the pores.

5 *Modification of the PILCs and the Influence on Adsorption*

In order to change the adsorption properties of pillared clays, these materials can be modified in various ways. Besides the possibility to choose a typical pillar to fine-tune the pore size, one can also introduce cations into the pillars or the pores of a pillared clay. As an example, we report two modification procedures and their influence on the adsorption capacity and selectivity of the final PILC. In the first case, several cations were introduced into the pillars during the synthesis of an iron pillared clay. Another technique shows the post-modification of an alumina pillared clay with cations. These cations are introduced in the pores of Al-PILCs by an ion exchange procedure.

5.1 Mixed Iron Pillared Clays. For the preparation of these mixed Fe-PILCs, the same procedure as for the parent Fe-PILC was followed. During the preparation of the pillaring precursor however, mixtures of 0.2 M iron(III)nitrate/chromium(III)chloride (ratio 1:1) and iron(III)nitrate/zirconylchloride (ratio 2:1) were used to obtain an Fe/Cr- and Fe/Zr-PILC, respectively. The porosity data and analysis of the elements of interest are shown in Table 4.

Table 4. Porosity data, elemental analysis and adsorption capacities (mmol/g) of mixed iron pillared clays.

	Ads. temp. (K)	Fe-PILC	Fe/Zr-PILC	Fe/Cr-PILC
SA (m^2/g)		198	287	190
μPV (cc/g)		0.082	0.092	0.051
d_{001}(*) (Å)		25.6	17.3	26.8
EPMA analysis (wt. %)		33.1 ($Fe^{2+/3+}$)	16.2 ($Fe^{2+/3+}$) 16.1 (Zr^{4+})	20.5 ($Fe^{2+/3+}$) 14.8 (Cr^{3+})
CO_2	273	0.29	0.32	0.40
N_2	194	0.03	0.12	0.25
C_6H_{12}(**)	273	0.11	0.56	0.80

(*) the thickness of a montmorillonite layer is 9.6 Å.
(**) cyclohexane was adsorbed at half of its vapour pressure.

From XRD data we know that Fe- and Fe/Cr-PILC have almost the same interlayer distance. The Fe/Zr-PILC has a lower d_{001} spacing (15–18 Å). Therefore, the presence of the Cr^{3+} and Zr^{4+} ions has a certain influence on the structure of the pillaring species, although the complete mechanism is not elucidated yet.

Adsorption results reveal the influence of the incorporated metal ions in the iron oxide pillars (Table 4). Nitrogen was adsorbed at 194 K, 440 mbar. CO_2 and cyclohexane were adsorbed at 273 K and 440 mbar for CO_2 and half of its vapour pressure for the organic gas.

Despite the lower interlayer spacing, more gas is adsorbed by the Fe/Zr-PILC, compared to the Fe-PILC. This can be understood by the higher electrical field in the smaller pores of the Fe/Zr-PILC and an additional induced field from the incorporated zirconium ions in the pillars. Also the chromium seems to act as an active adsorption site in the pillared clay. Although the porosity (SA and d_{001} spacing) of Fe- and Fe/Cr-PILC are almost identical, the presence of chromium species seems to increase the adsorption capacity for both organic and inorganic gases in the Fe/Cr-PILC. We think that the increased activity of the chromium, compared to the iron, is the result of their different appearence in the Fe/Cr- PILC. The iron is present as bonded species in the iron oxide pillars, while the chromium appears in the pillars as Cr^{3+} cations, and thus contributes to an induced electrical field in the pores of the Fe/Cr-PILC, compared to the parent Fe-PILC.

5.2 Cation Exchanged Pillared Clays. It is known that the cation exchange capacity (CEC) of montmorillonite decreases a lot after pillaring with alumina pillars. This is due to non-exchangeable H^+ cations in the clay structure that were formed during the conversion of the pillaring precursor into rigid Al_2O_3-pillars. It is however possible to restore the CEC of a PILC in two ways (Vaughan et al., 1981; Molinard et al., 1994). The direct procedure is the exchange of a desired cation from a basic solution. The indirect method consists of a first modification of the PILC with ammonia. The reaction of the gas with the H^+ results in the formation of NH_4^+ cations which can subsequently be exchanged for any other desired cation. These modifications have no effect on the structure of the PILC or do not alter the pillars. The ion exchange only results in the introduction of cations in the pores of the pillared clay. They can act as active adsorption sites and therefore change the adsorption properties of the substrate.

Two samples were exchanged with Sr^{2+} by the two different methods. The parent sample (Al-PILC) was prepared as described previously, but calcination took place at 673 K during two hours, at a heating rate of 10 K/min. This calcination procedure results in a higher micropore volume and surface area of the PILC and therefore an increased adsorption capacity. The Al-PILC was subsequently exchanged in a basic solution of $SrCl_2$ (0.05 M). The pH of the solution was adjusted with NaOH till pH = 12.17. After 2 days, equilibrium was reached and the exchanged PILC was separated by filtration, washed till Cl^--free and dried in air at 333 K. The sample was labelled Sr-Al-PILC(base).

Table 5. Adsorption capacities (mmol/g) on Al-PILC and Sr^{2+}-modified Al-PILC, at 0.45 atm. and 2 different adsoprtion temperatures.

Ads. temp.	194 K			273 K		
Sample	N_2	O_2	CO_2	N_2	O_2	CO_2
Al-PILC	0.14	0.10	2.36	0.02	0.01	0.36
Sr-Al-PILC(base)	0.28	0.20	2.24	0.04	0.01	0.46
Sr-Al-PILC(NH_3)	0.14	0.09	1.97	0.03	0.01	0.40

Another Sr^{2+} exchanged Al-PILC was also prepared. The parent pillared clay was first modified with NH_3 gas by an ordinary adsorption process at room temperature. Subsequently, the NH_4^+-Al-PILC was put in a 0.05 M solution of $SrCl_2$ for exchange during 24 hours. After filtration and washing, the PILC was dried at 333 K in air. The sample is labelled Sr-Al-PILC(NH_3). This method is preferred over the first one if cations should be exchanged which precipitate in basic solutions (Mg^{2+}, Ca^{2+}, Al^{3+}, ...).

Table 5 shows the adsorption of various inorganic gases at two different temperatures. It becomes clear that the incorporation of the Sr^{2+} cations in the structure has a positive influence on the adsorption capacity.

Although both modification procedures result in the same Sr^{2+} exchanged Al-PILC, the Sr-Al-PILC(base) shows a higher increase in adsorption capacity than the Sr-Al-PILC(NH_3). These cations act as active adsorption sites and therefore increase the potential field in the micropores. Especially the selectivity between N_2 and O_2 at 273 K changes significantly after the modification with Sr^{2+} in a basic solution. In general, nitrogen is always more adsorbed than oxygen since the quadrupole moment of the first contributes to an additional interaction with the adsorption sites in the PILC. This phenomenon is more pronounced at higher adsorption temperatures (273 K) since these localized interactions become also more important. At lower temperatures,

non-localized adsorption is the main mechanism (condensation), especially if the adsorption temperature reaches the boiling point of the adsorbed gas. This explains the high uptake of CO_2 at 194 K, which reflects in fact the condensation of the gas in the pores.

Conclusion

Pillared clays are microporous materials with a high surface area and pore volume. It is shown that various oxide pillars can be used to prop open the clay layers. Depending on the type of pillar that is used, the pore size, porosity and adsorption properties of these PILCs, change. A titania pillared clay has an interlayer distance of 16–20 Å, while the clay layers of a zirconia PILC are only 4 Å apart. This is reflected in the adsorption capacity of these substrates for gases such as N_2, O_2, CO_2 and Ar. An iron pillared clay has a large interlayer distance, but a low adsorption capacity. This is due to the high pillar density between the clay sheets. The iron oxide pillars occupy therefore a part of the available micropore volume which decreases the gas uptake.

The incorporation of specific elements in the pillars during the synthesis procedure, results in an increased adsorption capacity. This is the main reason why Fe/Cr- and Fe/Zr-PILCs have a higher adsorption capacity then the parent Fe-PILC, since the chromium and zirconium act as active adsorption sites.

Specific adsorption sites can also be introduced in the pores of the PILC by an ion exchange procedure. Post-modification of an Al-PILC with Sr^{2+} ions results in a substrate (Sr-Al-PILC) with an improved adsorption capacity and selectivity for N_2, O_2 and CO_2 at 273 K.

In general, it seems that the final adsorption properties of a pillared clay depend strongly on the pillars in three ways.

(1) The height of the pillaring species, which influences the pore volume, interlayer distance and potential adsorption field in the PILC.
(2) The distribution or density of the pillars between the clay layers, which has an influence on the stability, but also the pore volume.
(3) The nature of the pillaring species, which changes the adsorption field in the pores.

These three criteria should be kept in mind if a pillared clay is used for certain purposes. On the other hand, they offer an enormous flexibility and make it possible to fine-tune a pillared clay for specific applications.

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